Electronic Supplementary Material (ESI) for Chemical Communications.

Fine-tuning of metal work function by molecular doping

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Supplementary Material

1. Additional SEM, TGA and XRD data of the doped silver and gold

SEM images of doped silver indicate a broad particle size distribution ranging from ca. 100 nm to 1 µm. TGA presents weight loss traces the amount of dopant in the composites. Additional characterization of doped silver appeared in the literature[1,2].

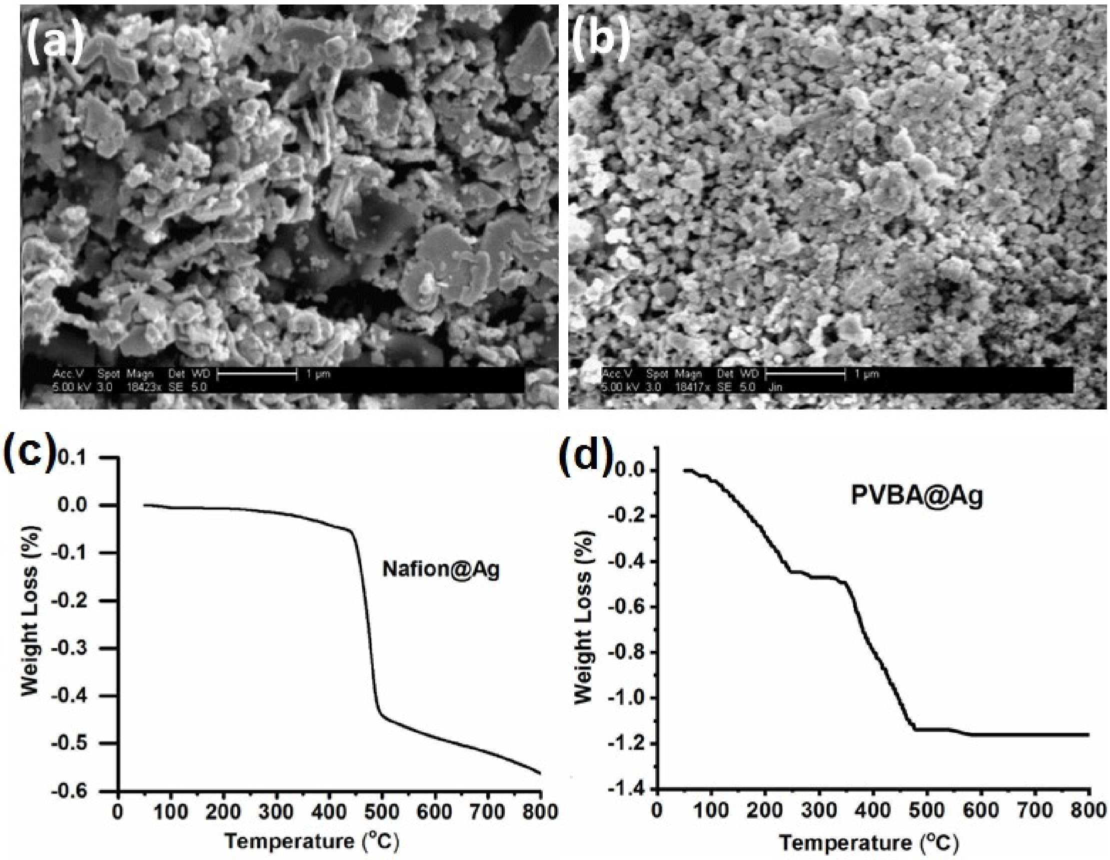

Figure S1. SEM image (bars: 1 µm) and TGA of (a, c) Nafion@Ag; (b, d) PVBA@Ag.

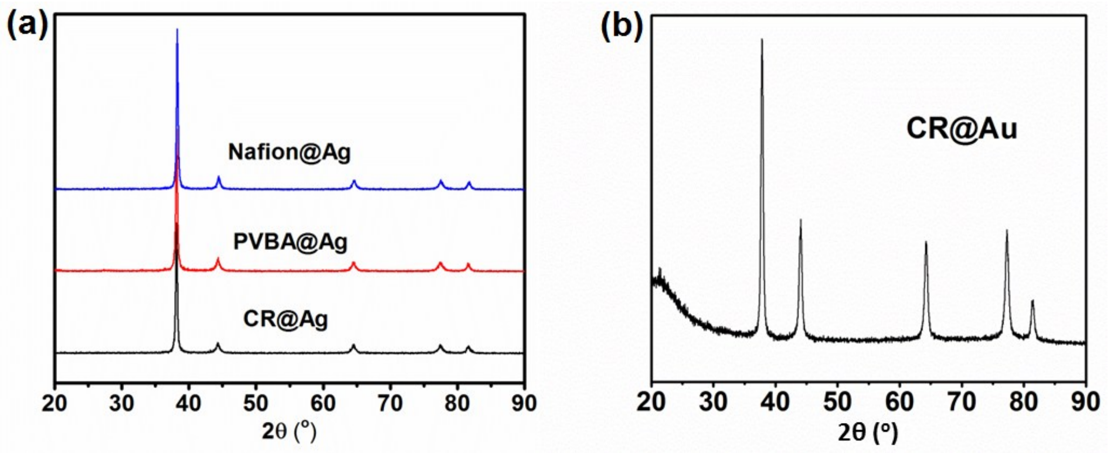

Figure S2. XRD patterns of the (a) doped silver and of (b) CR@Au powder

2. Resistivity and work Function values of the doped metals

Table S1. Resistivity values of representative doped samples

Sample (Disc)	**Resistivity** (Ω*cm)
Ag	$3.0 \pm 0.2 \times 10^{-6}$
CR@Ag	$3.3 \pm 0.2 \times 10^{-6}$
Nafion@Ag	$4.1 \pm 0.4 \times 10^{-6}$
PVBA@Ag	$4.8 \pm 0.3 \times 10^{-6}$
Au	$5.0 \pm 0.2 \times 10^{-6}$
CR@Au	$5.2 \pm 0.3 \times 10^{-6}$

Table S2. Work Function values of the doped metals

Sample (Disc unless described as film)	**WF** (eV)
1 Ag	4.26±0.05
2 CR adsorbed on Ag	4.30±0.04
3 CR@Ag	4.71±0.11
4 CR-extracted@Ag	4.41±0.05
5 CR-reduced@Ag	4.09±0.12
6 Ag treated with $Na_2S_2O_4$	4.20±0.10
7 Au	5.10±0.05
8 CR@Au	5.38±0.06
9 CR-reduced@Au	5.11±0.10
10 Au film	5.10±0.05
11 CR@Au film	5.33±0.07
12 CR-reduced@Au film	5.15±0.11
13 Th@Au film (conc. 3)	5.59±0.01
14 Th@Au film (conc. 1)	5.25±0.05
15 Th @Au film (conc. 2)	5.49±0.01
16 PVBA-OH@Ag	4.53±0.05
17 PVBA-OH adsorbed on Ag	4.28±0.05
18 PVBA-Cl@Ag	4.84±0.07
19 PVBA-OH@Ag after reverse ion-exchanging	4.56±0.06
20 Nafion-H@Ag	4.72±0.02
21 Nafion-H adsorbed on Ag	4.24±0.03
22 Nafion-Mg@Ag	4.62±0.03

3. The reactions of dopants

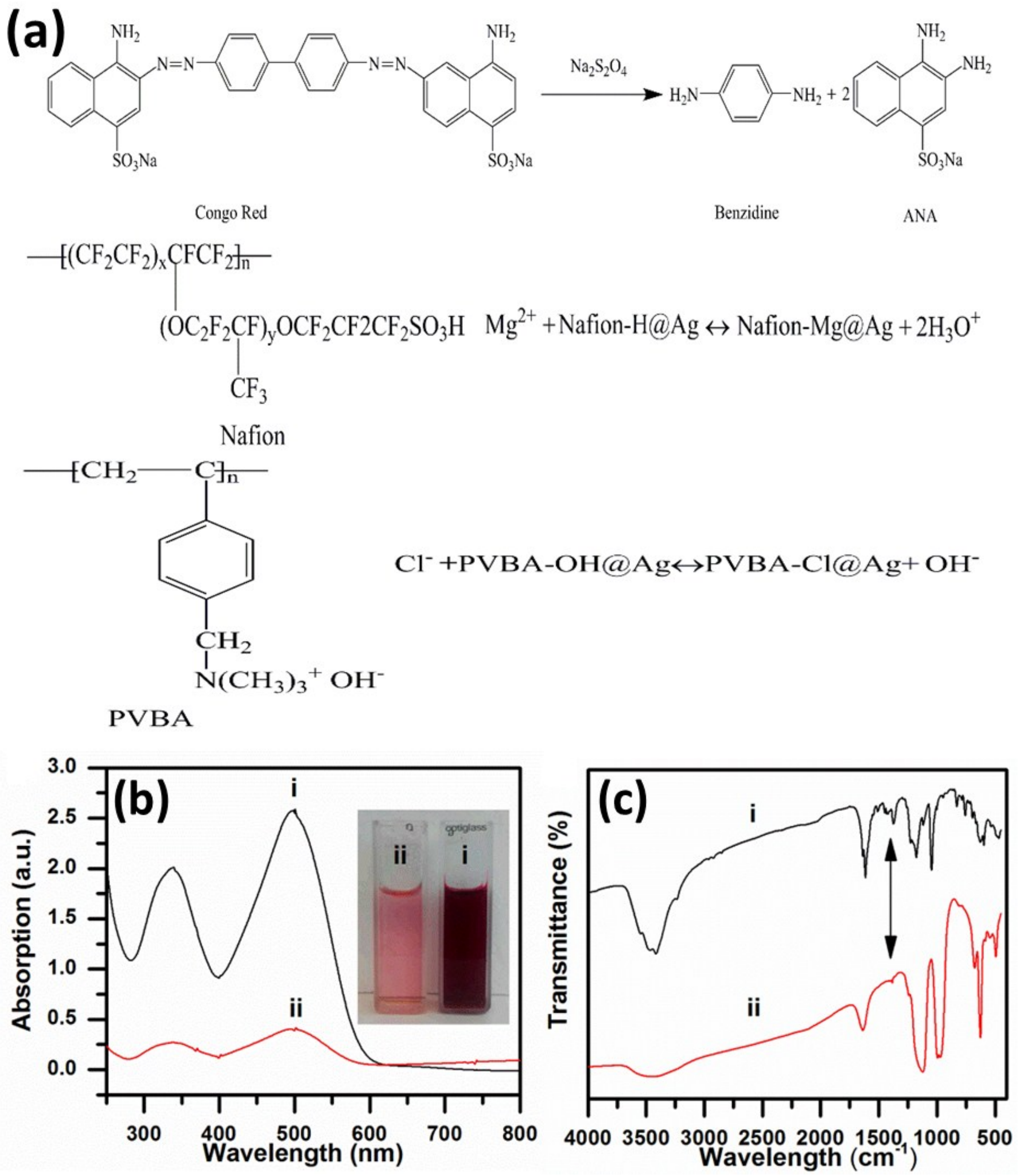

Figure S3. (a) Schemes of the reduction reaction of Congo red in CR@Ag and of the ion-exchange reactions of Nafion@Ag and PVBA@Ag; (b) Absorption spectra and (d) FTIR of CR before (i) and after (ii) reaction with $Na_2S_2O_4$ of the DMSO-extracted CR@Ag.

Table S3. Proton and hydroxyl-ion release from Nafion@Ag and PVBA@Ag

	Added salt	pH	%Exchange
Nafion@Ag	No added salt	6.53	
	$MgSO_4$	5.52	41.2%
PVBA@Ag	No added salt	8.33	
	NaCl	10.07	100%

3. SERS spectra of CR@Ag and Th@Au

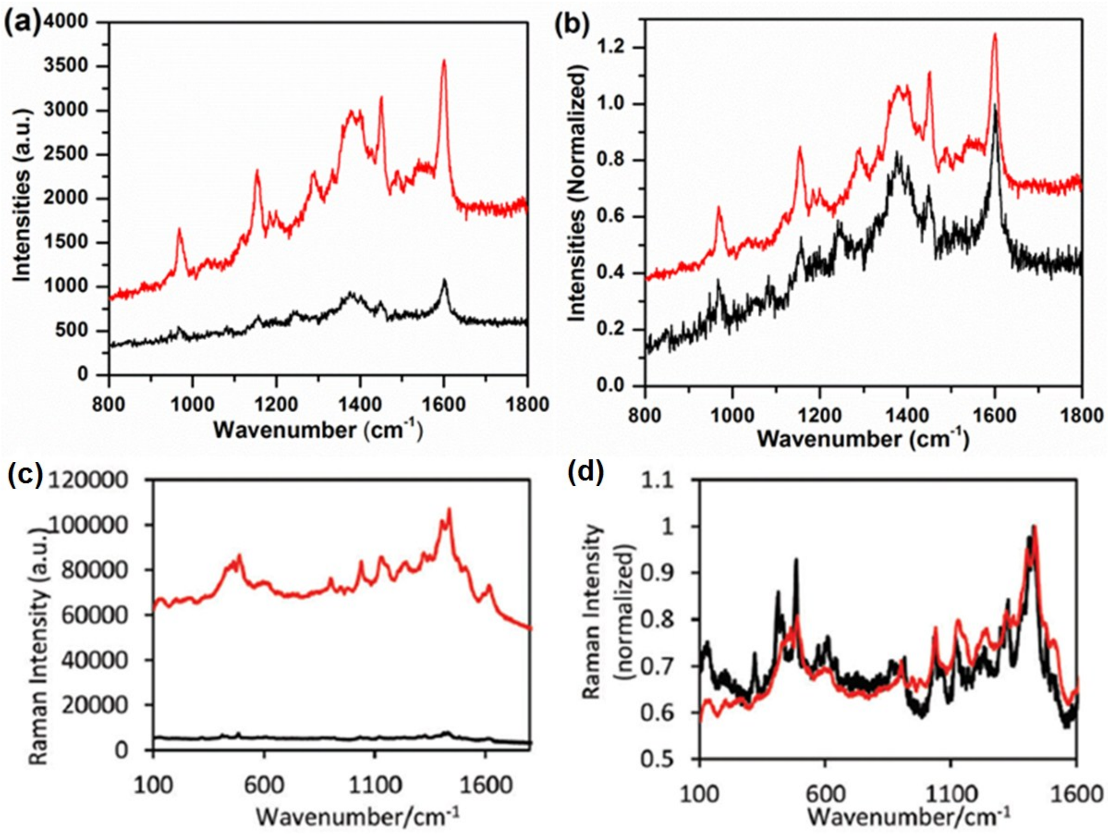

Figure S4. SERS proved to be an efficient analytical tool to determine the entrapment in the films[3]: (a) Congo red within silver (CR@Ag film, Red), compared to CR adsorbed on pure silver electroless layer (black). (b) The normalized intensity spectra of (a). (c) Thionine within gold (Th@Au film, con. 1, red) compared to Th adsorbed on the gold electroless layer (black). (d) The normalized intensity spectra of (c).

5. EDS spectra of Th@Au

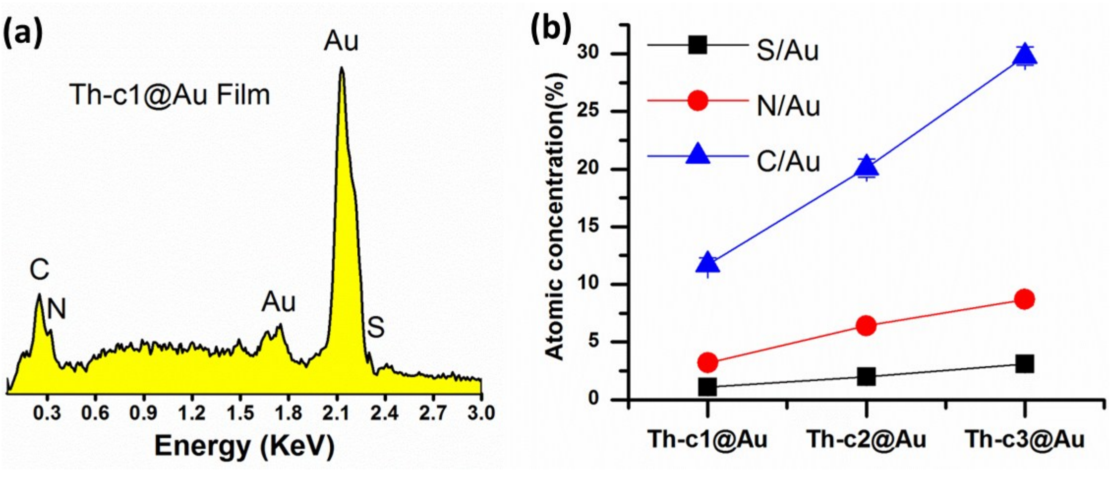

Figure S5. (a) Representative EDS spectrum of Th@Au film, showing the presence of Au, C, N and S. (b) Plot of the atomic concentrations in three Th@Au films.

6. Experimental Details

Chemicals: Congo red (sodium salt), thionine, poly(vinylbenzyltrimethylammonium chloride), silver nitrate and sodium hypophosphite were purchased from Sigma-Aldrich. Sodium tetrachloroaurate(III) dehydrate, sodium chloride, magnesium sulfate and Nafion (5 wt.-%, hydrogen-ion form, equiv. wt., 1100) were purchased from Alfa Aesar.

Materials preparations:

Entrapment of Congo red (CR) in silver or gold [1]: A 10 mL water solution with 0.51 g (3 mmol) $AgNO_3$ or 1.19 g (3 mmol) $NaAuCl_4 \cdot 2H_2O$, 0.161 g (1.8 mmol) NaH_2PO_2 and 0.01 g (0.03 mmol) of CR was stirred at RT for 48 h. The precipitate, (CR@Ag or CR@Au), was filtered and washed with 10 mL distilled water for three times, then dried in vacuum for 24 hours at RT. TGA results prove that 100% of the dye was entrapped in the resulting powders, thus the ratio of CR/Ag or Au is 1:100.

Entrapment of Nafion in silver [2]: Nafion (16 uL, 0.1 mmol), NaOH (18 uL, 1M), and H_2O (2.0 mL) were stirred for half an hour (in order to facilitate cation exchange with Na^+). This solution was then mixed with 6 mL $AgNO_3$ (0.51 g, 3 mmol) aqueous solution. Then, NaH_2PO_2 (0.161 g, 1.8 mmol) was added into the combined solution and stirred for 24 h at room temperature. The reduction, according to Equation 1:

$$2AgNO_3 + NaH_2PO_2 + H_2O \rightarrow 2Ag + NaH_2PO_3 + 2HNO_3 \qquad (1)$$

results in high acidity (pH 1.2), which ensured Nafion is entrapped in the free-acid form (Nafion-H). The precipitate was filtered, washed with distilled water (10 mL) three times and dried for 24 h in vacuum at RT. The resulting material, 0.3 g of Nafion@Ag, contained ~100% of the added polymer in the synthesis, as determined via TGA. The composition therefore is 0.6% wt./wt. (polymer/metal); or by the atomic S/Ag ratio, which is 0.5:100.

Entrapment of PVBA in silver [2]**:** PVBACl (0.084g, 0.1 mmol of monomer) was mixed with $AgNO_3$ (0.51 g, 3 mmol) and NaH_2PO_2 (0.161 g, 1.8 mmol) in 10 mL distilled water, and the solution was stirred at room temperature for 24 h. The precipitate was filtered, washed with three portions of distilled water (10 mL), and dried for 24 h in vacuum, producing 0.27 g of the doped metals. To convert the chloride to the hydroxide, the powder was transferred into a NaOH solution (10 mL, 0.1 M), stirred for 1 h at room temperature, filtered, washed three times with water (10 mL), and dried in vacuum at room temperature, resulting in the basic PVBA@Ag (PVBA-OH@Ag). Based on TGA analysis, the percentage of the entrapped polymer (out of the initial amount) is 36%±5%, i.e., the doping in the final material is 1.2% wt./wt., the monomer/silver ratio is 1:149 and the atomic C/Ag ratio is 1:25.

Preparation of doped metal disc: For the WF measurements, 13 mm diameter disks were prepared by compressing 200 mg of the composite powder at 9,000 PSI for 5 min by using an infra-red (IR) pellet. The pure metals were prepared as described above but without the dopant. For the consistency of the result, all the unreacted disks were re-grinded to powders after WF measurement for further reaction. For comparison with adsorption, one drop of the dopant solution (CR, Nafion and PVBA) (at concentrations of 10 mM) was cast on the silver disc and dried.

Fabrication of the doped gold thin films [3]: The cleaned glass slides were immersed in 0.01 M PDDA solution for 2 hours, rinsed again with water and dried under a nitrogen stream. The polymer-coated slides were subsequently incubated overnight in the colloidal gold solutions and the Au NPs self-assembled on it. The gold layer was rinsed with water and then dried under a nitrogen stream. The improvement of the adhesion and the uniformity of the catalytic layer were achieved by dipping the Au NPs-coated slide in an electroless solution containing 3.8 mL of 1.0 M $NaAuCl_4$ and 10.0 mL of 0.40 mM hydroxylamine hydrochloride for 15 minutes under agitation. The slide was then taken out from the solution and immediately used for the metal doping process: the slide was dipped again in a fresh electroless solution (3.8 mL of 1.0 M $NaAuCl_4$ and 10.0 mL of 0.40 mM hydroxylamine hydrochloride) to which desired amount of 5.0 mM solution of the dopant (12.5 uL for CR and three volume of 12.5, 25 and 50 uL for Th) was added and the slides were then agitated for 60 minutes in that combined solution.

The reactions with the dopants:

Reduction of entrapped CR: A total of 0.1 g of the powdered silver doped with CR was stirred in a solution of 0.1 g (0.049 mmol) of $Na_2S_2O_4$ in 5.0 mL of water for 48 h. The solids were then filtered and washed with three portions of 10 mL distilled water and dried in vacuum at RT. The content of the doped metal after reaction was extracted with 5.0 mL DMSO, and the amount of extractable unreacted dye was determined spectroscopically and compared to unreacted doped silver, which was extracted similarly. The pure home-made silver powder has also been treated with $Na_2S_2O_4$ by the same procedure for comparison.

Ion exchange with Nafion@Ag: Nafion@Ag (0.1 g) was added to an aqueous solution (10 mL) of $MgSO_4$ (0.01 M). The slurry was stirred for two hours to liberate the hydronium ions and the amount releases was measured (pH meter). The percentage of accessible, exchangeable hydronium ions was calculated by dividing the number of moles of hydronium ions that 1g of Nafion released in salt solution by dividing the number of moles of hydronium ions that 1g of Nafion@Ag contains.

Ion exchange with PVBA@Ag: A similar procedure of ion exchange with Nafion@Ag was used to affect the release of hydroxyl ions. NaCl solution was used here as a Cl^- source.

Instrumentation:

Work function measurements: The macroscopic Kelvin probe (KP) technique was performed under ambient conditions using a 0.5 mm diameter gold tip amplifier (Ambient Kelvin Probe Package from KP Technology Ltd.) with vibrating at fixed frequency of 150 Hz. The disc or film of dopant@metal placed on a conducting support is grounded. A steady AC current develops in the tip-sample capacitor and an additional DC bias is then applied between the electrodes to nullify the AC current. KP techniques provide a voltage resolution of about 5 mV, while the lateral resolution is a few millimeters for KP, respectively. Calibration of the probe was performed against a freshly cleaved High Oriented Pyrolytic Graphite surface for both techniques. In order to check the stability of the sample, KP measurements were performed on three different points of the same sample.

Other instrumentation: High resolution scanning electron microscopy (HR-SEM) observations were performed with a Sirion (FEI) or Magellan (400L) microscopes, operating at 5 or 10 kV. Powders or metal thin film coated on glass were mounted on an aluminum stub using carbon double side tape. Thermogravimetric analysis was performed by using a Mettler–Toledo TGA/SDTA 851e from 50 to 800 ^{o}C with a heating rate of 10 ^{o}C in flowing air. Surface enhanced Raman spectroscopy (SERS) measurement were taken using a Renishaw InVia Raman Microscope with a maximum output of 25 mW and 300 mW at a wavelength of 514 nm for CR and 785 nm for Th for excitation (only 0.0001% power of the laser was used). UV-vis absorption spectroscopy was carried out with a Jasco V-630 spectrophotometer and FTIR spectroscopy with a Bruker Vector 22 FTIR instrument. XRD measurements were carried out on a Philips automated powder diffractometer with a Cu Kα1 (1.5406 °A) radiation source. The source tension and current are 40 kV and 40 mA, respectively. The electrical resistivity was measured using an in-line Four Point Probe (Lucas Labs S-302-4).

References:

1. H. Behar-Levy and D. Avnir, *Chem. Mater.* **2002**, 14, 1736-1741.
2. H. Behar-Levy and D. Avnir, *Adv. Funct. Mater.* **2005**, 15, 1141-1146.
3. H. Naor, Y. Divon, L. Iagher, L. Etgar and D. Avnir, *J. Mater. Chem. C.* **2016**, 4, 11548-11556.