Supplementary Material (ESI) for Chemical Communications

Supplementary material

Chemisorption of fluorous copper(II)-carboxylates complexes on SiO_2 surfaces: Versatile binding layers applied to the preparation of porphyrin mono- and multilayers

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1. General

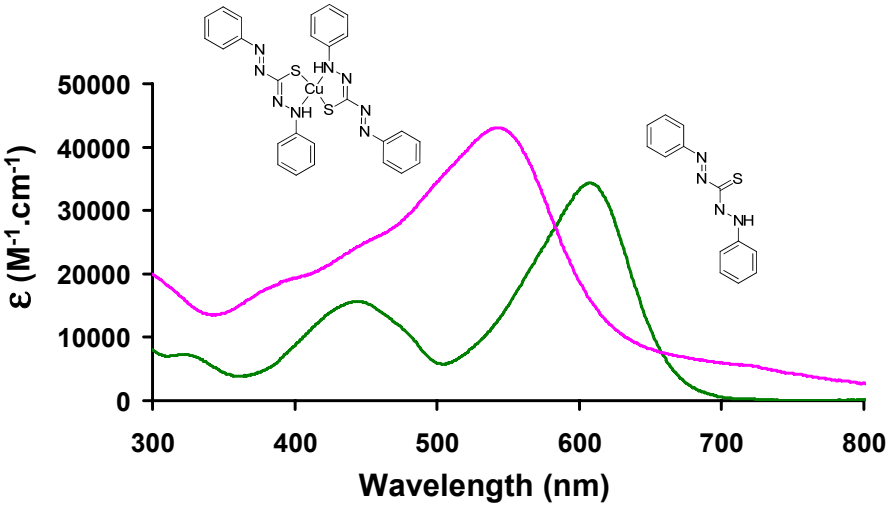
All reagents were obtained from commercial sources and used as received unless noted otherwise**.** The acetone and NEt_3 used for the synthesis of **2** were dried over K_2CO_3 and CaH_2, respectively, and distilled prior to use. The chloroform (stabilised over amylen) used for the adsorption of the porphyrins was first passed through a column of basic alumina and then distilled over K_2CO_3 to remove any traces of acid. Two types of glass substrates were employed in the study: cover glass (20 x 20 x 0.15 mm) purchased from Roth or quartz slides (25 x 25 x 0.2 mm) purchased from Electron Microscopy Sciences. Before use the glass substrates were cleaned using the piranha solution under ultrasound followed by copious rinsing with milliQ water and drying under a nitrogen flow. The confocal fluorescence microscope (CFM) is a Picoquant Microtime 200 based on a modified inverted IX71 from Olympus. The samples are excited on average at ~1 kW/cm^2 with a Ti-Sa laser chain including a Coherent Mira, a pulse-picker and a frequency doubler that affords pulses of 4 – 6 ps at 428 nm at 4.75 MHz repetition rate. The emitted light is collected by transmission through beam-splitting optics and is filtered by a 500 nm long pass interference filter to completely reject the reflected excitation laser light before being focused on a pinhole. It is then detected by a steady-state CCD-spectrometer (Andor) or an avalanche photodiode (MPD) coupled to a time-resolved photon counter set-up. The room is thermostated at 23°C with air-conditioning. The Picoquant Symphotime software is used to extract average fluorescence lifetimes at each pixel of the image and obtain the FLIM images. All the lifetimes are collected and displayed in a histrogram where the number of occurrences of each lifetime is plotted versus the lifetime. This histogram reflects the distribution of lifetimes on the whole image.For a description of the experimental set-up used for the second harmonic microscopy (μ-SHG) imaging see the reference [1]. The water contact angles were measured on a DSA 100 goniometer from Krüss. HRSEM images were recorded at the Centre de Ressource en Microscopie Electronique et Microanalyse (CREMEM) of the University of Bordeaux on a JSM 6700F microscope. The AFM images were recorded in a tapping mode on an Agilent5500 microscope. All images were recorded in air at constant temperature (23 °C). The infrared spectrum was recorded directly on the oil of **2** using a Perkin Elmer Spectrum 100 FTIR spectrometer equipped with a Pike Miracle™ single reflection ATR system. The spectra (from 4000 to 650 cm^{-1}) were obtained from 20 scans, with a resolution of 1 cm^{-1}. Electronic absorption spectra were recorded on a Hitachi U3300 spectrophotometer (300 – 800 nm scan range). Elemental analysis were performed by the Service Central d'Analyses, Vernaison, France. Results are expressed in weight percent.

2. Synthesis of $[Cu_2(C_{14}F_{29}O_4CO_2)_4(acetone)_2]$ (2)

A dry acetone solution (2 mL) of a mixture of NEt_3 (0.499 g, 4.93 mmol) and $C_{14}F_{29}O_4CO_2H$ (2.045 g, 2.47mmol) is stirred for 30 min at room temperature whereupon the solvent and the excess of NEt_3 are evaporated under vacuum to afford $C_{14}F_{29}O_4CO_2HNEt_3$ as a viscous and lightly brown oil (2.291 g, 99.8%). The oil is then dissolved in dry acetone (2mL) to which a dry acetone (2mL) solution of $Cu(OTf)_2$ (0.459 g, 1.27 mmol) is added dropwise with stirring. Rapidly, the complex **2** is formed, which separates from the acetone solution as a blue oil. After standing for 2 hours at 4°C for few hours, the colorless acetone upper phase is removed and the blue oil is washed twice with dry and cold acetone. After removal of the residual acetone under vacuum, **2** is obtained as an oil in 91% yield (1.939 g). FTIR (oil) 1714, 1692, 1428, 1302, 1226, 1196, 1140, 1125, 1041, 993, 980, 829, 809, 746, 732, 712, 667; UV-visible (MeOH) [λ_{max}, nm (ε, M^{-1} cm^{-1})], 767 (157) ; Anal. Calcd for $(C_{14}F_{29}O_4CO_2)_4Cu_2$, $(CH_3)_2CO$, $2H_2O$: C, 21.44; Cu, 3.60. Found: C, 21.33; Cu, 3.74.

3. Copper titration by dithizone assay

Four glass slides (2 x 2 x 0.1 cm) modified by **1** or **2** are dipped in a biphasic system consisting of 5 mL of milliQ water at a pH of 2-3 (adjusted with acetic acid) and 5 mL of a dichloromethane solution of dithizone (7.10^{-7} M). The system is then vigorously stirred for 5 min. After standing for 10 min, the two phases are separated and the absorption spectrum (300-800 nm scan range) of the organic phase is recorded. The formation of dithizonate copper(II) complex was indicated by the colour change from green to pink. Copper(II) ions are titrated using the molar extinction coefficient at 620 nm of the dithizone and of the dithizonate copper(II) complex which are 31100 and 12400 $M^{-1}.cm^{-1}$, respectively.



4. HRSEM of the copper(II) modified glass surfaces

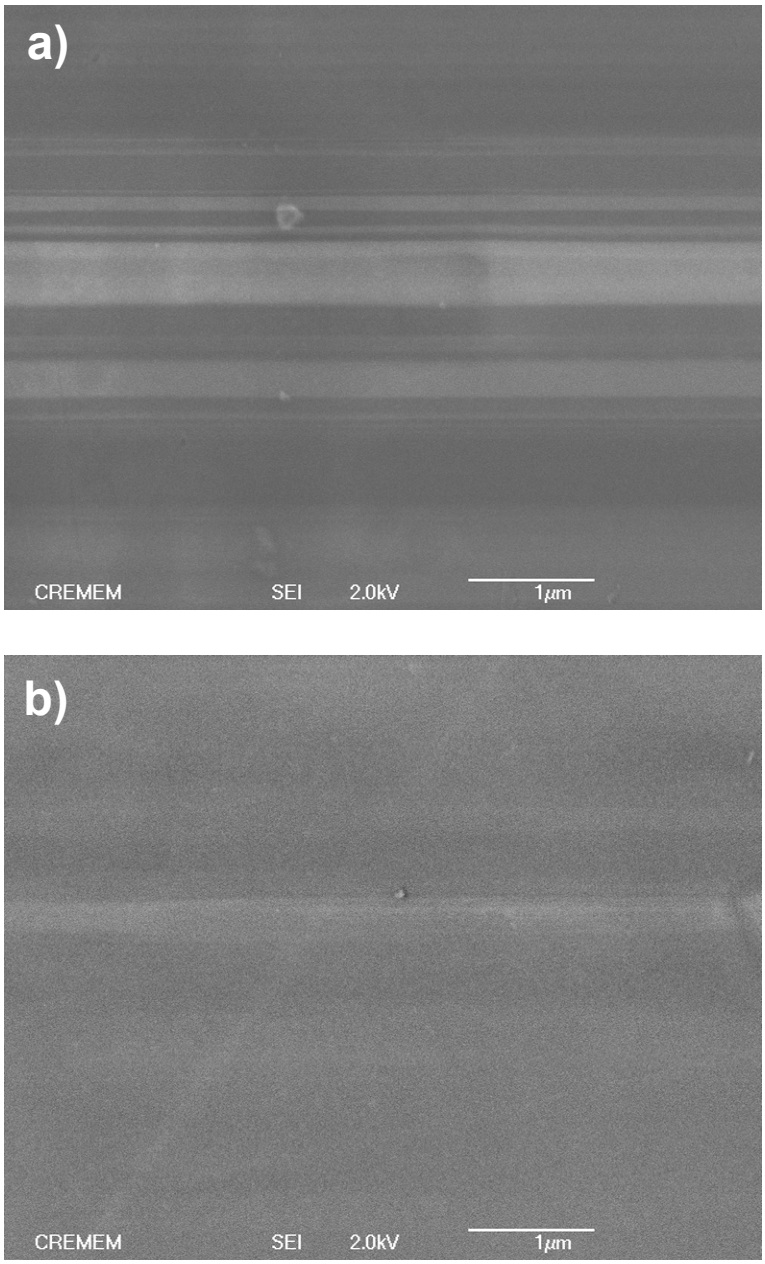


Figure S1. HRSEM images of glass substrates modified by a) complex **1**, b) complex **2**.

5. Fluorescence microscopy images

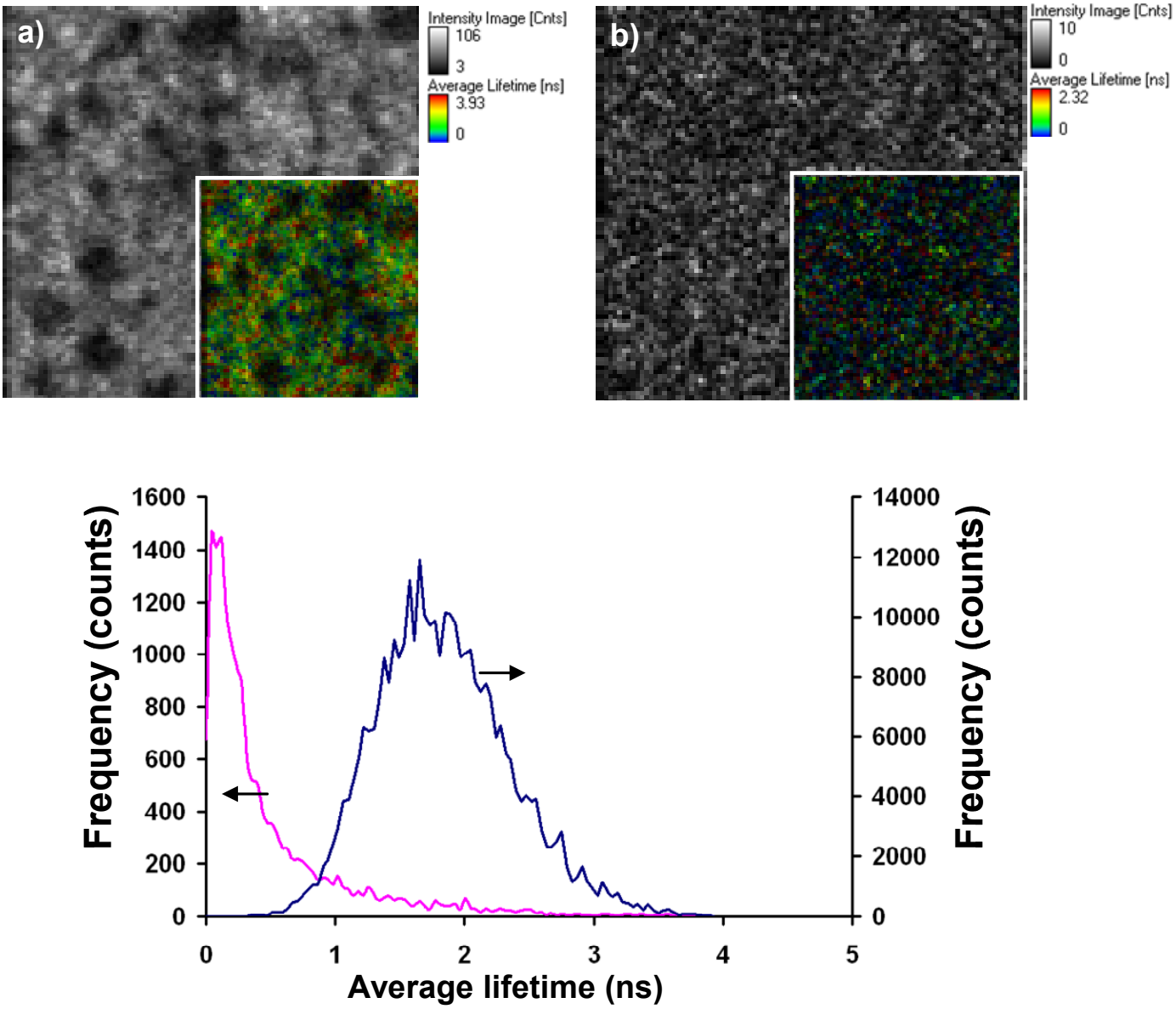


Figure S2. Intensity and lifetime fluorescence images (20 x 20 μm) of a) commercial cover glass (no cleaning, Roth) and b) the same cover glass modified with a monolayer of **2**. Below is presented the fluorescence lifetime histograms of the commercial cover glass (blue) and modified cover glass (pink).

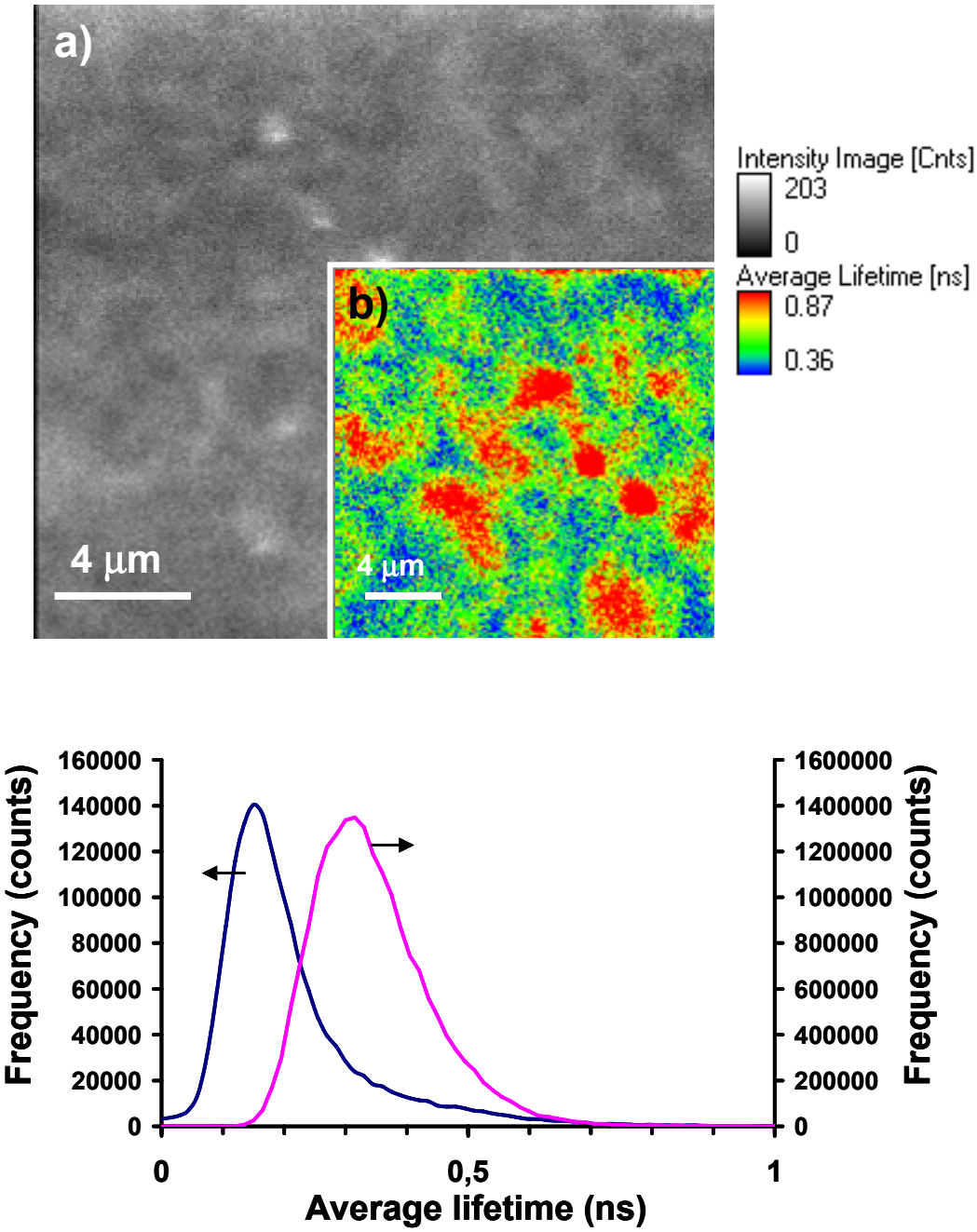


Figure S3. a) Intensity and b) life time fluorescence images (20 x 20 µm) of a dense film (immersion time 60 s, $\Gamma \sim 4 \times 10^{-10}$ mol cm^{-2}) of **3** on a glass substrate first modified with **2**. Below is presented the fluorescence lifetime histogram of the whole image (in pink). For comparison, the histogram obtained for a film at lower coverage (presented in the manuscript in the figure 3) is also given (in blue).

[1] V. Rodriguez, D. Talaga, F. Adamietz, J. L. Bruneel, M. Couzi, *Chem. Phys. Lett*. 2006, **431**, 190.