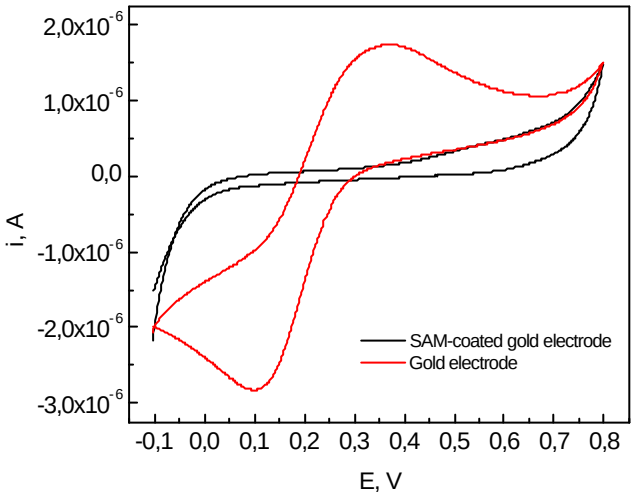
CYCLIC VOLTAMMETRY:
insulating behaviour of the SAM

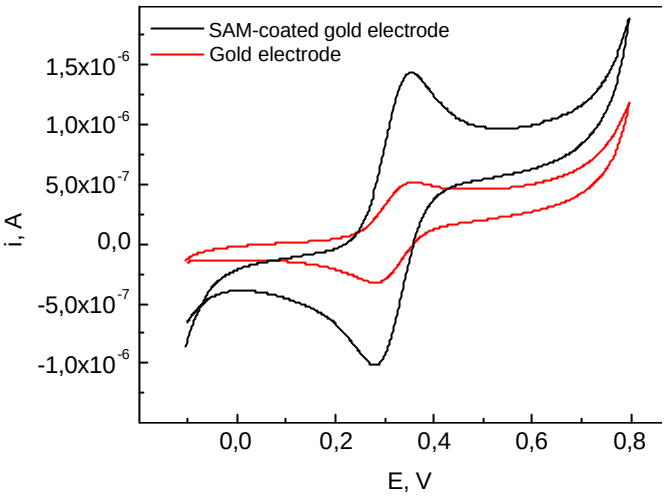
Cyclic Voltammograms of **$K_4Fe(CN)_6$** and **Fc-COOH** in solution at a *bare* gold electrode **or** at a gold electrode *modified with a SAM of OM (C 8)*

$K_4Fe(CN)_6$



The OM SAM **insulate** the electrode from $K_4Fe(CN)_6$ in solution

Fc-COOH

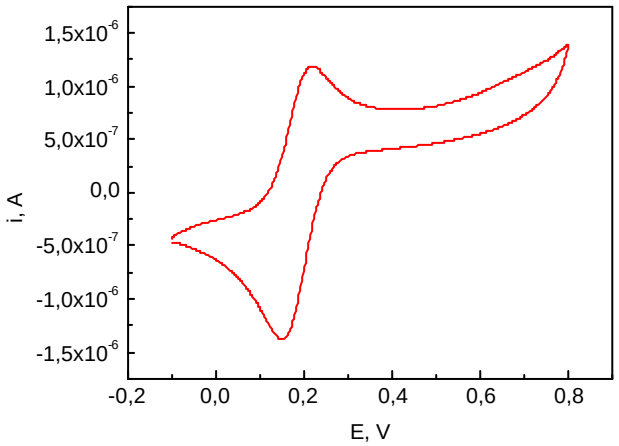


The OM SAM **does not insulate** but causes the electrochemical signal of Fc-COOH in solution to increase

*The **insulating behaviour** of the SAM depends on the **affinity** between the electrode surface and the molecules in solution*

Cyclic Voltammograms of **Fc** in solution at a gold electrode *modified with a SAM of ODM (C 18)*

Fc



*Increasing the **length of the alkyl chain** of the SAM*

NO INSULATING BEHAVIOUR

HYBRID FILMS (SAM/LB):
1. Characterization

Preparation of hybrid films on gold
(SAM and LB procedures)
with and without **redox mediator**

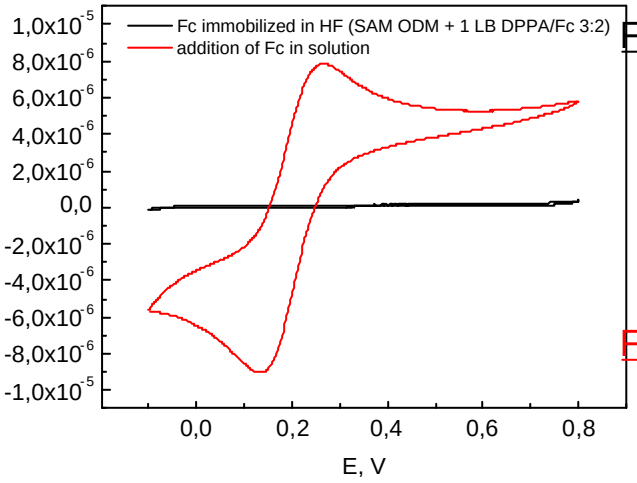
Characterization by means of:

- Ellipsometric thickness
- Contact angle
- Transfer ratio

	SAM (ODM)	HF (ODM+2 LB pure DPPA)	HF (ODM+2 LB DPPA/Fc)	HF (ODM+2 LB DPPA/TMB)
s	10-13 Å	42-58 Å	48-60 Å	31-43 Å
q	100-106°	105-107°	97-101°	101-107°
TR	-	1.000	0.809	1.058

s = thickness; q = contact angle of water; **TR** = transfer ratio

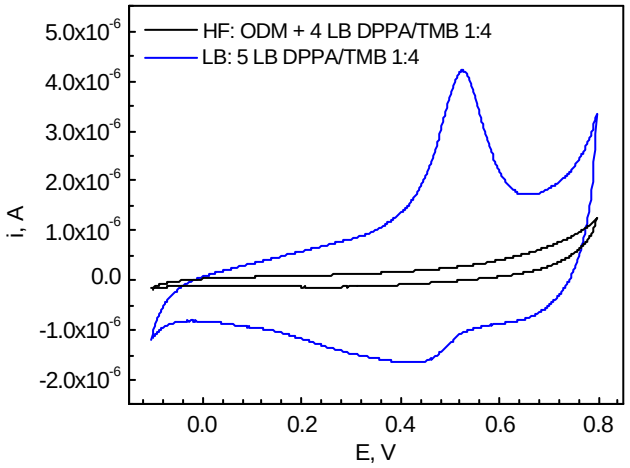
2. Insulating behaviour of the film



Fc immobilized in HF → **No** electrochemical signal

Addition of Fc in solution

- Electrode coating with **2 layers** → No insulation
- Electrode coating with **4 layers or more** → HF acts as an insulating film



TMB immobilized in HF → **No** electrochemical signal

TMB immobilized in LB film → **Significant** electrochemical signal

TMB: optimal mediator

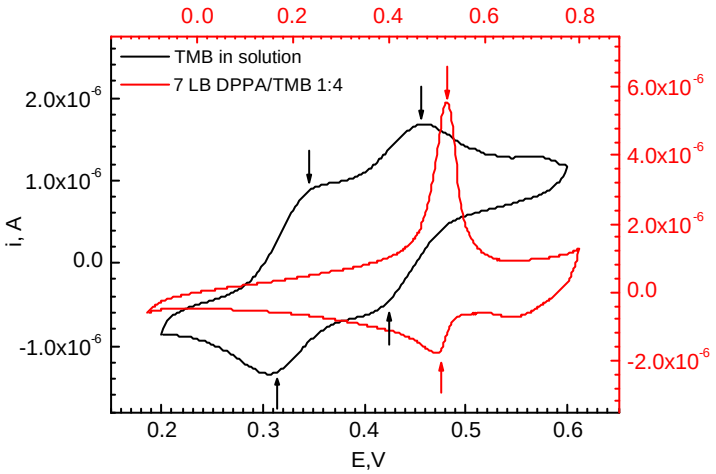
IMMOBILIZED TMB: Cyclic Voltammograms

Preparation of LB films of DPPA/TMB 1:4 on gold (**co-spreading**)

Characterization recording **cyclic voltammograms** as a function of:

- layer number
- π transfer
  - π_{tr} = 25 mN/m — before the TMB transition
  - π_{tr} = 40 mN/m — after the TMB transition

1. Redox features of free diffusing TMB in solution and immobilized TMB

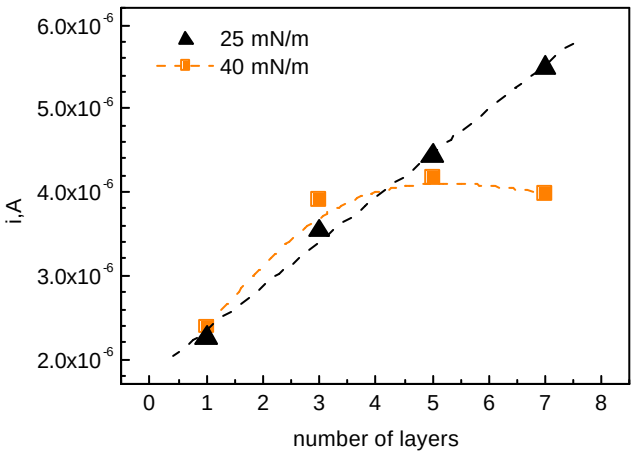


TMB immobilized in LB films maintains its electroactive behaviour even if:

- In solution: **two-steps** oxidation
- In LB films: **one-step** oxidation

Reduced mobility *of TMB in LB films with respect to the solution*

2. Intensiy of the oxidation peak at 0.525 V for TMB immobilized in LB layers



π_{tr} = **25** mN/m — Less compact LB film → **Linear relationship** between current intensity (**i**) and layer number

π_{tr} = **40** mN/m — More compact LB film → **Saturation treshold** of **i** values against layer number

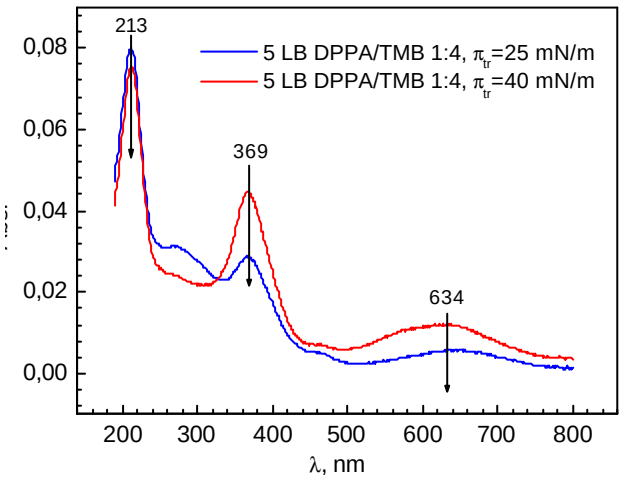
IMMOBILIZED TMB: UV-Vis Spectra

Preparation of LB films of DPPA/TMB 1:4 on quartz (**co-spreading**)

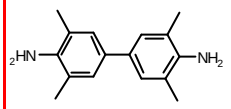
Characterization recording **UV-Vis spectra** as a function of:

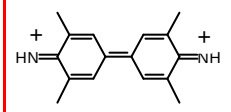
- layer number
- π transfer
  - π_{tr} = 25 mN/m — before the TMB transition
  - π_{tr} = 40 mN/m — after the TMB transition

immobilized TMB



TMB in solution

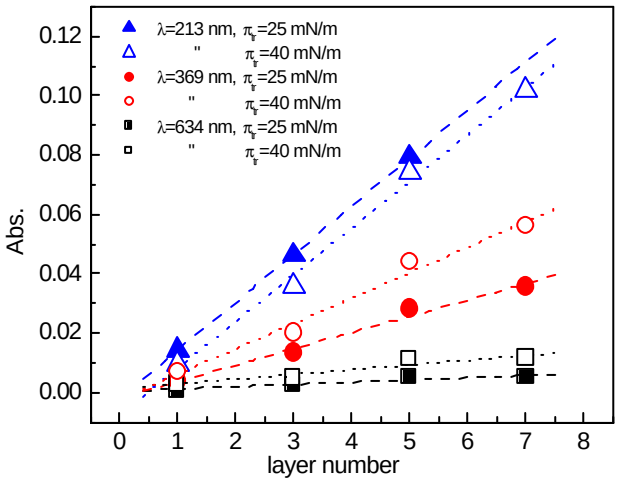
TMB	λ_1 (nm)	λ_2 (nm)	λ_3 (nm)	λ_4 (nm)
	211	292	370	-
	e_1 (mM)	e_2 (mM)	e_3 (mM)	e_4 (mM)
	≈ 20	≈ 22	« 0.1	

TMB_{ox}	λ_1 (nm)	λ_2 (nm)	λ_3 (nm)	λ_4 (nm)
	211	294	370	644
	e_1 (mM)	e_2 (mM)	e_3 (mM)	e_4 (mM)
	≈ 20	≈ 25	≈ 57	≈35

M.Vernois, G.Friedmann, M.Brini et P.Federlin, *Bull. Soc. Chim.*, 5, **1973**, 1793

*LB films of DPPA/**TMB** contain simultaneously **TMB** and **TMBox*** → **Photochemical oxidation of TMB**

Intensity of absorption bands for immobilized TMB



Linear relationsheep between **Abs.** and **layer number**

QUANTITATIVE TRANFER OF TMB IMMOBILIZED IN THE DPPA MONOLAYER

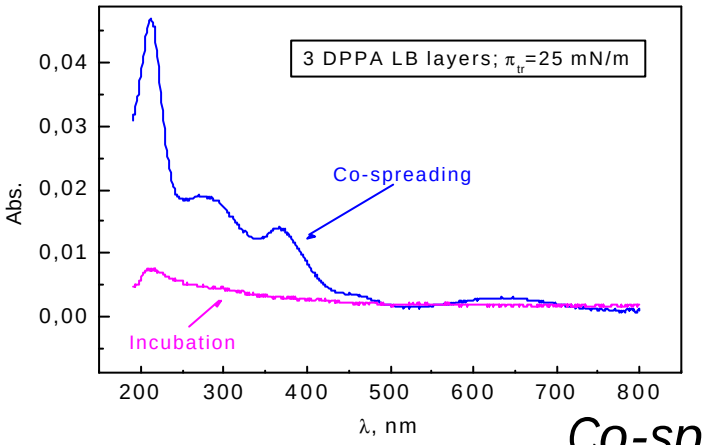
INCUBATION:
alternative procedure to immobilize TMB in LB films

DPPA LB films were immersed overnight in solutions of:

- **reduced TMB** 0.2 mM in phosphate buffer
- **oxidized TMB** $1.4*10^{-2}$ mM in acetate buffer

and UV-Vis spectra were recorded on the extracted slides

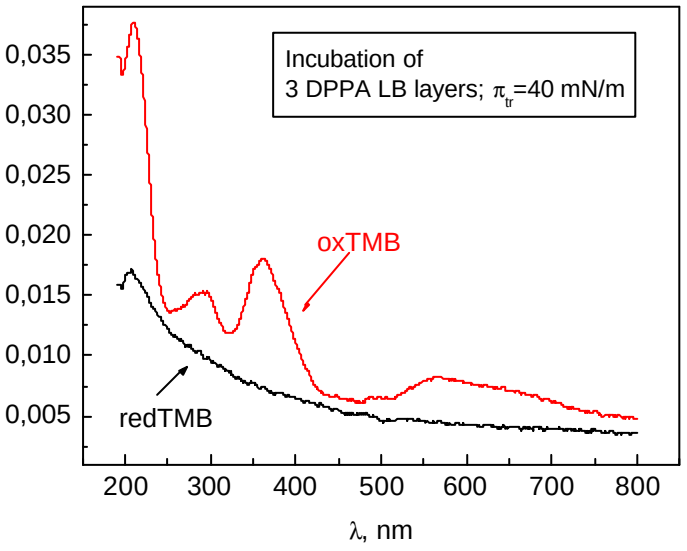
❖ CO-SPREADING AND INCUBATION



Immobilized TMB **by co-spreading** shows a higher UV-Vis signal than immobilized TMB **by incubation**

Co-spreading procedure makes TMB ***more ordered*** *into the LB film*

❖ OXIDIZED AND REDUCED TMB



oxTMB shows a stronger tendency to interact with the LB film surface than red**TMB**

BUT

It is noteworthy the buffer effect

Electrochemical tests demostrated that the mobility of free diffusing TMB iin the acetate buffer is higher than in the phosphate one: ***the migration towards the LB film surface is favoured***

CONCLUSIONS

The **electrode coating,** with SAMs, LB films and HF, allow to modify the features of electrode surface so as to decrease interferences (*insulating behaviour*) and to immobilize electroactive molecules (*redox mediators*)

- **Hybrid films** (HF), built-up combining SAM and LB procedures, are *compact and robust structures*, which allow to **immobilize electroactive molecules** ,TMB in particular

  → **but** TMB cannot penetrate the SAM: loss of electrochemical signal

- **TMB**, immobilized in LB films by co-spreading with a DPPA matrix,maintains its **elecroactive behaviour**

  → The electrochemical signal in CV is correlated with the number of LB layers and strongly depends on the **mobility** of TMB in the film

- Independent spectroscopical investigation of TMB immobilized in LB films confirms the **presence** of the mediator in LB layer