

Type of the Paper (Supplementary Material)

# Excellent cooperation between carboxyl-substituted porphyrins, k-carrageenan and AuNPs for extended application in CO<sub>2</sub> capture and manganese ion detection

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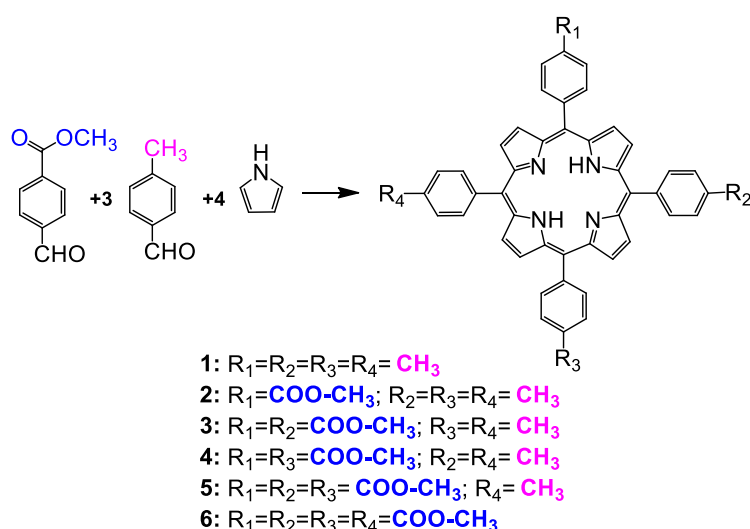
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## 2.3. Synthesis of 5-(4-methoxy-carbonyl-phenyl)-10,15,20-tris-(4-methyl-phenyl)-porphyrin (5-COOCH<sub>3</sub>-3MPP)

To a quantity of 2.25 g (13.70 mmol) methyl-4-formylbenzoate and 4.93 mL (41.11 mmol) 4-methylbenzaldehyde dissolved in 280 mL propionic acid 7.13 mL (54.82 mmol) propionic anhydride were added, for the consumption of the water generated during the reaction in order to favour the shift of the equilibrium to the right. The mixture was brought to reflux at 141.2 °C under intense stirring. Then, a mixture of 3.6 mL (54.82 mmol) pyrrole dissolved in 6.45 mL propionic acid was added dropwise and the reflux was maintained for 3.5 hours more.

The mixture of reaction products (Figure S1) was then left overnight to cool to room temperature and a purple precipitate was formed. The precipitate was filtered, repeatedly washed with portions of 50 mL of hot distilled water (90 °C) and dried. The filtrate was collected and 100 mL hexane was added. The next day another round of precipitate was filtered, washed and dried. The second filtrate was also washed with hot water and dried. The reunited precipitates were all subjected to TLC analysis in dichloromethane.



**Figure S1.** The multicomponent synthesis of 5-(4-methoxycarbonyl-phenyl)-10,15,20-tris-(4-methyl-phenyl)-porphyrin and the mixture of six resulted porphyrins

It can be noticed that by using as eluent  $\text{CH}_2\text{Cl}_2$  (Figure S2), 4 main components were separated by thin layer chromatography (TLC) from the reaction mixture, at the following  $R_f$ : 0.94; 0.76; 0.55; 0.39. The separation of the four components was then performed on chromatographic column, using Silica gel (0.04 - 0.06 mm, 230 - 400 mesh) from Scharlab and dichloromethane as eluent. The component that eluted first was proven by NMR to be tetratolylporphyrin, and the second, having  $R_f$  at 0.76, was the 5-(4-methoxy-carbonyl-phenyl)-10,15,20-tris-(4-methyl-phenyl)-porphyrin, that is our desired compound.



**Figure S2.** The TLC plate presenting the four separated compounds from the multicomponent synthesis of 5-(4-methoxycarbonyl-phenyl)-10,15,20-tris-(4-methyl-phenyl)-porphyrin, eluted with  $\text{CH}_2\text{Cl}_2$

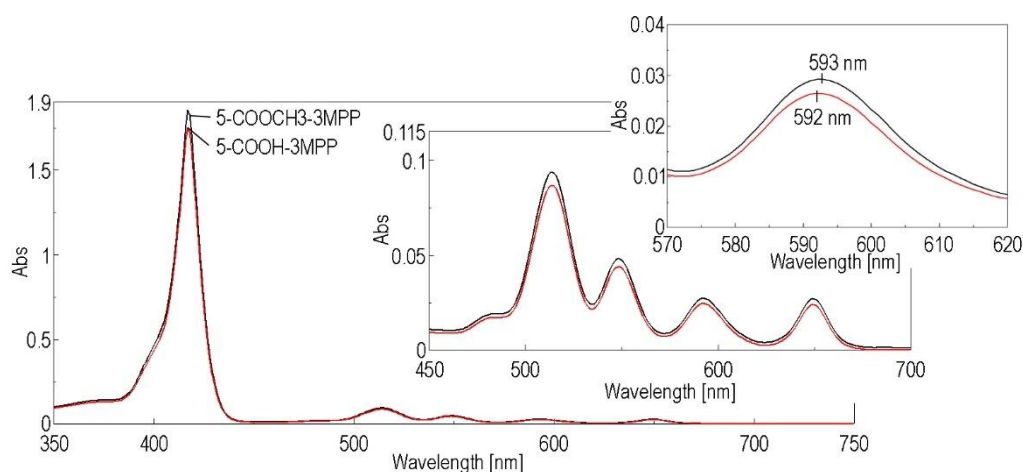
#### 2.4. Hydrolysis of porphyrin ester (5-COOCH<sub>3</sub>-3MPP) to 5-(4-carboxy-phenyl)-10,15,20-tris-(4-methyl-phenyl)-porphyrin (5-COOH-3MPP)

The porphyrin ester 5-(4-methoxy-carbonyl-phenyl)-10,15,20-tris-(4-methyl-phenyl)-porphyrin was hydrolysed [37, 38] into the carboxyl-porphyrin derivative (Figure 2, main text) using a mixture of KOH and ethanol (strong alkaline catalysis), as follows: to a quantity of 0.21 g (0.29 mmol) of 5-(4-methoxy-carbonyl-phenyl)-10,15,20-tris-(4-methyl-phenyl)-porphyrin dissolved in 100 mL THF a mixture of 50 mL KOH ( $c = 2$  M, 10 mmol) and 60 mL ethanol was added dropwise under reflux. The reflux was maintained for 4 hours. After the reaction mixture was cooled to room temperature, a solution of HCl ( $c = 1$  M) was added to reach  $\text{pH} = 6.8$ . The porphyrin was then repeatedly extracted with portions of 50 mL chloroform. The organic extracts were unified and washed with saturated sodium carbonate solution, then twice with distilled water. After drying with anhydrous sodium sulfate, the organic extract is filtered and the solvent is removed at low pressure.

#### 2.5. Physical-chemical characterization of the obtained compounds

##### 2.5.1. UV-Vis comparison of (5-COOCH<sub>3</sub>-3MPP) and (5-COOH-3MPP)

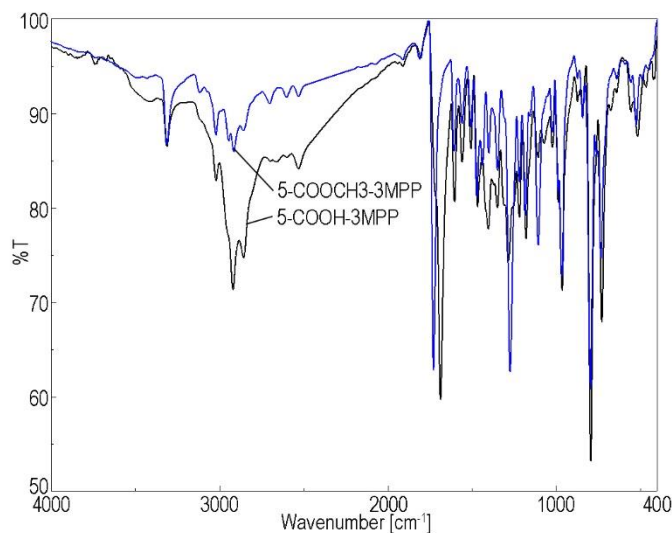
Figure S3 presents the overlapped UV-Vis spectra of the porphyrin ester (5-COOCH<sub>3</sub>-3MPP) and the carboxy-porphyrin (5-COOH-3MPP). It can be observed that the hydrolysis of the ester group leads to the diminishing of the absorption intensity of the Soret band, although the molar extinction coefficients of Soret bands of both derivatives have similar values, and to a slight hypsochromic shift of the QII band (Figure S3-detail). This minor change addressing only to the intensity of absorption and to a small blue shift of QII band is expected due to the little modification of only one peripheral substituent of the porphyrin macrocycle from an ester to a carboxyl functional group [39].



**Figure S3.** Superposed UV-Vis spectra of (5-COOCH<sub>3</sub>-3MPP) and (5-COOH-3MPP) in THF, both solutions of equal concentration,  $c = 4.095 \times 10^{-6} \text{ M}$ , 1 cm optical path length, scan speed of 1000 nm/min and blank line was obtained in bare THF.

### 2.5.2 FT-IR comparison of (5-COOCH<sub>3</sub>-3MPP) and (5-COOH-3MPP)

Analysing the FT-IR spectra of the two porphyrins (Figure S4), it can be observed that the C-O stretching vibration present in the porphyrin ester (5-COOCH<sub>3</sub>-3MPP) located at  $1272 \text{ cm}^{-1}$  [40] and the band located at  $1728 \text{ cm}^{-1}$  representing the stretching of the C=O group in the ester [41] are no longer noticed in the FT-IR spectrum of the carboxylic porphyrin (5-COOH-3MPP), where the bands located at  $1686 \text{ cm}^{-1}$  and  $1283 \text{ cm}^{-1}$  stand for the C=O stretching frequencies of carboxyl group [42]. Besides, the medium intensity bands located in the range of  $1440 - 1395 \text{ cm}^{-1}$  and the band located at  $796 \text{ cm}^{-1}$  are belonging to N-H vibrations in pyrrole [43]. The common bands located around  $965 \text{ cm}^{-1}$  in both FT-IR spectra are assigned to C-H and C=C bending vibrations [44].

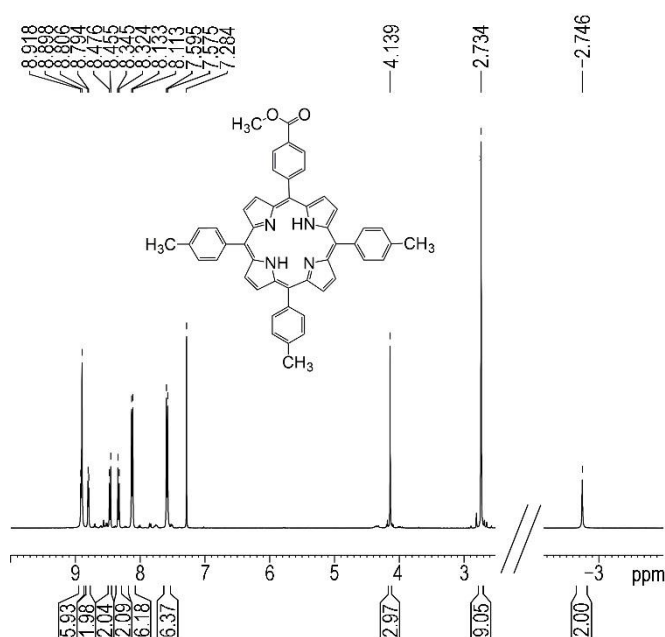


**Figure S4.** Overlapped FT-IR spectra of (5-COOCH<sub>3</sub>-3MPP) and (5-COOH-3MPP) in KBr pellets

### 2.5.3. NMR analysis for (5-COOCH<sub>3</sub>-3MPP) and (5-COOH-3MPP)

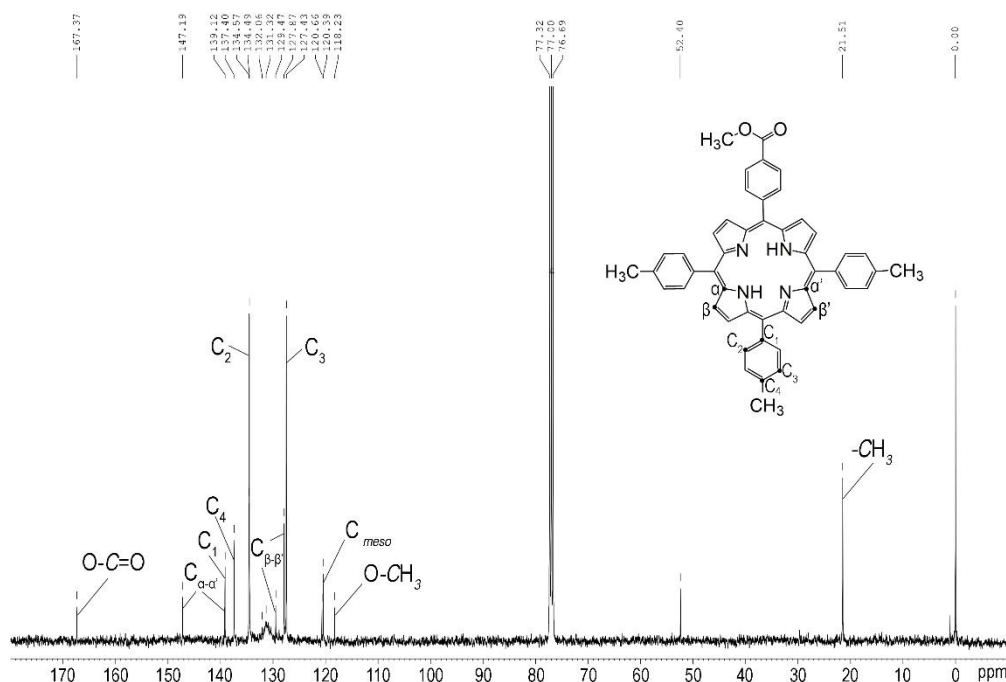
Analysing the <sup>1</sup>H-NMR of compound 5-(4-methoxy-carbonyl-phenyl)-10,15,20-tris-(4-methyl-phenyl)-porphyrin (Figure S5) it can be concluded that the signals location and the ratios between all types of protons are correct, thus justifying the proposed structure. The  $\beta$ -pyrrolic protons present a double doublet in the 8.91 - 8.79 ppm interval; the *ortho*-phenyl protons belonging to the methyl-benzoate group give signal in the 8.47 - 8.45 ppm interval; the *meta*-phenyl protons of the methyl-benzoate group resonate between 8.34 and 8.32 ppm; the doublet in the 8.13 - 8.11 ppm range is attributed to *ortho*-phenyl protons from the tolyl group; the *meta*-phenyl protons from the tolyl functional group can be identified also as doublet, in the interval of 7.59 to 7.57 ppm. The aliphatic protons of -OCH<sub>3</sub> substituent appear as

singlet signal at 4.13 ppm; The singlet at 2.73 ppm is assigned to the protons belonging to the  $-CH_3$  group and the internal  $-NH$  protons are distinctively placed at  $-2.74$  ppm, due to shielding.



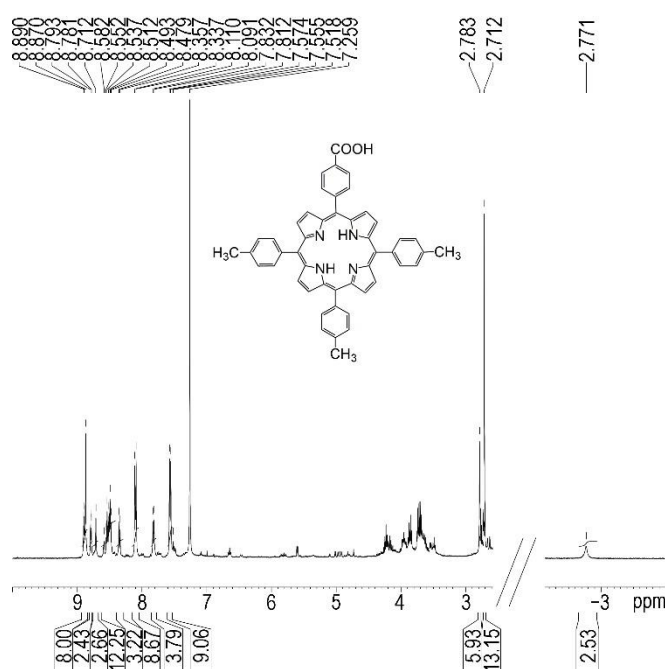
**Figure S5.**  $^1H$ -NMR spectrum of (5-COOCH<sub>3</sub>-3MPP)porphyrin in  $CDCl_3$

In the  $^{13}C$ -NMR spectrum of 5-(4-methoxycarbonyl-phenyl)-10,15,20-tris-(4-methyl-phenyl)-porphyrin (Figure S6) the triplet signal around 77 ppm is attributed to  $CDCl_3$  solvent. The signal of the aliphatic  $-CH_3$  carbon atom is present at 21.51 ppm; the other aliphatic carbon atoms of the  $-O-CH_3$  group resonate at 118.23 ppm; the pyrrolic carbon atoms give signal at 147.19 ppm; and the carbon atoms from the benzene rings are present in the 120.39 - 139.12 ppm interval. The carbon atom linked to  $O-C=O$  in the ester group gives signal at 167.37 ppm.



**Figure S6.**  $^{13}C$ -NMR spectrum of 5-(4-methoxycarbonyl-phenyl)-10,15,20-tris-(4-methyl-phenyl)-porphyrin

The carboxyl porphyrin (5-COOH-3MPP) was also investigated by  $^1H$ -NMR spectroscopy (Figure S7) and it can be observed that the singlet signal specific for the three protons of the  $-OCH_3$  group found in the ester at 4.13 ppm is no longer present, fact that confirms the hydrolysis of the ester to carboxylic acid.



**Figure S7.**  $^1\text{H}$ -NMR spectrum of (5-COOH-3MPP) porphyrin in  $\text{CDCl}_3$

### 2.6. Method of obtaining (5-COOH-3MPP)-*k*-carrageenan composite material

A quantity of 40 mg k-carrageenan ( $5.07 \times 10^{-2}$  mmol) and 4 mg ( $5.71 \times 10^{-3}$  mmol) of 5-(4-carboxyphenyl)-10,15,20-tris-(4-methyl-phenyl)-porphyrin were stirred together vigorously in 35 mL dimethylformamide (DMF) and refluxed for 2 hours. Then, after cooling, the mass was centrifuged and the gel deposited at the bottom of the flasks was collected.

### 3.1. The installation for capturing CO<sub>2</sub> gas by the (5-COOH-3MPP)-k-carrageenan composite material, in DMF/water mixture

Figure S8 presents the used installation for bubbling the CO<sub>2</sub> gas into the porphyrin-k-carrageenan composite.

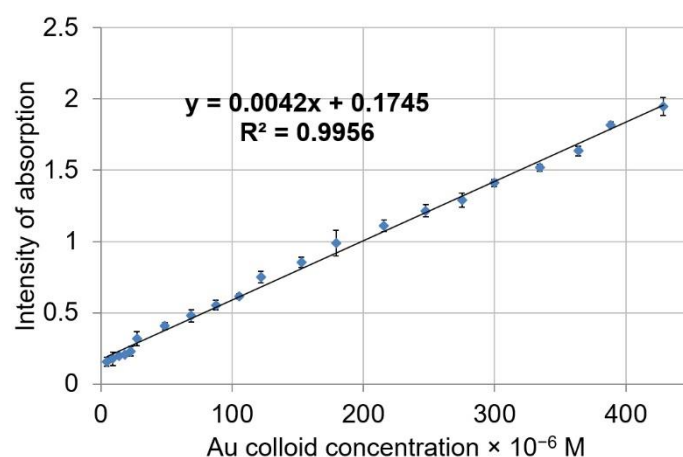


**Figure S8.** The installation for the capturing of CO<sub>2</sub> gas by the porphyrin-k-carrageenan composite material

### 3.2.1. The capacity of the 5-COOH-3MPP porphyrin-k-carrageenan composite material to detect AuNPs

A conclusion after the formation of plasmonic material 5-COOH-3MPP porphyrin-k-carrageenan-AuNPs is that the 5-COOH-3MPP porphyrin-k-carrageenan composite material is able to detect gold nanoparticles over a large concentration domain:  $4 \times 10^{-6}$  M to  $4 \times 10^{-4}$  M (Figure S5) very useful for the monitoring of gold nanoparticles in fibroblasts.

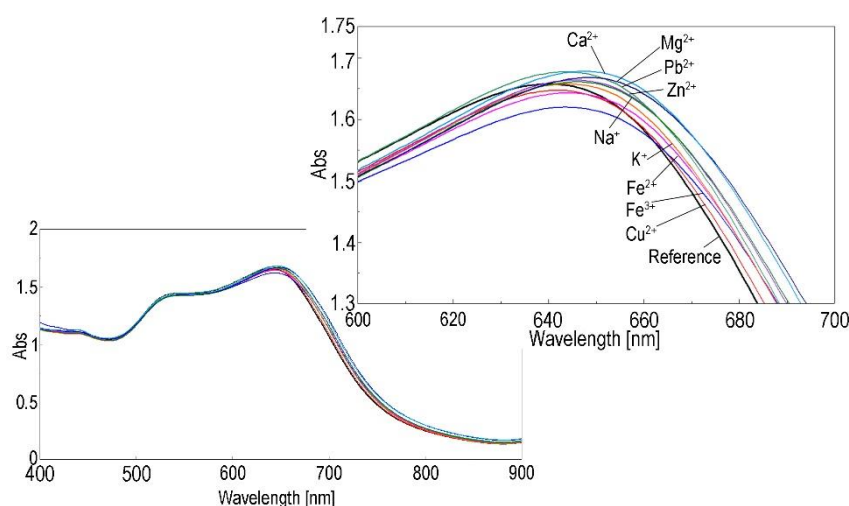
AuNPs particles above 4–5 nm in diameter are nontoxic after acute exposures [45] but induce more gene expression changes than the chronic counterpart. Smaller particles of AuNPs become catalytically active and can induce cytotoxicity. Longterm low doses of AuNPs (0.1 nM) applied during 20 weeks to a commonly used human skin cell model (human dermal fibroblasts) are able to induce hypoxia, oxidative stress, and inflammation in fibroblasts, that have an essential role in cell homeostasis [46, 47].



**Figure S9.** Linear dependence between the intensity of absorption of 5-COOH-3MPP porphyrin-k-carrageenan material measured at 520 nm and the AuNPs concentration.

### 3.4. Interference study

The UV-Vis study to reveal the effect of interfering cations to  $\text{Mn}^{2+}$  detection is presented in Figure S10.



**Figure S10.** Overlapped UV-vis spectra for the reference and for the presence of each interfering metallic salt:  $\text{CuCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{FeSO}_4$ ,  $\text{KCl}$ ,  $\text{NaCl}$ ,  $\text{ZnCl}_2$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{MgSO}_4$ ,  $\text{CaCl}_2$

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