

# Supporting Information

## Highly Networked Capsular Silica–Porphyrin Hybrid Nanostructures as Efficient Materials for Acetone Vapor Sensing

*Izabela Osica<sup>1,2</sup>, Gaku Imamura<sup>1</sup>, Kota Shiba<sup>1</sup>, Qingmin Ji<sup>1</sup>, Lok Kumar Shrestha<sup>1</sup>,  
Jonathan P. Hill<sup>\*1</sup>, Krzysztof J. Kurzydłowski<sup>2</sup>, Genki Yoshikawa<sup>1</sup>, Katsuhiko Ariga<sup>\*1</sup>*

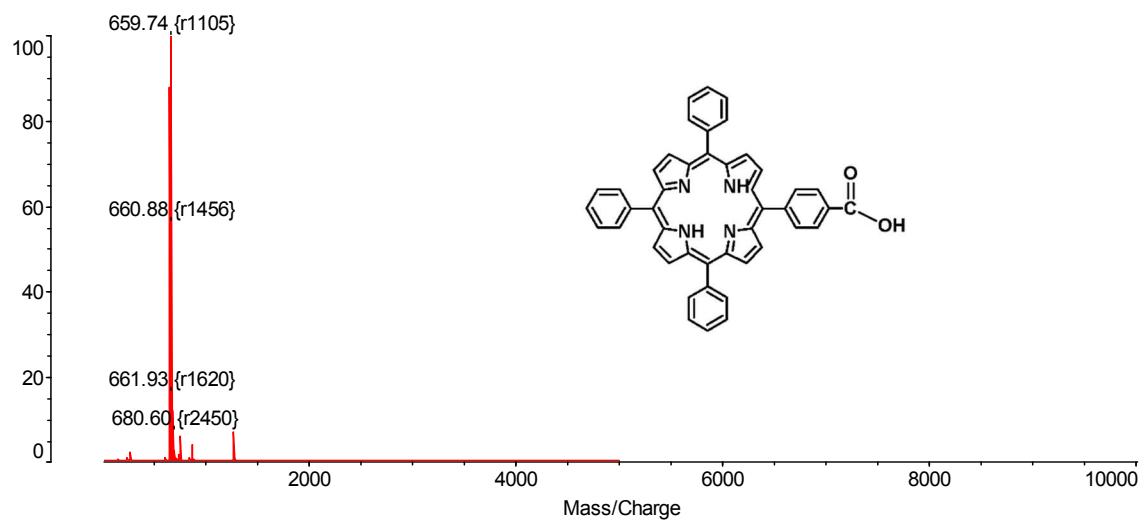
1. World Premier International (WPI) Research Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba 305-0044, Japan

2. Faculty of Materials Science and Engineering, Warsaw University of Technology, Warsaw, Poland

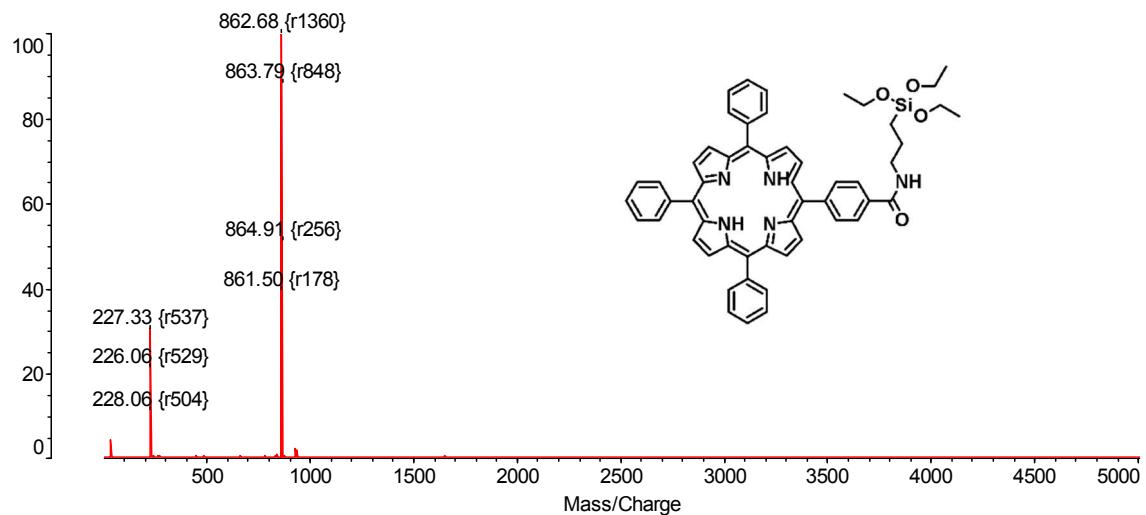
Corresponding authors: Jonathan P. Hill and Prof. Dr. Katsuhiko Ariga

E-mail: [Jonathan.HILL@nims.go.jp](mailto:Jonathan.HILL@nims.go.jp)

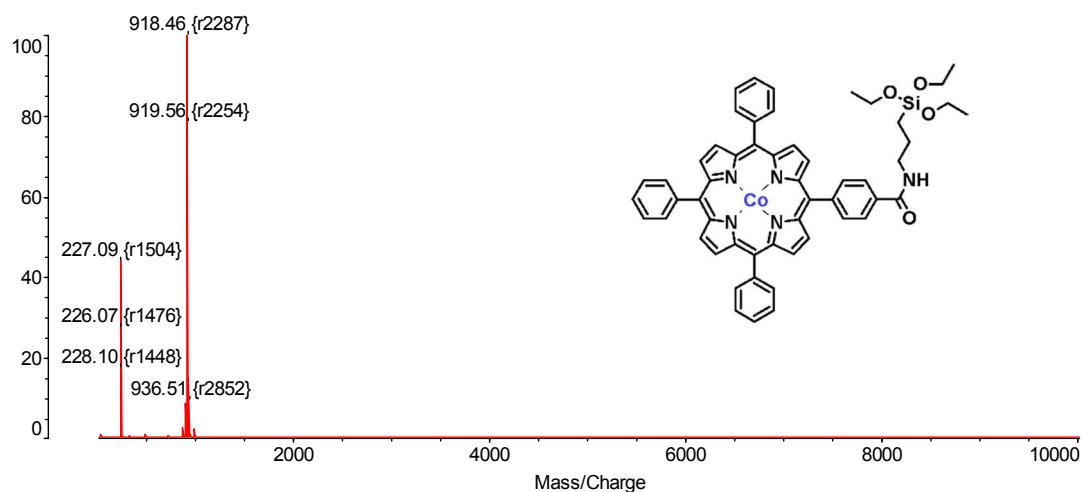
[ARIGA.Katsuhiko@nims.go.jp](mailto:ARIGA.Katsuhiko@nims.go.jp)



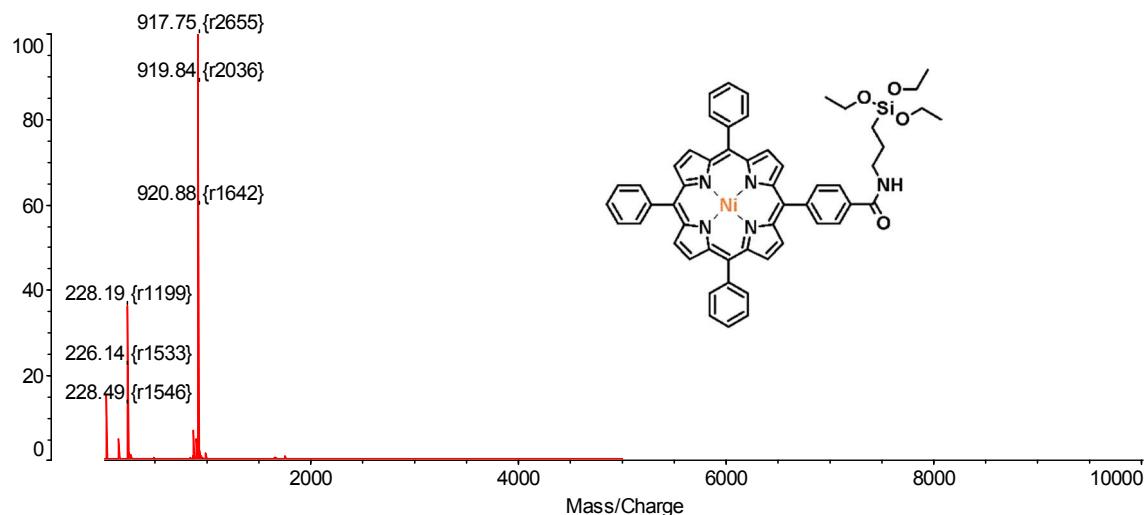
**Figure S1.** MALDI-TOF MS spectrum of 5-(4-Carboxylphenyl)-10,15,20-triphenylporphyrin (**2**).



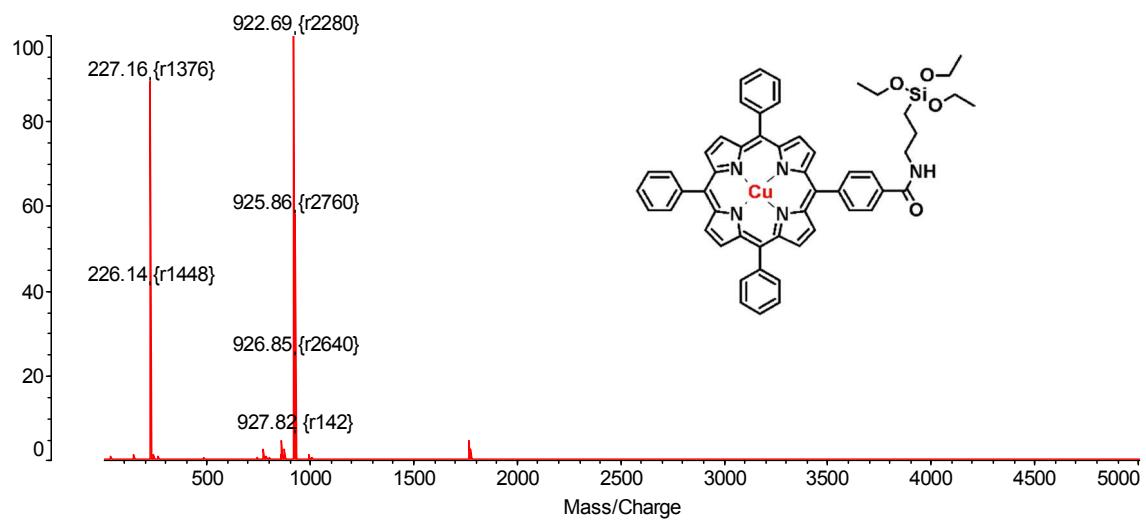
**Figure S2.** MALDI-TOF MS spectrum of 5-[4-(N-(3-Triethoxysilylpropylbenzamido))-]10,15,20-triphenylporphyrin (**4**).



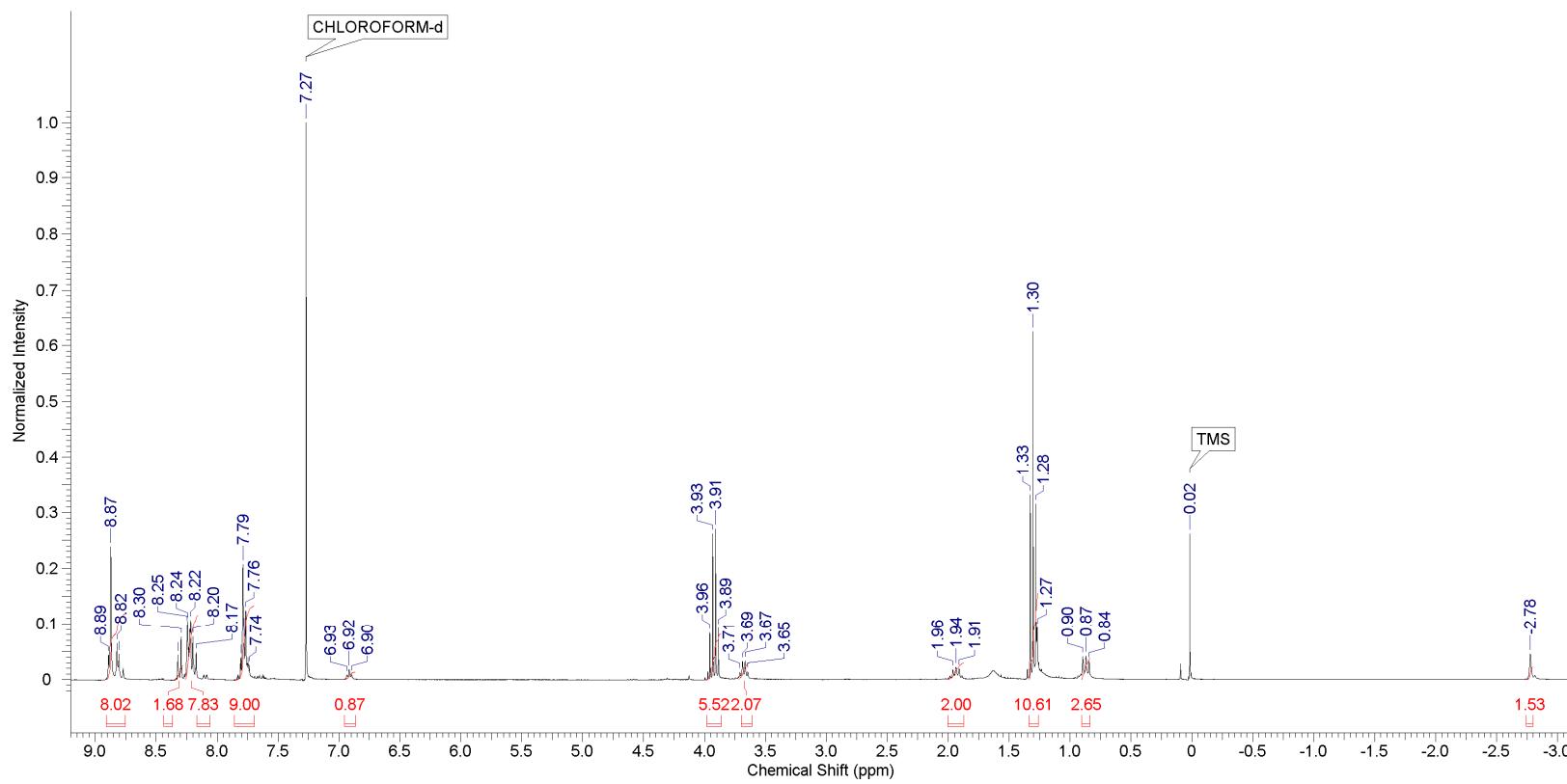
**Figure S3.** MALDI-TOF MS spectrum of 5-[4-(N-(3-Triethoxysilylpropylbenzamido))-10,15,20-triphenylporphinato cobalt(II) (**4Co**).



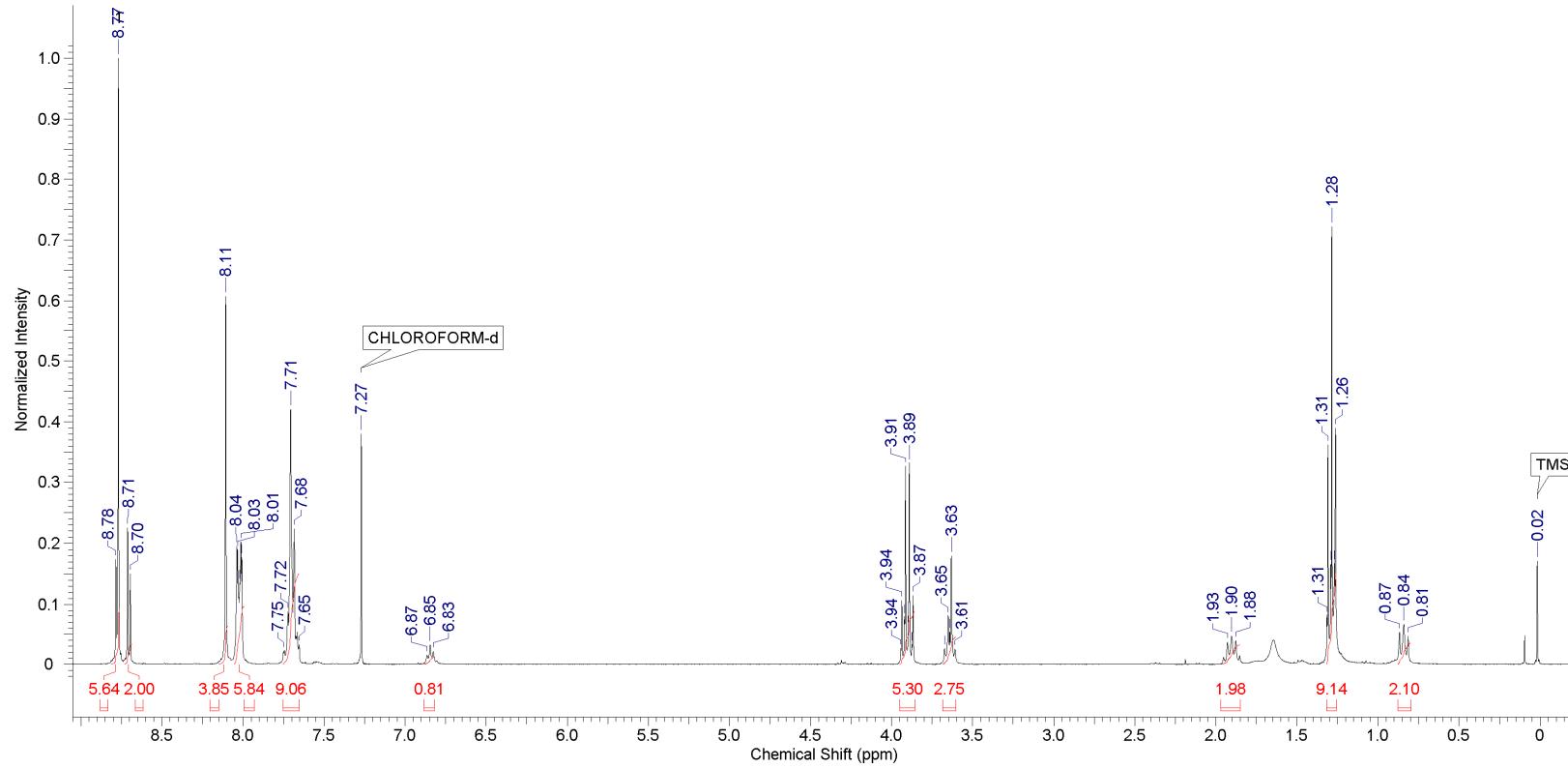
**Figure S4.** MALDI-TOF MS spectrum of 5-[4-(N-(3-Triethoxysilylpropylbenzamido))-10,15,20-triphenylporphinato nickel(II) (**4Ni**).



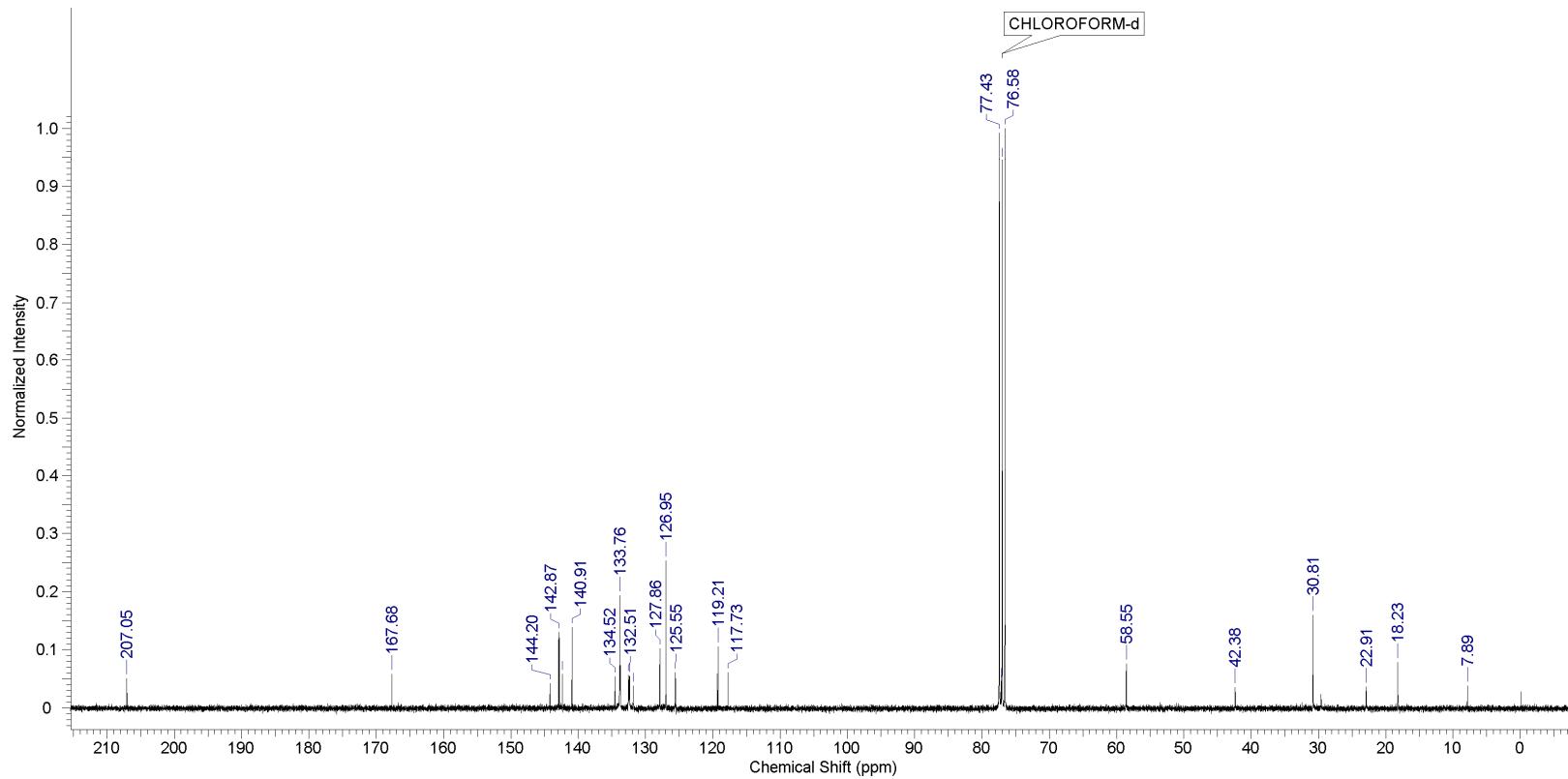
**Figure S5.** MALDI-TOF MS spectrum of 5-[4-(N-(3-Triethoxysilylpropylbenzamido))-10,15,20-triphenylporphinato copper(II) (**4Cu**).



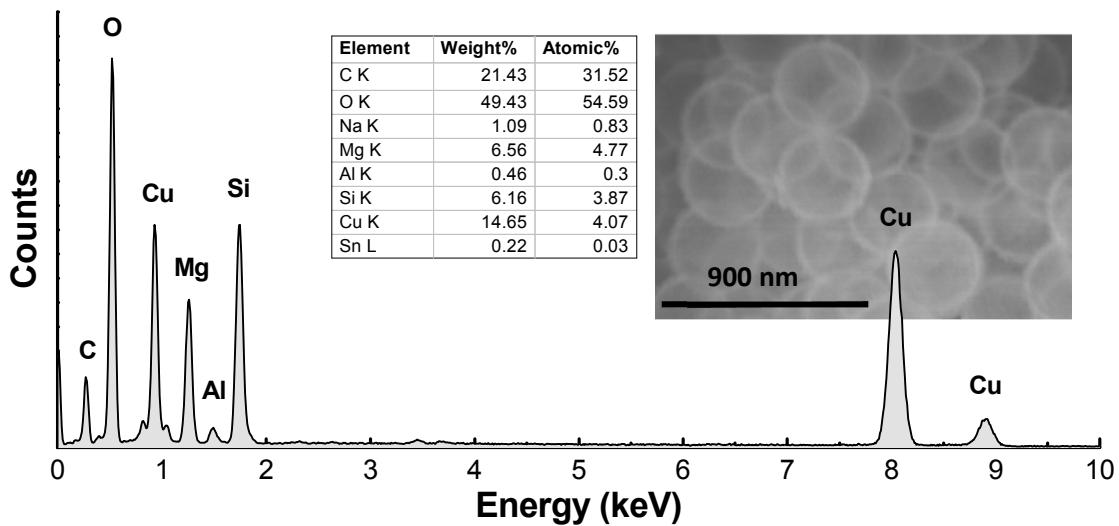
**Figure S4.**  $^1\text{H}$  NMR spectrum of 5-[4-(N-(3-Triethoxysilylpropylbenzamido))]-10,15,20-triphenylporphyrin (**4**).



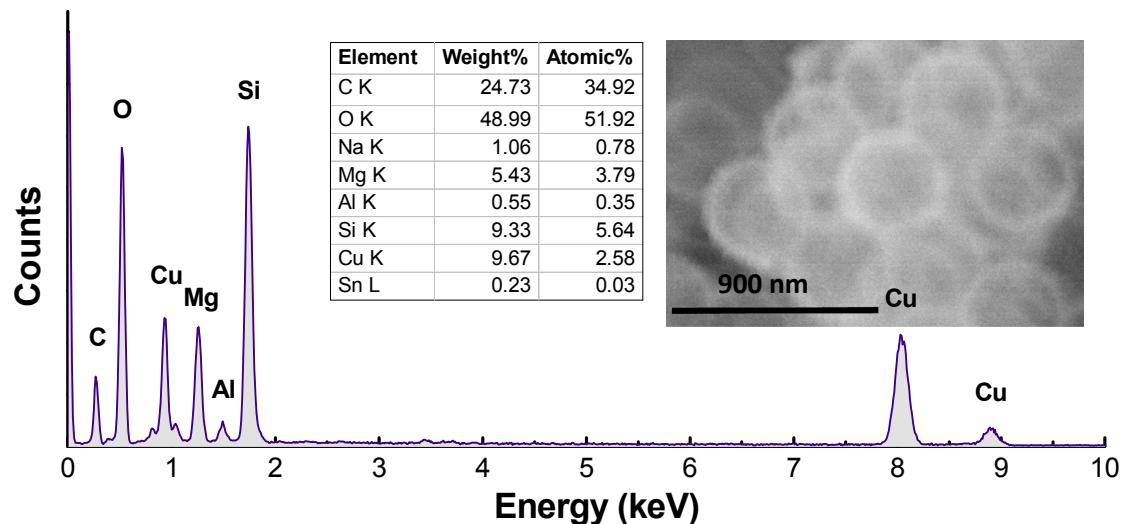
**Figure S5.** <sup>1</sup>H NMR spectrum of 5-[4-(N-(3-Triethoxysilylpropylbenzamido))] - 10,15,20-triphenylporphinato nickel(II) (**4Ni**).



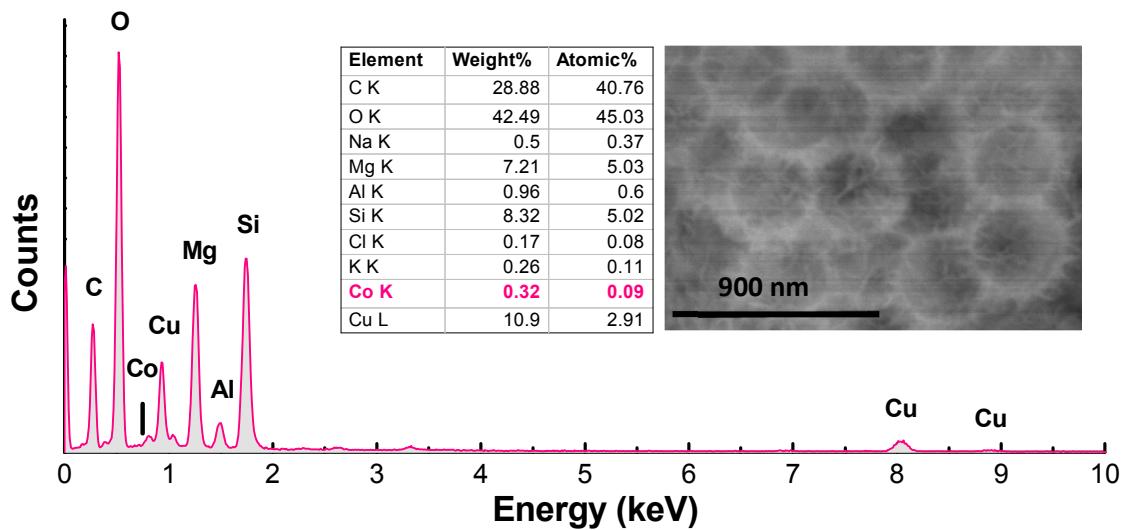
**Figure S6.**  $^{13}\text{C}$  NMR spectrum of 5-[4-(N-(3-Triethoxysilylpropylbenzamido))] -10,15,20-triphenylporphinato nickel(II) (**4Ni**) recorded at 25 °C.



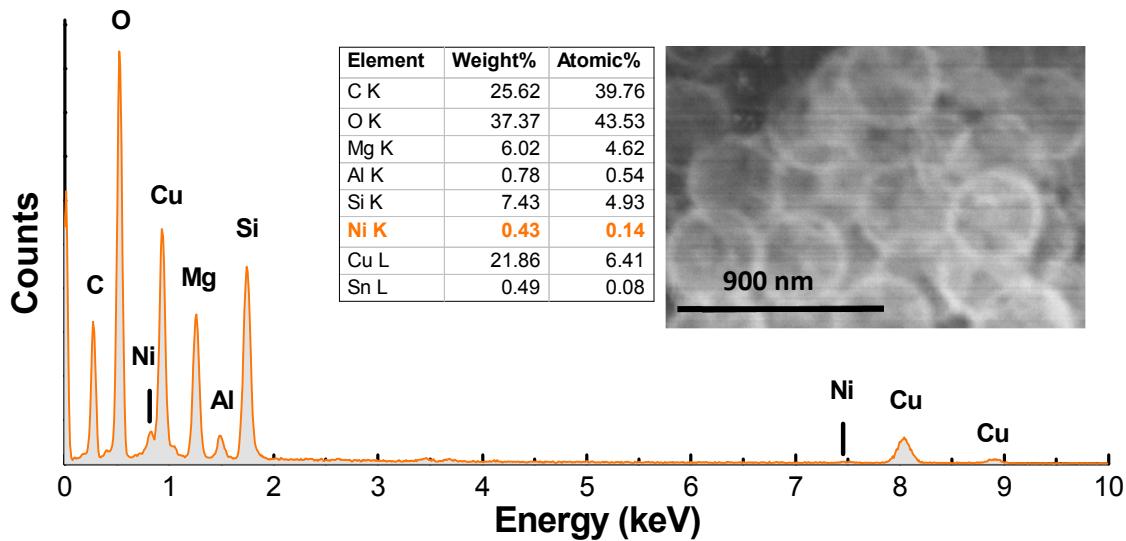
**Figure S7.** EDX spectra of SFS compound. Carbon and copper appear as a background of a copper gird coated with carbon film.



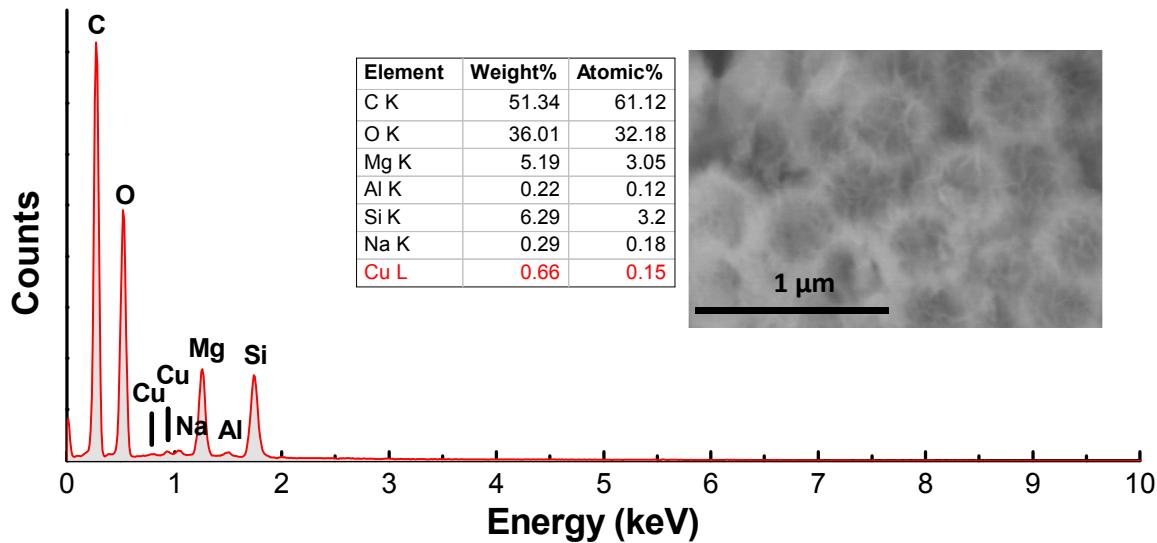
**Figure S8.** EDX spectra of SFS4 compound. There is no significant difference observed after SFS functionalization with free base porphyrin (**4**), although slight increase of carbon content was observed.



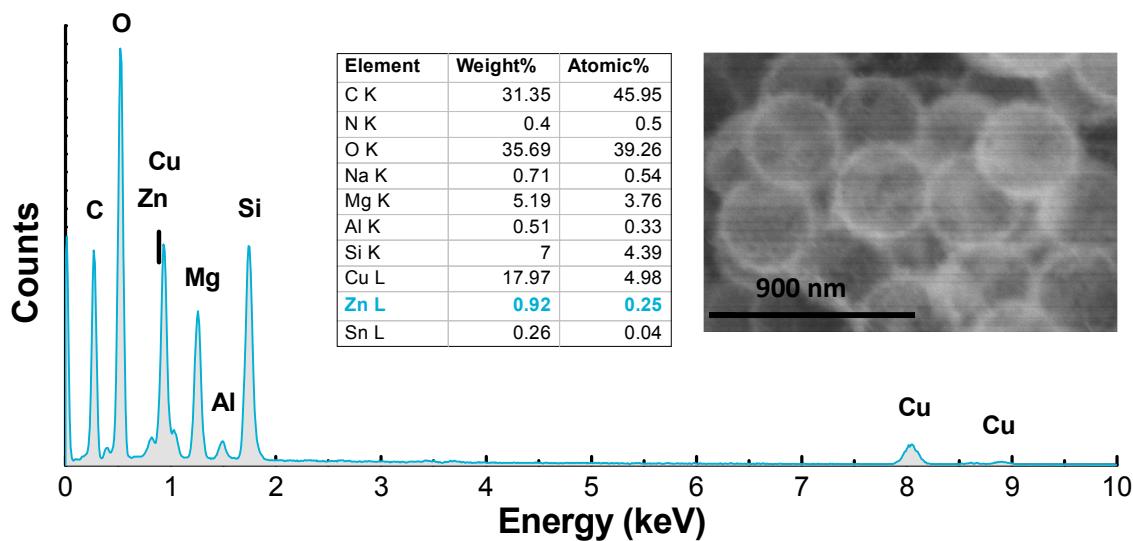
**Figure S9.** EDX spectra of SFS4Co compound. The spectrum showed evidence for successful cobalt porphyrin complex (**4Co**) functionalization of SFS material.



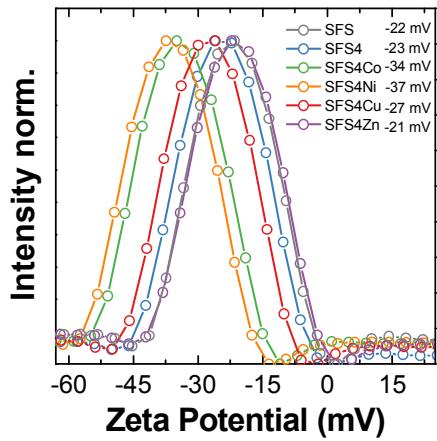
**Figure S10.** EDX spectra of SFS4Ni compound. A slight amount of nickel could be recognized as an evidence of successful SFS functionalization with nickel porphyrin complex (**4Ni**).



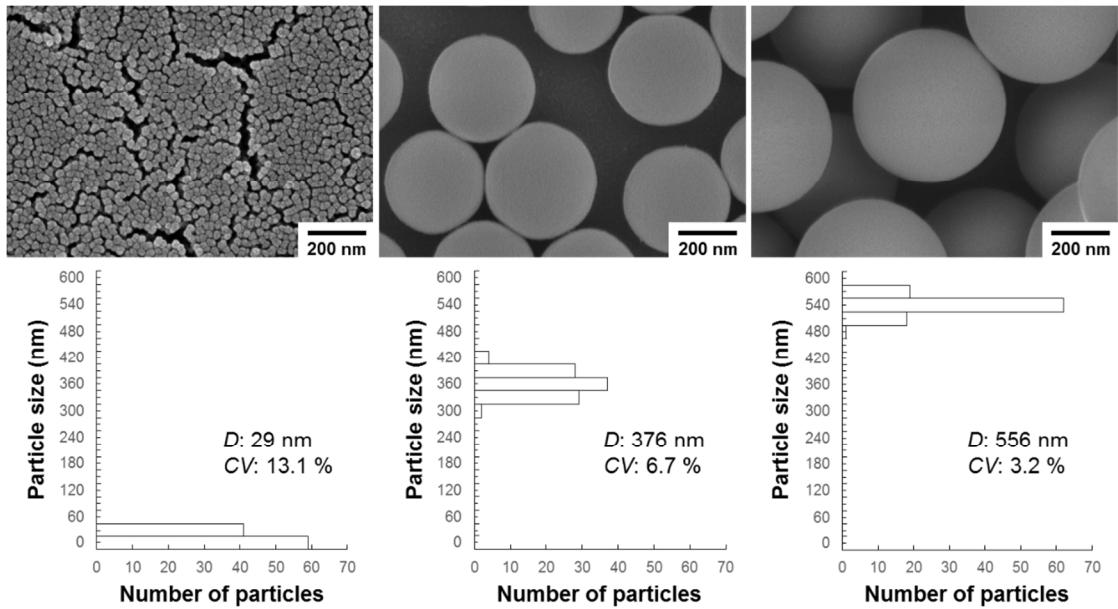
**Figure S11.** EDX spectra of SFS4Cu compound. The sample was placed on carbon tape, in results carbon appeared predominantly on spectrum. Copper was detected as an evidence of successful SFS functionalization with Cu porphyrin.



**Figure S12.** EDX spectra of SFS4Zn compound. Zinc element could be found in the composition and showed the successful functionalization of SFS with nickel porphyrin complex (4Ni).

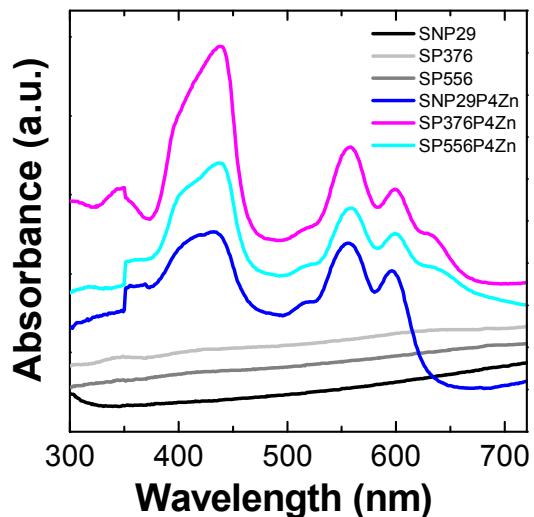


**Figure S13.** The zeta potential distribution of SFS4M capsules dispersed in pure water (pH 7).

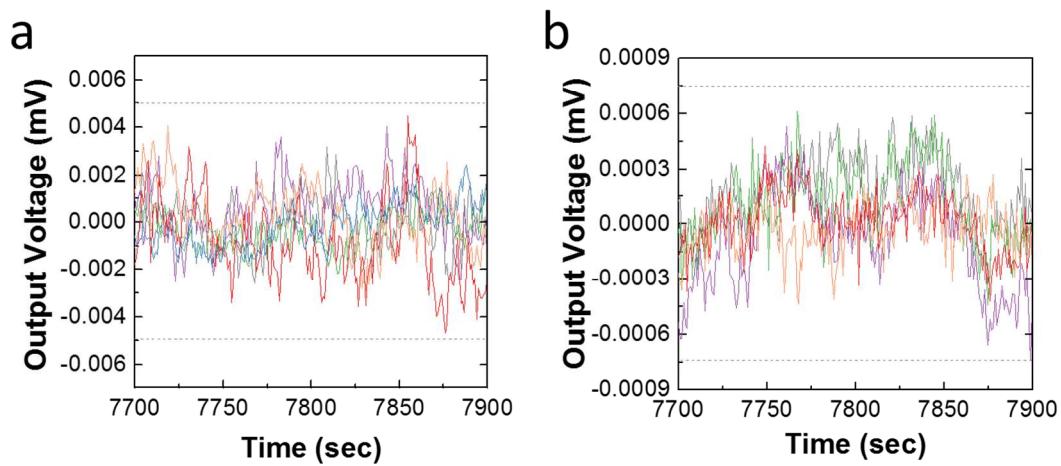


**Figure S14.** SEM images of monodispersed silica particles synthesized with MeOH (left), EtOH (middle) and IPA (right). The corresponding particle size distributions are also shown below each SEM image. The average particle size (D) and coefficient of variation

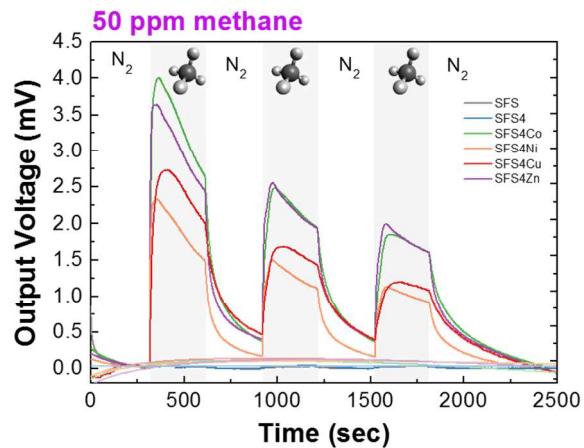
(CV) values were derived from the SEM images by counting 100 particles. CV values were estimated from the following formula,  $CV = \frac{\sqrt{\sigma^2}}{D}$ , where  $\sigma$  is standard deviation.



**Figure S15.** UV-vis spectra of unmodified silica solid particles and functionalized with zinc porphyrin: (**SNP29P4Zn**)  $\lambda_{\text{max}}(\text{nm})$  430, 555, 596 nm; (**SP376P4Zn**)  $\lambda_{\text{max}}(\text{nm})$  439, 558, 599 nm; (**SP556P4Zn**)  $\lambda_{\text{max}}(\text{nm})$  437, 558, 599 nm.



**Figure S16.** The MSS signal noise of 0.005 mV and 0.00075 for (a) SFS-porphyrin hybrids and (b) porphyrin, respectively, was accepted.



**Figure S17.** Real-time response curve of prepared MSS sensor to 50 ppm of methane gas.

**Table S1.** Quantities of reagents used for the silica synthesis.

	Solution A		Solution B		
	TEOS (mL)	Alcohol (g)	NH <sub>3</sub> aq (g)	H <sub>2</sub> O (g)	Alcohol (g)
29 nm	1.418	MeOH: 8.7	0.758	2.84	MeOH: 6.98
376 nm	1.418	EtOH: 8.7	0.758	2.84	EtOH: 6.98
556 nm	1.418	IPA: 8.7	0.758	2.84	IPA: 6.98