

Towards metal free supported quaternary ammonium halides catalysts for an optimized cycloaddition of CO₂ onto styrene oxide

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MATERIALS AND METHODS

Thermogravimetric analyses (TGA) were performed on a SDT Q600 system (TA Instruments, Inc.) under air flow (100 mL/min) at a heating rate of 5 °C/min, in the temperature range 25-700°C or on a Toledo instrument with temperature increment of 10°C/min in air from 25°C to 800°C.

The X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D8 diffractometer or on a D8-Advance operated at 30 kV and 30 mA using the Cu K α radiation ($\alpha = 1.54184 \text{ \AA}$) as X-ray source. For the low-angles diffraction experiments, the data were collected in the 2θ range from 0.5 to 7° with a step of 0.02° and a counting time of 6 s/step.

N₂ adsorption-desorption isotherms were obtained on an ASAP 2020 (Micromeritics) after degassing samples at 150°C for 3 h. The specific surface area of the sample was calculated from the adsorption data points obtained at P/P^0 between 0.05 and 0.3 or 0.25 using the Brunauer-Emmett-Teller equation (BET). The pore diameter and distribution were estimated from the desorption branch of the isotherms using the Barret-Joyner-Halenda model (BJH).

Elemental composition analyses were carried out on an ED-XRF EPSILON (PANALYTICAL) to determine the amount of both Zn and halide on silica. Metal contents in silica for Zn/SBA-15 and Zn/KIT-6 were determined by inductively-coupled plasma optical emission spectroscopy (HORIBA Jobin Yvon Activa).

XPS analyses were performed using an Omicron Argus X-ray photoelectron spectrometer, equipped with a monochromated AlK α radiation source ($h\nu = 1486.6$ eV) and a 280 W electron beam power. The emission of photoelectrons from the sample was analyzed at a takeoff angle of 45° under ultra-high vacuum conditions ($\leq 10^{-9}$ mBar). Spectra were carried out with a 100-eV pass energy for the survey scan and 20 eV pass energy for the C_{1s}, O_{1s}, N_{1s}, Br_{3d} regions. Binding energies were calibrated against the Si 2p peak at 103.3 eV, and element peak intensities were corrected by Scofield factors. The peak areas were determined after subtraction of a Shirley background. The spectra were fitted using Casa XPS v.2.3.15 software (Casa Software Ltd, UK).

Solid state NMR spectra were recorded on a BRUKER AVANCE III (500 MHz) spectrometer equipped with a 4 mm double-bearing probe head so as to observe the grafting of organic compounds on silica. ¹H-²⁹Si CP/MAS experiments were carried out at 10 kHz with 5 ms contact time and 10 s delay. Chemical shifts were referenced to TMS.

Table S1: Experimental parameters and results of ex-situ quaternization of tertiary amines with silylated organosilanes (3-bromopropyl trimethoxysilane and the corresponding iodo and chloro derivatives). The reactions were conducted at the reflux of the different solvents.

Entry	Amine	Halide	Dry solvent	Time (h)	NMR yield (%)
1	Me ₂ EtN	Br	MeCN	17	98
2	MeEt ₂ N	Br	MeCN	17	95
3	Et ₃ N	Br	MeCN	17	92
4	Pr ₃ N	Br	MeCN	17	42
5	Bu ₃ N	I	MeCN	17	99
6	Et ₃ N	Cl	THF	24	0
7	Et ₃ N	Cl	MeCN	24	0
8	Et ₃ N	Cl	Toluene	64	0
9	Et ₃ N	Cl	-	16	0

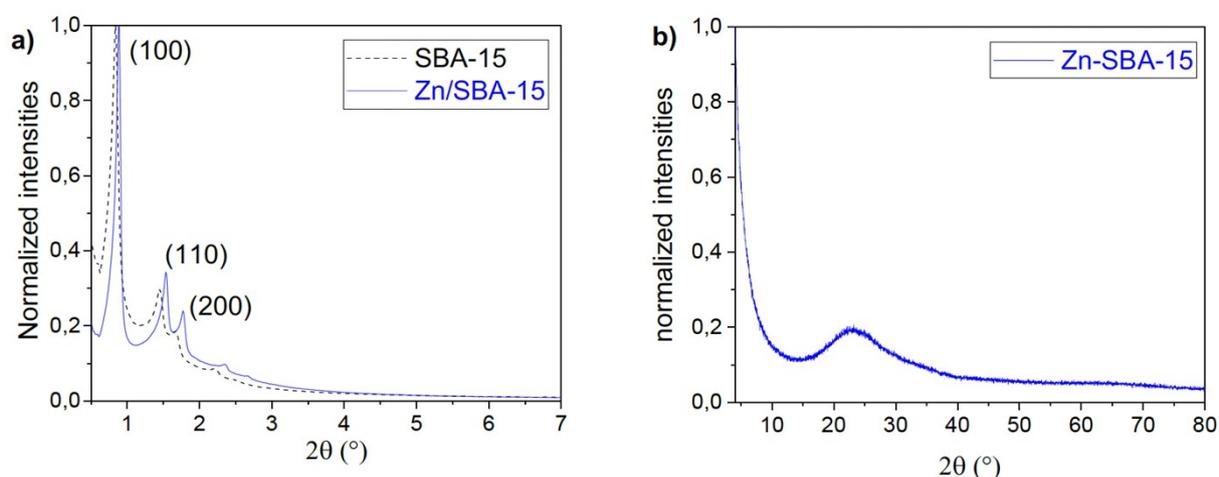


Figure S1. a) Low-angle XRD patterns of SBA-15 and Zn/SBA-15 and b) standard XRD patterns of Zn/SBA-15.

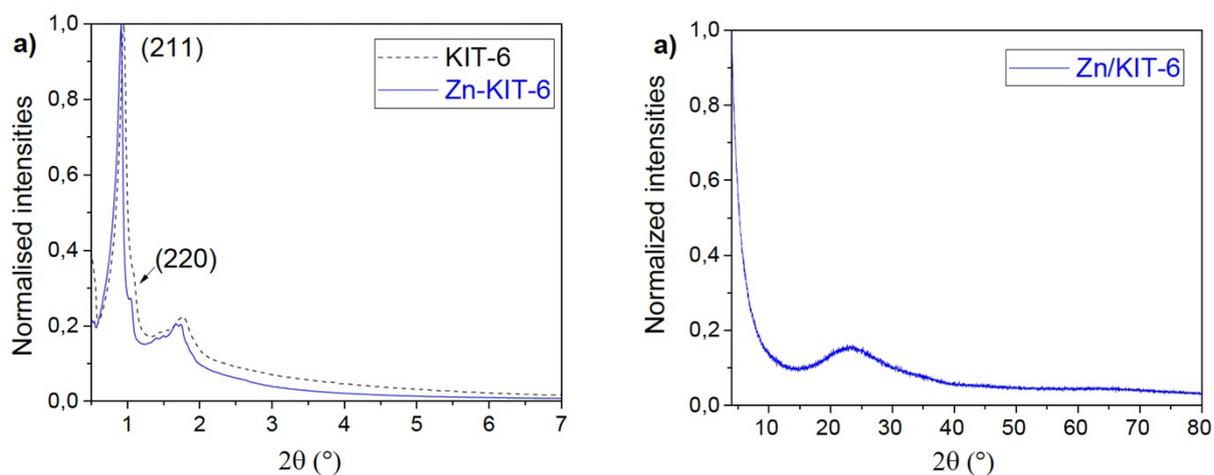


Figure S2. a) Low-angle XRD patterns of KIT-6 and Zn/KIT-6 and b) standard XRD patterns of Zn/ KIT-6.

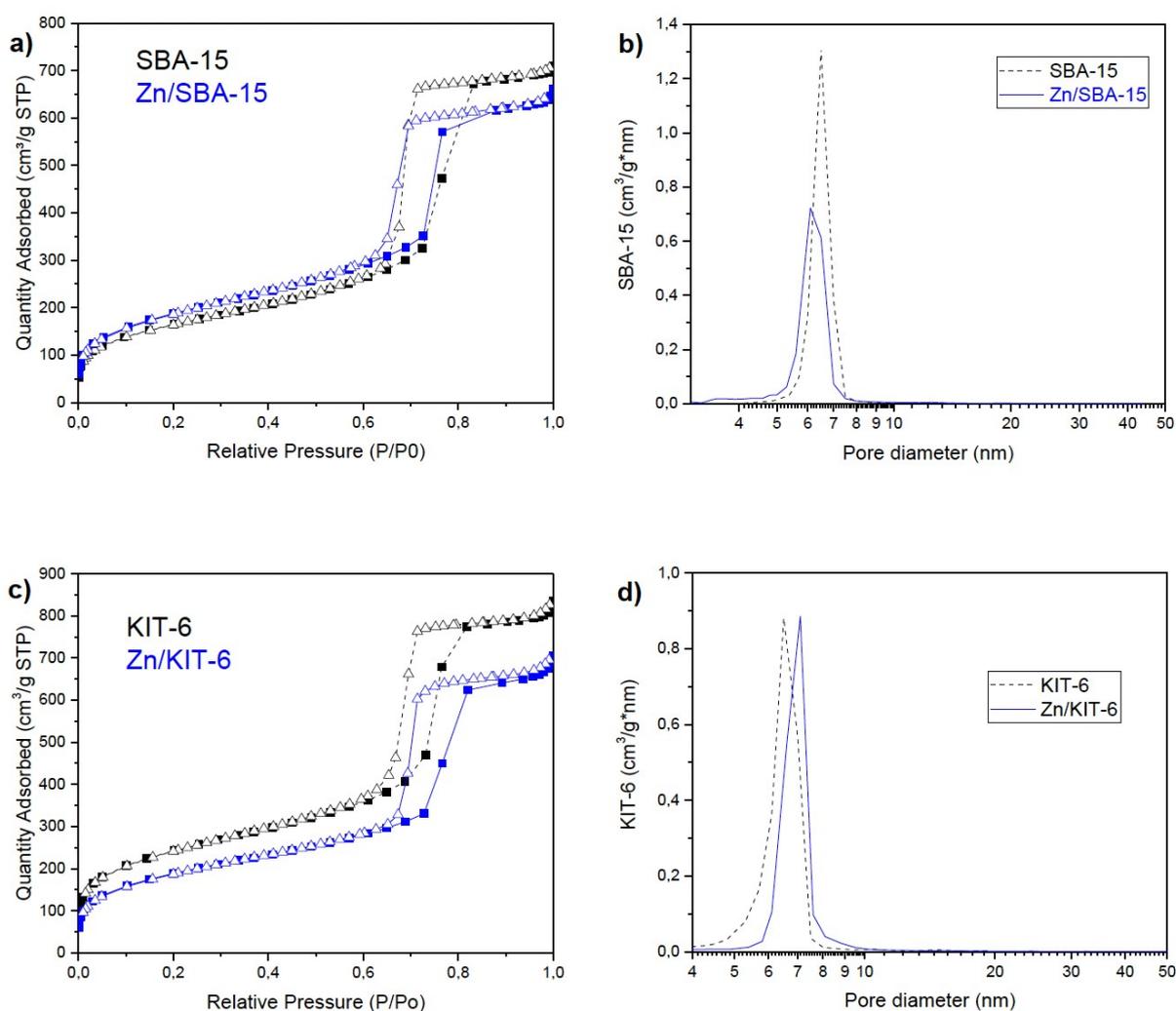


Figure S3. a) N_2 sorption isotherms and b) pore size distribution of SBA-15 and Zn/SBA-15. c) N_2 sorption isotherms and d) pore size distribution of KIT-6 and Zn/KIT-6.

Method for the determination of the $NR_3^+X^-$ loading by thermogravimetric analysis (TGA).

The determination of halides loadings on silica was carried out using both the TGA curve and its derivative. Thanks to the derivative, it was possible to estimate the temperature where the

ammonium halide is completely burned. It should be noticed that further weight loss at higher temperature was attributed to the dehydroxylation (the loss of water by the condensation of two hydroxyls from silanols). A representative example is shown below (Figure S4) for $\{NBu_3^+I\}@SBA-15$. Hence, the mass% of ammonium halide could be calculated as the difference between the mass% of the dehydrated material and the mass% of the silica after burning the organic moieties (in the example: mass% of ammonium iodide = 99 - 75 = 24), if all organics are supposed to come from grafted ammonium halides. Then, the mass% of halide could be determined knowing the molecular mass of the halide [MM iodine = 126.90 g/mol] and the molecular mass of the ammonium halide [MM $-(CH_2)_3-NBu_3I$ = 354.34]: mass% iodide = $(126.90/354.34) \times 24\% = 8.6\%$.

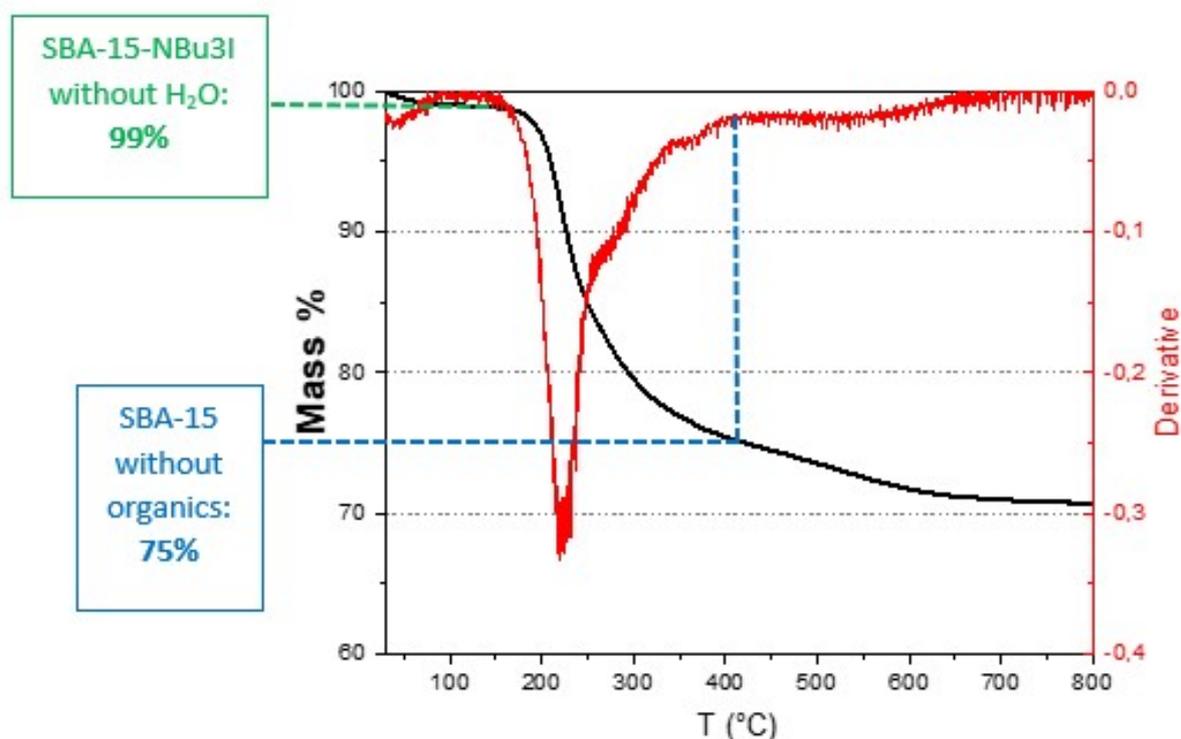


Figure S4. TGA curve used for the estimation of the QAS loading in $\{NBu_3^+I\}@SBA-15$

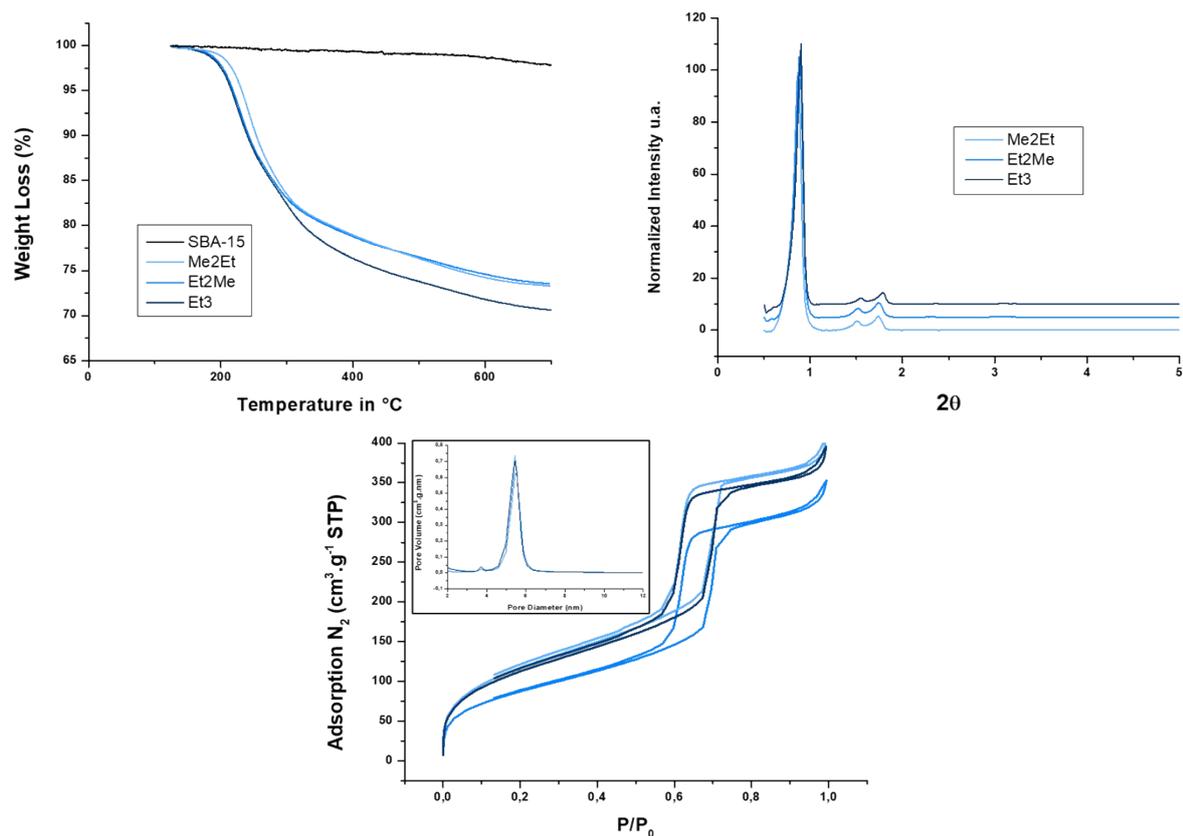


Figure S5: (top left) TGA (All curves were normalized at 100°C), (top right) Low-angle XRD patterns and (bottom) N₂ adsorption-desorption isotherms (77K) with pore size distribution curves (inset) for {Me₂EtN⁺Br}@SBA-15 (light blue), {Et₂MeN⁺Br}@SBA-15 (blue) and {Et₃N⁺Br}@SBA-15 (dark blue).

X-ray fluorescence spectroscopy. For each halogen (Cl, Br and I), a calibration curve was required (Figures S6). Therefore, different amounts of ZnX₂ (X = Cl, Br or I) were supported on SBA-15. To carry that out, the desired amount of ZnX₂ was dissolved in water (2 mL), SBA-15 (500 mg) was added along with 5 mL of water. The solution was evaporated at 45°C for 18. Then, the resulting powder was dried at 80°C in an oven for 3h. To be sure of the quantity of ZnX₂ supported on SBA-15, an IPC-AES analysis was carried out for each sample to better calculate the calibration curve.

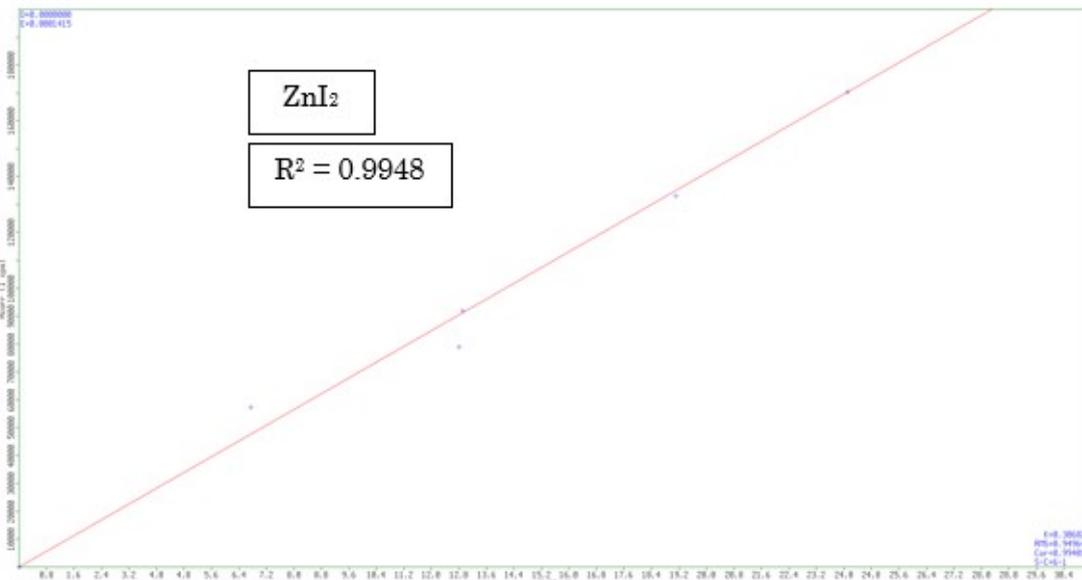
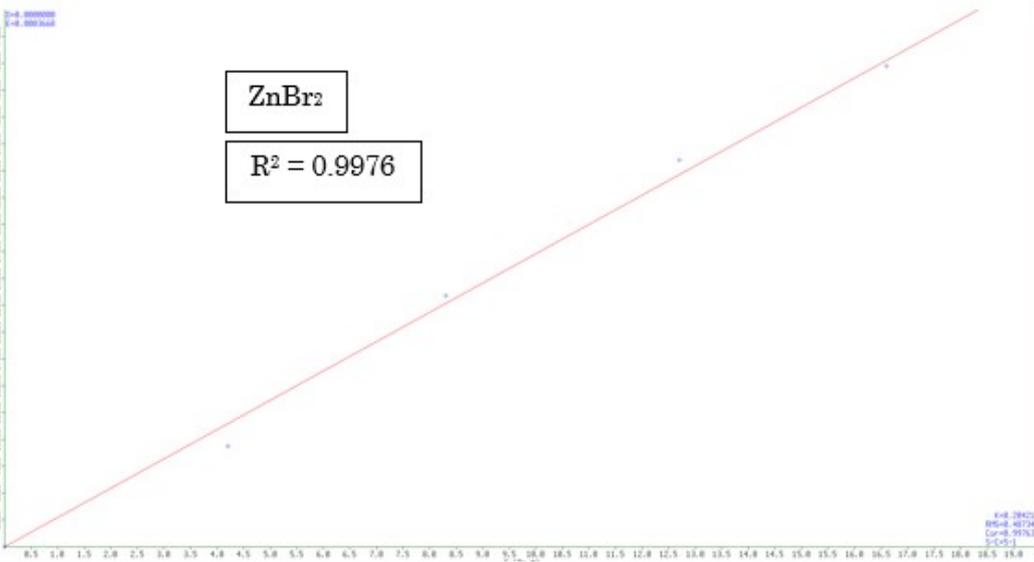
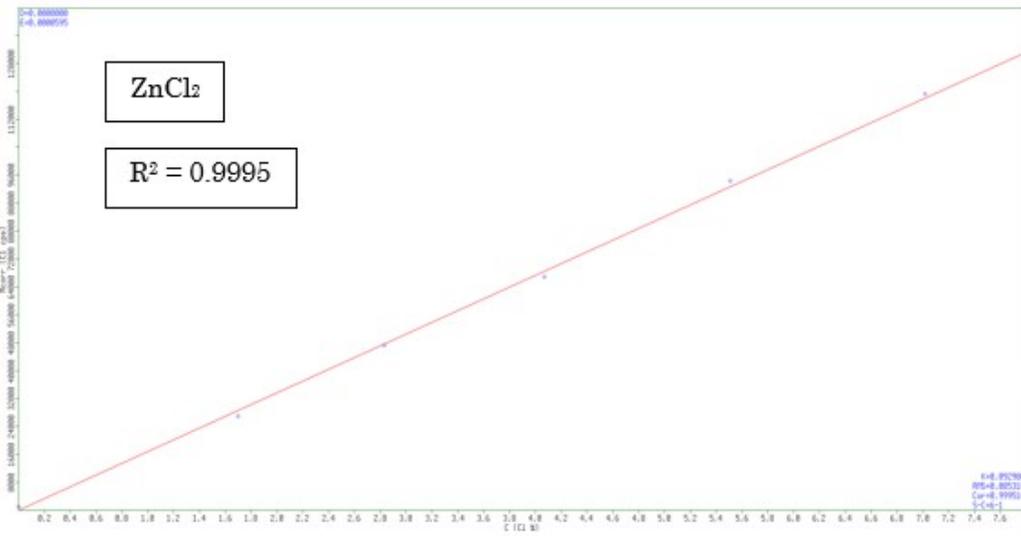


Figure S6. Fluorescence X calibration curves of ZnCl₂ (top), ZnBr₂ (middle), ZnI₂ (bottom) on silica.