Electronic Supplementary Information (ESI)

Photochemical grafting of diazoniums salts on metals

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Experimental section

The substrates were gold-plated wafers (100 nm of gold on a silicon wafer, Aldrich), thereafter referred as gold wafers; iron and copper plates were polished with alumina slurry (0.04 µm, Presi). The gold wafers were cleaned with 98% H_2SO_4 and ultrasonicated in ultra pure water for 380 s. The copper plates were first rinsed in 5% citric acid for 1 min. The iron and copper plates were rinsed by ultrasonication in ultra pure water for 180 s.

1,4-dimethoxybenzene (99%) and 4-nitrobenzenediazonium tetrafluoroborate (97%) were obtained from Aldrich and used without further purification. Acetonitrile (Chromasolv grade) was from Aldrich (99.9%).

The charge-transfer complex (CT) was prepared in acetonitrile + 0.1 M 4-nitrobenzenediazonium tetrafluoroborate and 0.3 M or 0.9 M 1,4-dimethoxybenzene (except when indicated).

Grafting under visible light was performed in a temperature-controlled cell purged with dinitrogen and covered by a glass Petri dish filled with water as a thermal filter; a 500 W visible halogen lamp was placed ~ 11 cm above the sample. This sample was placed in the bottom of the cell and covered with a constant volume of the charge transfer complex solution.

Grafting under UV light was achieved via wide spectrum UV irradiation mercury Pen Ray lamp UVPC-86079 (20 mA AC, 4400 µW cm^{-2} at 254 nm for a distance of ~ 4 cm) with emission at 184.9 (3%, ~ 150 µW cm^{-2}) , 253.6 (100%) , 312.5-313.1, 356.0-356.3, 407.7, 435.8 nm.

After irradiation, the plates and wafers were rinsed three times for 380 s with acetone and then one time for 380 s with ultra pure water, under ultrasonication.

IR spectra of modified plates were recorded using a purged (low CO_2, dry air) Jasco FT/IR-6100 Fourier Transform Infra Red Spectrometer equipped with a MCT (mercury-cadmium-telluride) detector. For each spectrum, 1000 scans were accumulated with a spectral resolution of 4 cm^{-1}. The background recorded before each spectrum was that of a clean substrate. The profiles were recorded with an IRRAS Jasco IRT 700S microscope equipped with a RAS-

5000 objective, using a 80 x 80 μm^2 beam size and 800 accumulations with a spectral resolution of 4 cm^{-1}.

Ellipsometry was used to measure the thickness of the films on Au and Cu with a mono wavelength ellipsometer Sentech SE400. The following values were taken for gold: ns = 0.192, ks = 3.493; for copper: ns= 0.101, ks = 3.513. These values were measured on clean surfaces before photografting and the film thicknesses were determined from the same plates after modification, taking n_s = 1.49, ks = 0 for the polymeric layer.

Electrochemical experiments were performed with a potentiostat/galvanostat (CH660 A, CH Instruments, USA) in ACN + 0.1 M NBu_4BF_4 in a three-electrode cell : platinum counter electrode , Ag/AgCl reference electrode and a working electrode that was either a modified gold wafer shard or a 1 mm diameter gold disk electrode. The voltammogram of nitrobenzene was recorded with the disk electrode in a 1mM solution of nitrobenzene.

Influence of the 4-DNB/DMB ratio

We have examined the intensity of the IR band of the nitro group as a function of the 4-DNB/MBD ratio. In the following, a 9-fold excess of DMB was used all along this investigation in agreement with Fig. ESI 1.

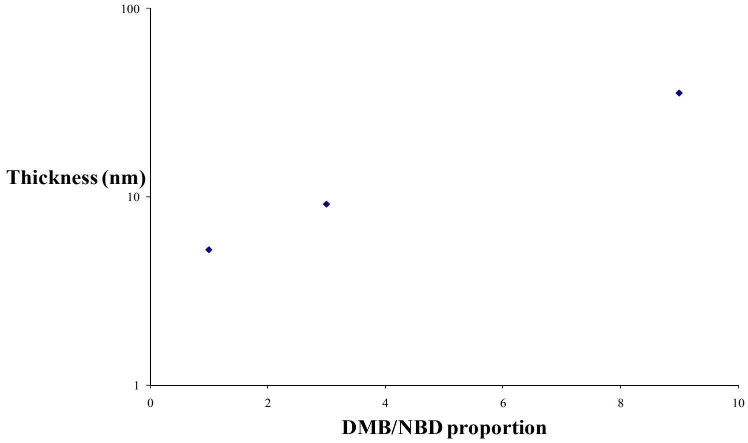

Fig. ESI 1. Influence of the DMB/4-DNB ratio on the thickness of the film

Influence of the temperature

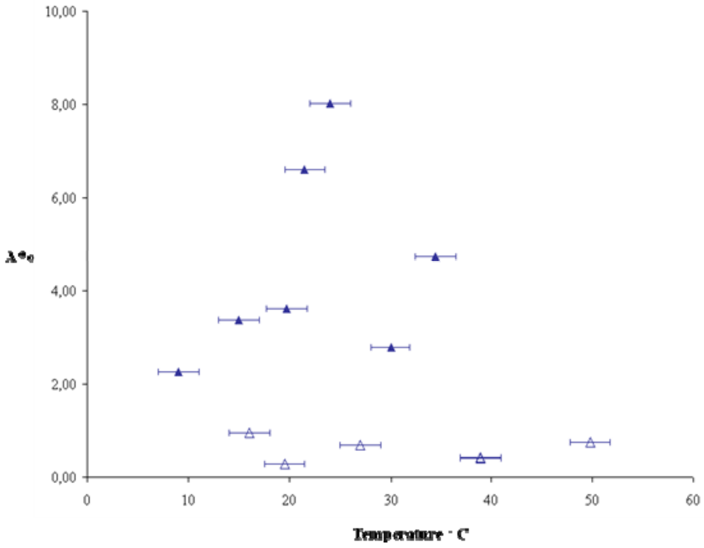

Fig. ESI 2. Intensity of the 1351 cm^{-1} symmetric stretching band of the NO_2 group vs temperature (°C): ▲ photografting under visible light, △ spontaneous grafting. Gold wafer, 20 min irradiation, CT (0.1M 4-DNB, 0.9 M DMB) in ACN.

The intensity of the IRRAS band at 1351 cm^{-1} (symmetric NO_2 stretching) is linearly dependant on the thickness of the layer and the number of attached phenyl groups produced during the experiment (20 min). Fig. ESI 5 brings forward two interesting points: i) the variation of the intensity of the IRRAS band is not significant for the spontaneous reaction whatever the temperature as this reaction is rapidly self-limited, and ii) this intensity goes through a maximum for the photografting reaction at ~ 22°C. This maximum is likely related to the involvement at higher temperature of another reaction that outruns the grafting reaction. This reaction could be the dimerization of the aryl radicals that should be produced in larger and larger amounts as the temperature increases. The increase of the concentration should favor a dimerization (second order in radicals) over the grafting reaction (first order in radicals).

Photografting on copper and iron.

Fig. ESI 2 presents the IRRAs spectra recorded on iron and copper plates photografted by the CT complex. The spectra are similar to the spectrum on gold; they present the same NO_2 stretching and ring breathing vibration.

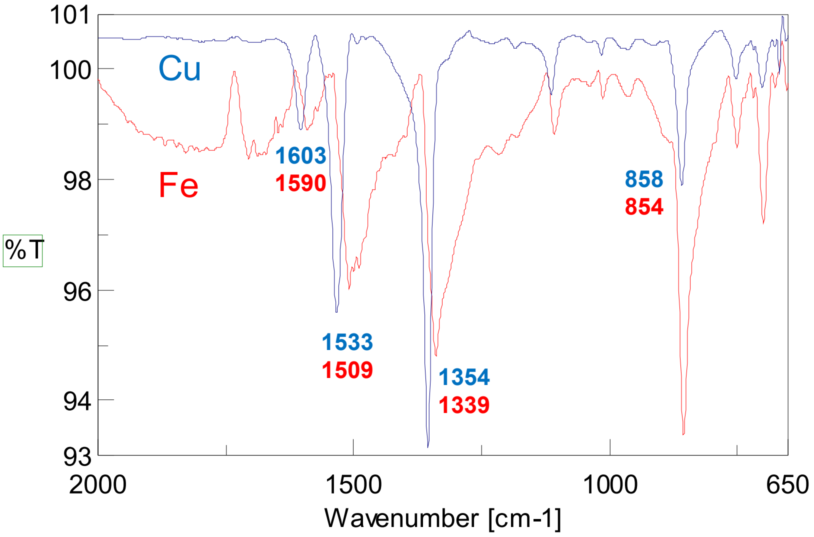

Fig. ESI 3. IRRAS spectra of Cu and Fe plates modified at 20 ± 2°C by irradiation (20 min) under visible light of a charge transfer complex between 4-nitrobenzenediazonium (0,1 M) and 1,4-dimethoxybenzene (0,9 M) in ACN.

Patterning of a gold wafer.

A gold wafer was patterned by applying a PDMS stamp with 100 x 100 µm^2 square pillars that had been dipped into a water soluble but solvent insoluble ink. This gold surface was then irradiated in the CT complex for 20 min. After rinsing in hot ultrapure water under sonication for 380 s, the surface was examined by IR microscopy, using the smallest aperture of the IRRAS setup (80 x 80 µm^2 beam size, see experimental section). Since the size of the IR beam is similar to that of the mask, a very low resolution is expected for images.

The 2D image of Fig. ESI.3 is recorded at the wavelength of the asymmetric vibration of the nitro group (1526 cm^{-1}). It shows a low absorbance zone (blue) that has not been grafted and a high absorbance zone (red) that has been grafted with 4-nitrophenyl groups. Owing to the limited imaging conditions, the size of the observed pattern correlates satisfactorily with that of the mask.

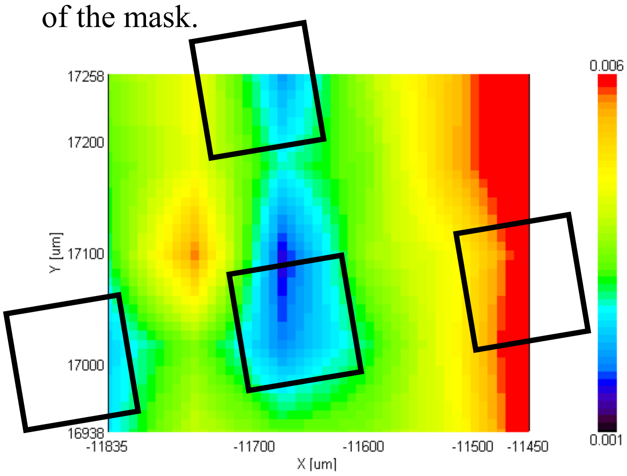

Fig. ESI 4. FTIR image of a gold wafer modified by a 100 x 100 µm^2 pattern. The low absorbance corresponds to the ungrafted part of the pattern, the high absorbance corresponds to the grafted part of the wafer. The black squares indicate the positions of the pillars.

UV irradiation

As 4-NBD absorbs at 315 nm, we have irradiated a copper wafer in a 4-DNB solution (0.3 M, 20 min) under UV light. The IRRAS spectrum obtained after careful rinsing is presented in Fig. ESI 4. It is identical to that of Fig. 2 recorded on gold (see for example the nitro symmetric and asymmetric bands respectively at 1351 and 1526 cm^{-1}), indicating that grafting has occurred.

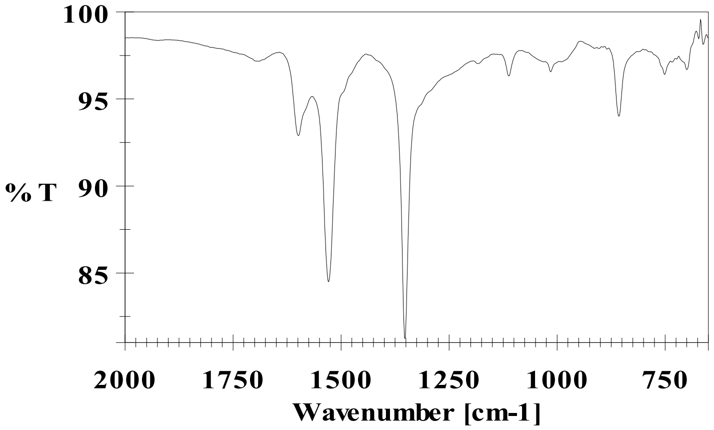

Fig.ESI 5. IRRAS spectrum of a copper wafer UV irradiated for 20 min in 0.3 M 4-DNB.