Electronic Supplementary Material (ESI) for Dalton Transactions.

Mesoporous silica nanoparticles functionalised with a photoactive ruthenium(II) complex: Exploring the formulation of a metal-based photodynamic therapy photosensitiser

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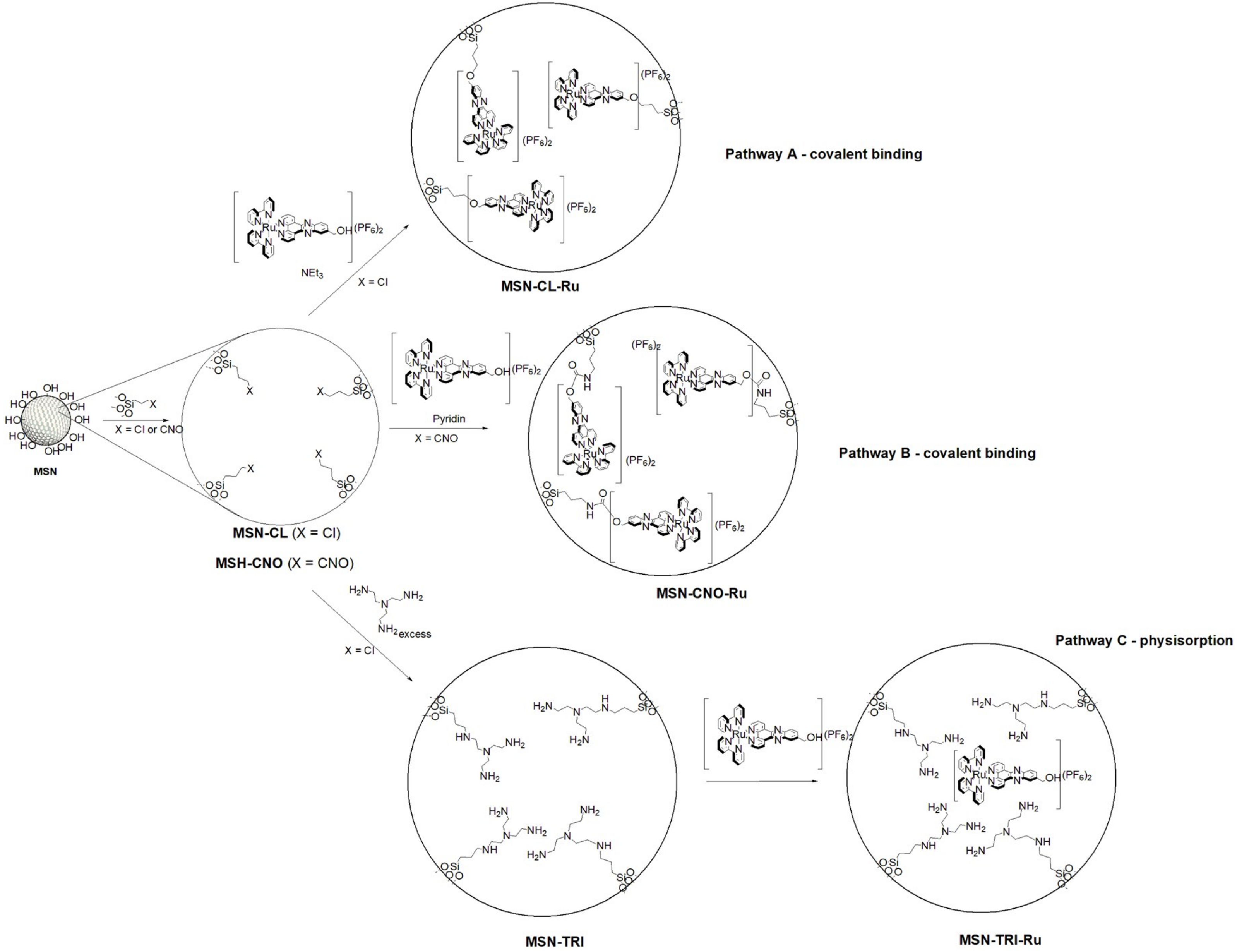
Supplementary Material

This supplementary material contains:

1) Main Scheme of the reactions carried out in this study.
2) Experimental description of additional reactions for incorporation of ruthenium complex with low functionalization rates.
3) Pore size distribution of the studied materials
4) DR-UV spectra of the studied materials
5) FT-IR spectra of the studied materials, MSN and ruthenium complex
6) Emission and lifetime spectra of **MSN-TRI-Ru** in CH_3CN

1. Main Scheme of the reactions carried out in this study.

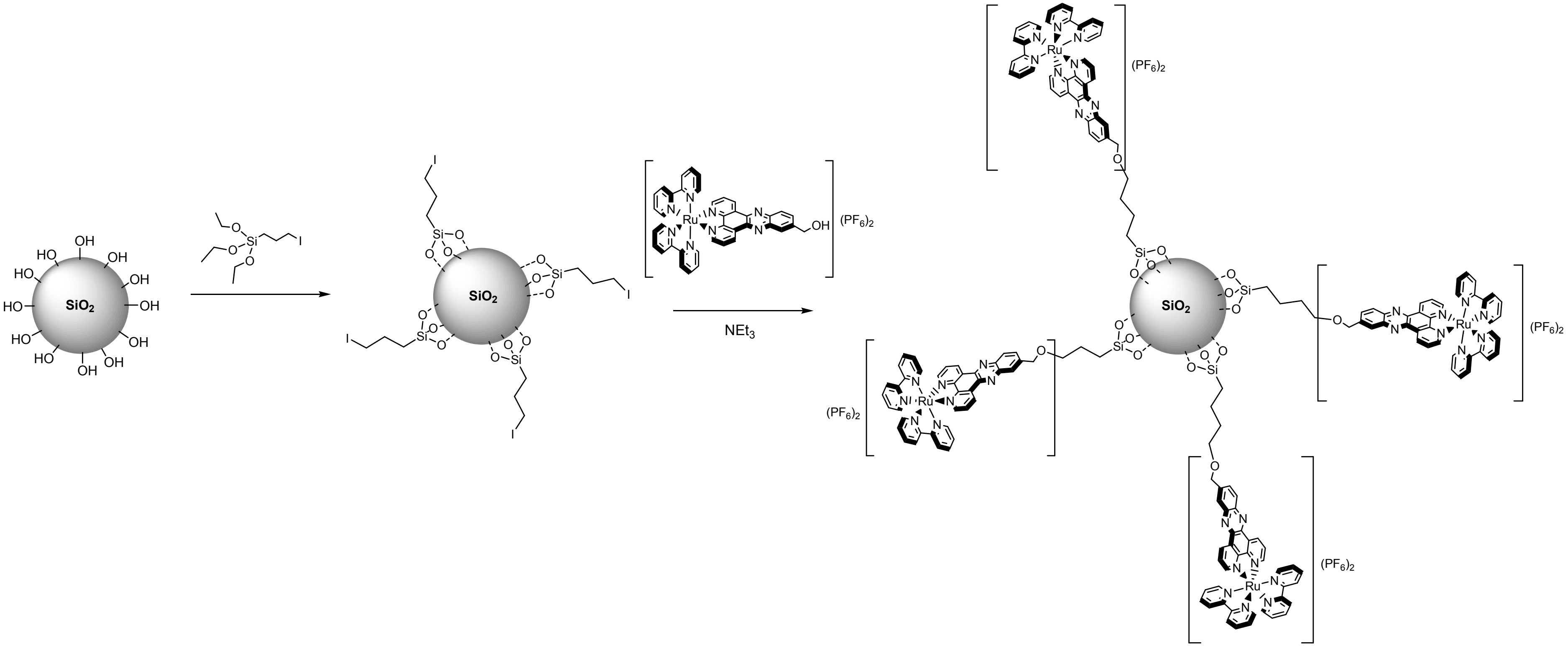


Scheme S1. Synthesis of materials studied in biological tests

2. Experimental description of additional reactions for incorporation of ruthenium complex with low functionalization rates.

2.1. 3-iodopropyltriethoxysilane approach

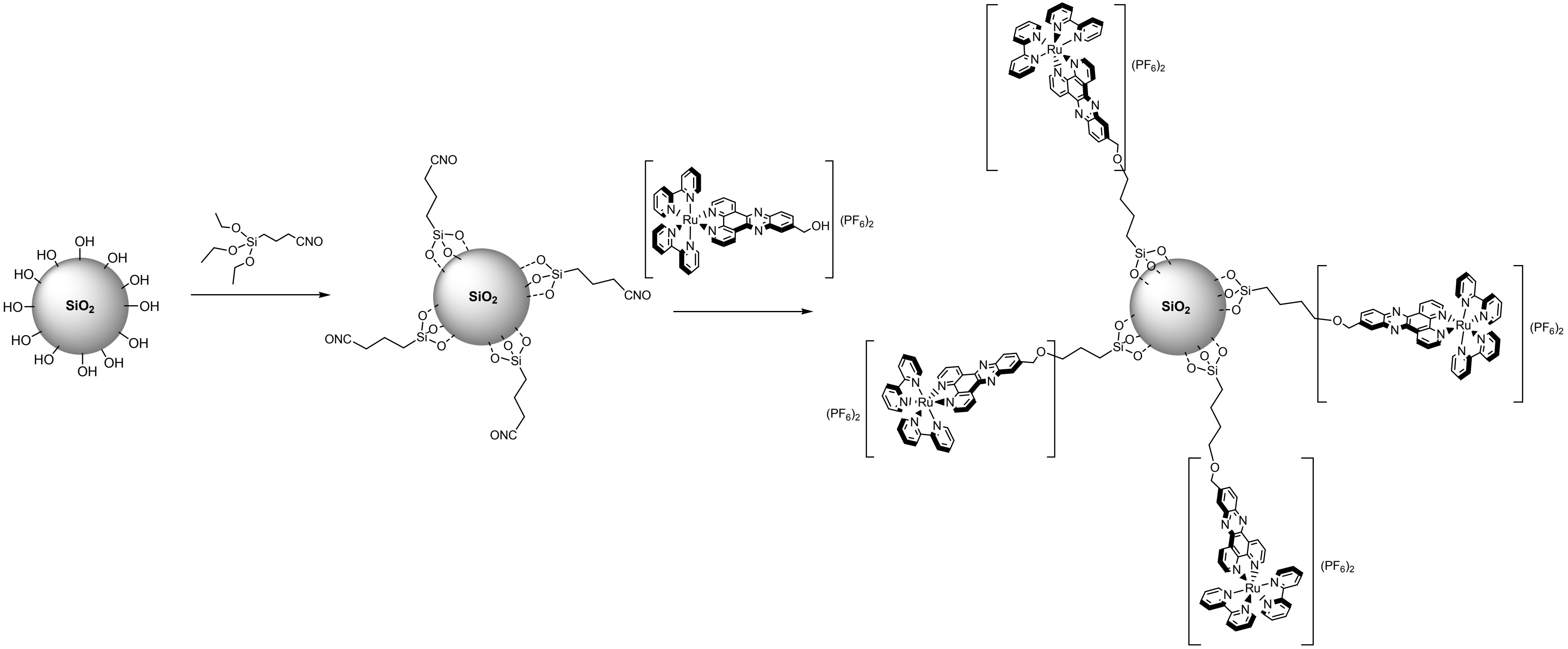
A solution of 3-iodopropyltriethoxysilane (1.00 g) in toluene (30 mL) was added to dehydrated MSN (1.00 g) and the mixture was stirred 48 h at 110 ºC. The slurry was filtered through fritted discs and the solid residue washed with toluene (5 × 50 mL) and diethylether (5 × 50 mL). The resultant solid was dried under vacuum at room temperature for 24 h to give a pale yellow free flowing powder (**MSN-I**). Subsequently, a suspension of ruthenium compound (10 mg) (to obtain a theoretical level of 5% Ru/MSN-I) in ethanol (100 mL) was added to **MSN-I** (190 mg, respectively) and the mixture was stirred at room temperature for 10 minutes, subsequently the stoichiometric amount of trimethylamine (1:1 molar ratio with ruthenium complex) was added to the mixture which was then stirred under reflux during 48 h. The slurry was filtered through fritted discs and the solid residue was washed several times with ethanol (5 × 100 mL) water (5 × 100 mL) and diethylether (5 × 100 mL) and then dried under vacuum at room temperature for 24 h to give a pale orange free flowing powder.



Scheme S2. Synthesis of material **MSN-I-Ru**

2.2. 3-isocyanatopropyltriethoxysilane approach (without organic base)

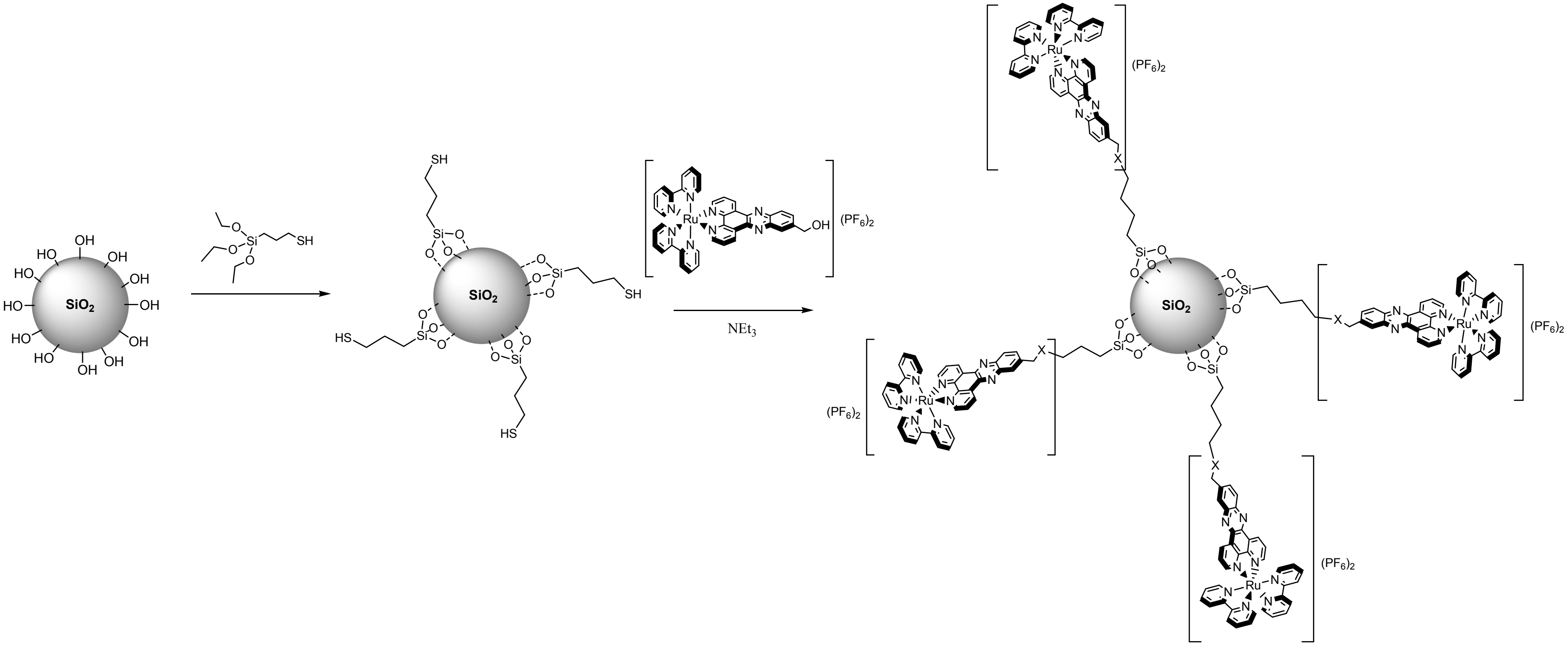
A solution of 3-isocyanatopropyltriethoxysilane (1.00 g) in toluene (30 mL) was added to dehydrated MSN (1.00 g) and the mixture was stirred 48 h at 110 ºC. The slurry was filtered through fritted discs and the solid residue washed with toluene (5 × 50 mL) and diethylether (5 × 50 mL). The resultant solid was dried under vacuum at room temperature for 24 h to give a white free flowing powder (**MSN-CNO**). Subsequently, a suspension of ruthenium compound (10 mg) (to obtain a theoretical level of 5% Ru/MSN-CNO) in ethanol (100 mL) was added to **MSN-CNO** (190 mg, respectively) and the mixture was stirred at room temperature for 10 minutes and then stirred under reflux during 48 h. The slurry was filtered through fritted discs and the solid residue was washed several times with ethanol (5 × 100 mL) water (5 × 100 mL) and diethylether (5 × 100 mL) and then dried under vacuum at room temperature for 24 h to give a pale orange free flowing powder.



Scheme S3. Synthesis of material **MSN-CNO-Ru-2**

2.3. 3-mercaptopropyltriethoxysilane approach

A solution of 3-mercaptopropyltriethoxysilane (1.00 g) in toluene (30 mL) was added to dehydrated MSN (1.00 g) and the mixture was stirred 48 h at 110 ºC. The slurry was filtered through fritted discs and the solid residue washed with toluene (5 × 50 mL) and diethylether (5 × 50 mL). The resultant solid was dried under vacuum at room temperature for 24 h to give a white free flowing powder (**MSN-SH**). Subsequently, a suspension of ruthenium compound (10 mg) (to obtain a theoretical level of 5% Ru/MSN-SH) in ethanol (100 mL) was added to **MSN-SH** (190 mg, respectively) and the mixture was stirred at room temperature for 10 minutes, subsequently the stoichiometric amount of triethylamine (2:1 molar ratio with ruthenium complex) was added to the mixture which was then stirred under reflux during 48 h. The slurry was filtered through fritted discs and the solid residue was washed several times with ethanol (5 × 100 mL) water (5 × 100 mL) and diethylether (5 × 100 mL) and then dried under vacuum at room temperature for 24 h to give a pale orange free flowing powder.



X = S or O

Scheme S4. Synthesis of **MSN-SH-Ru**

Table S1. Ruthenium content in the materials determined by XRF.

Material	%Ru (theoretical)	%Ru (found)
MSN-I-Ru	5	2.3
MSN-CNO-Ru2	5	1.8
MSN-SH-Ru	5	0.6

3. Pore size distribution of the studied materials

Figure S1 shows the pore size distribution of the studied materials measured by BET isotherms. It is clearly observed that the pore size distribution of unmodified MSN is very narrow with a maximum at ca. 2.5 nm. After functionalization with ruthenium complex in materials MSN-CL-Ru and MSN-CNO-Ru, the pore size distribution is lower than 2.0 nm, although, due to the limitations of the porosimeter (with measurements only for pore sizes higher than 2.0 nm) only one of the faces of the distribution is shown. For material MSN-TRI-Ru that is not porous because of the blocking of the mesopores by the tris-amine and the ruthenium complex, the pore size distribution is not relevant.

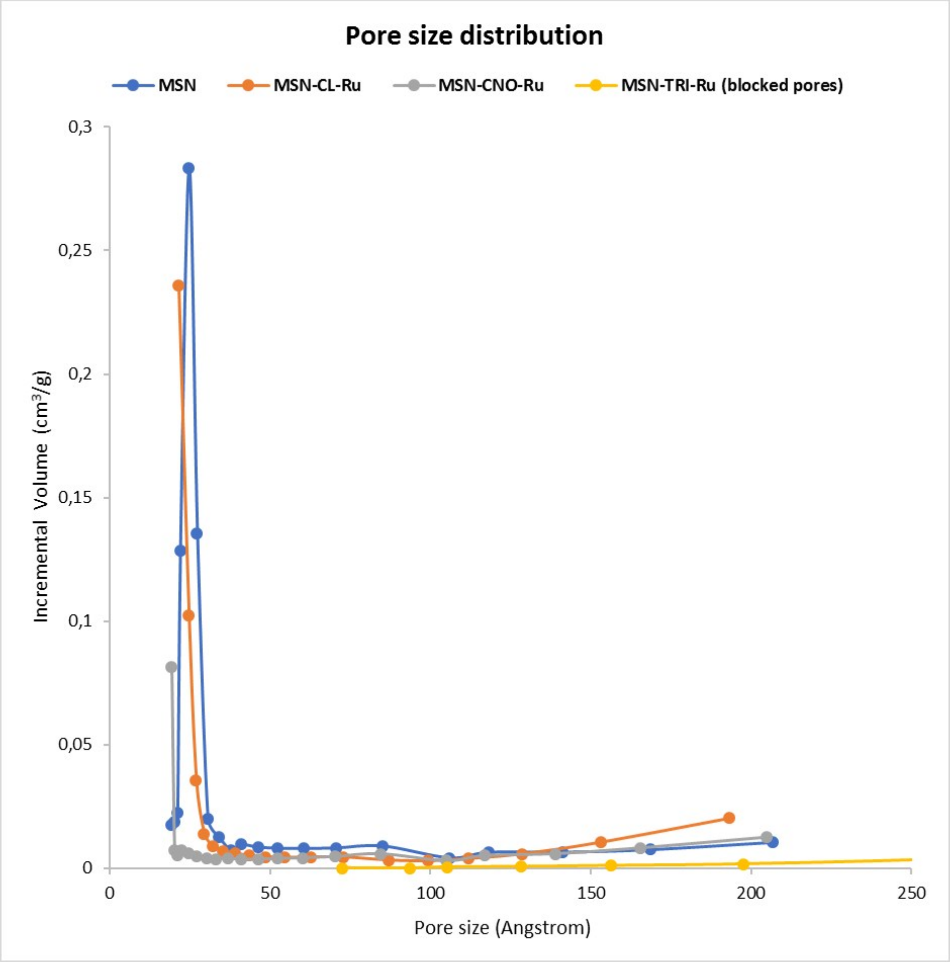


Figure S1. Pore size distribution of the studied materials MSN, MSN-CL-Ru, MSN-CNO-Ru and MSN-TRI-Ru

4. DR-UV spectra of the studied materials

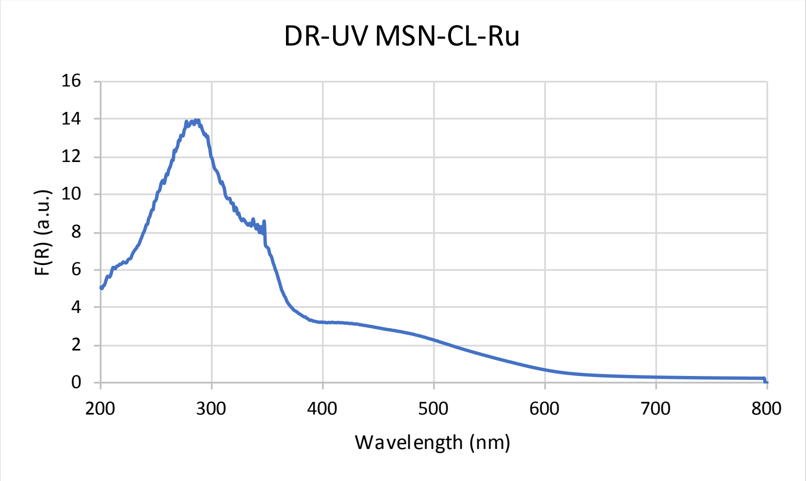


Figure S2. DR-UV spectrum of MSN-CL-Ru

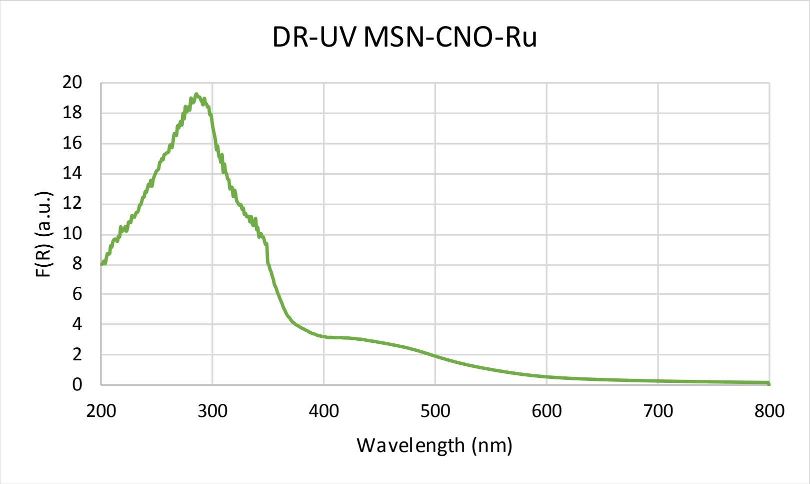


Figure S3. DR-UV spectrum of MSN-CNO-Ru

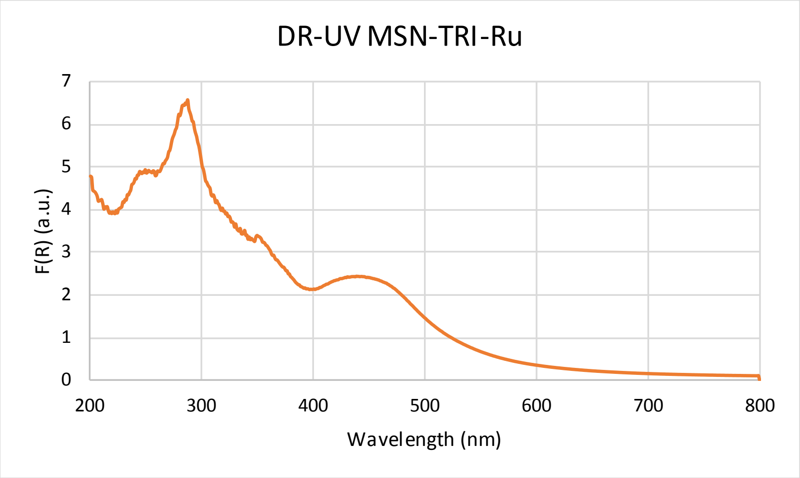


Figure S4. DR-UV spectrum of MSN-TRI-Ru

5. FT-IR spectra of the studied materials, MSN and ruthenium complex

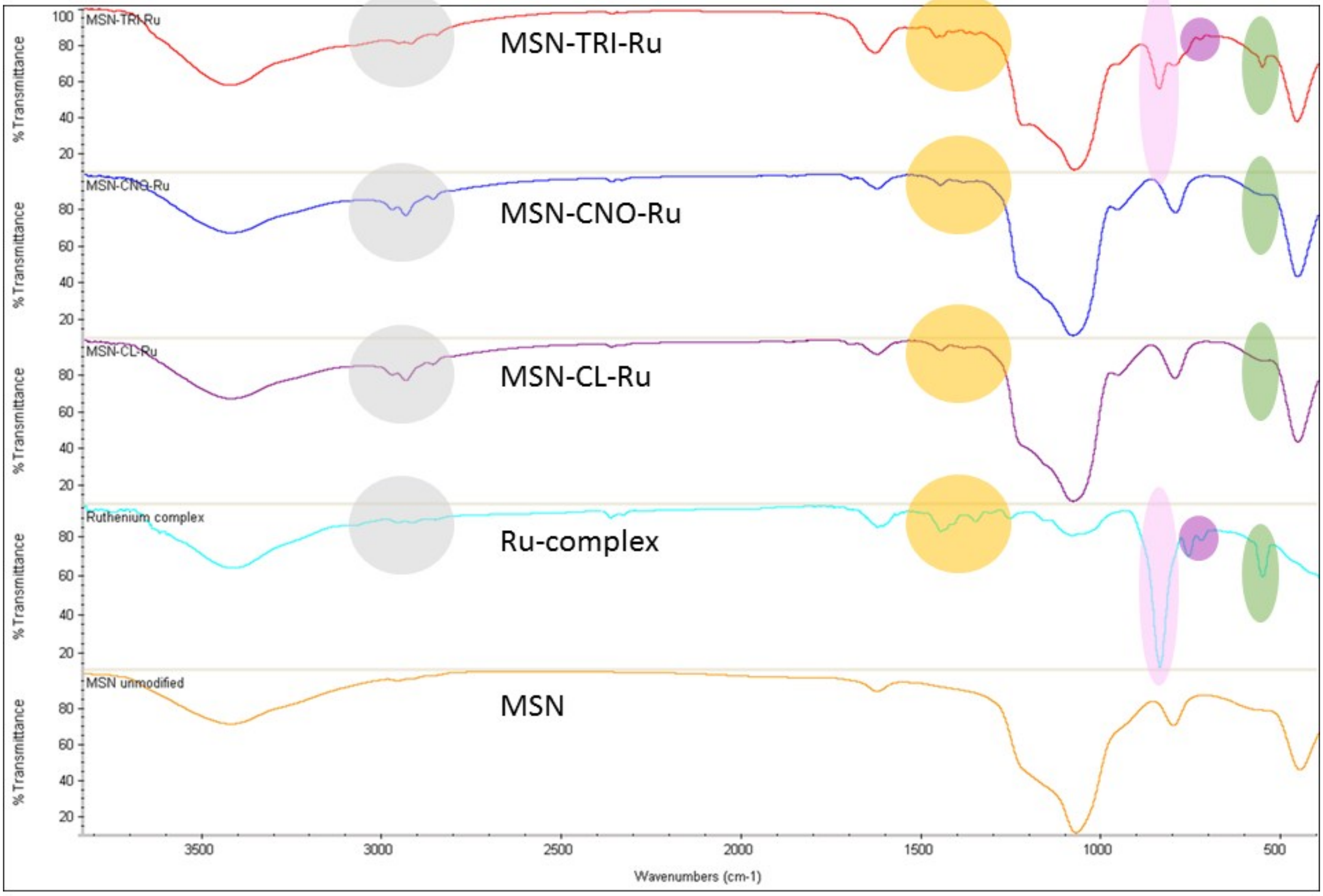


Figure S5. FT-IR spectra of the ruthenium complex and the studied materials MSN, MSN-CL-Ru, MSN-CNO-Ru and MSN-TRI-Ru.

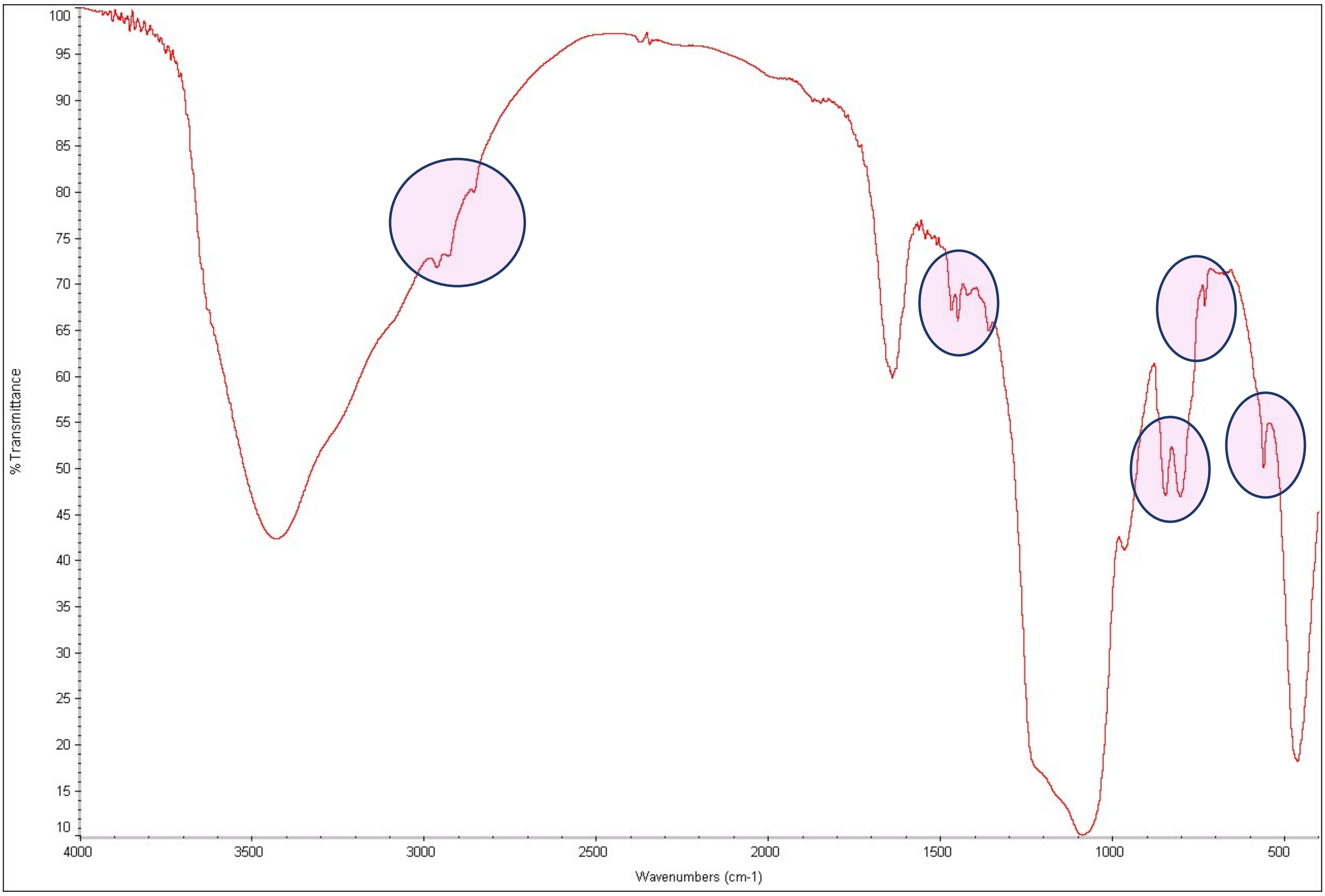


Figure S6. FT-IR spectrum of MSN-CL-Ru in a very concentrated KBr pellet.

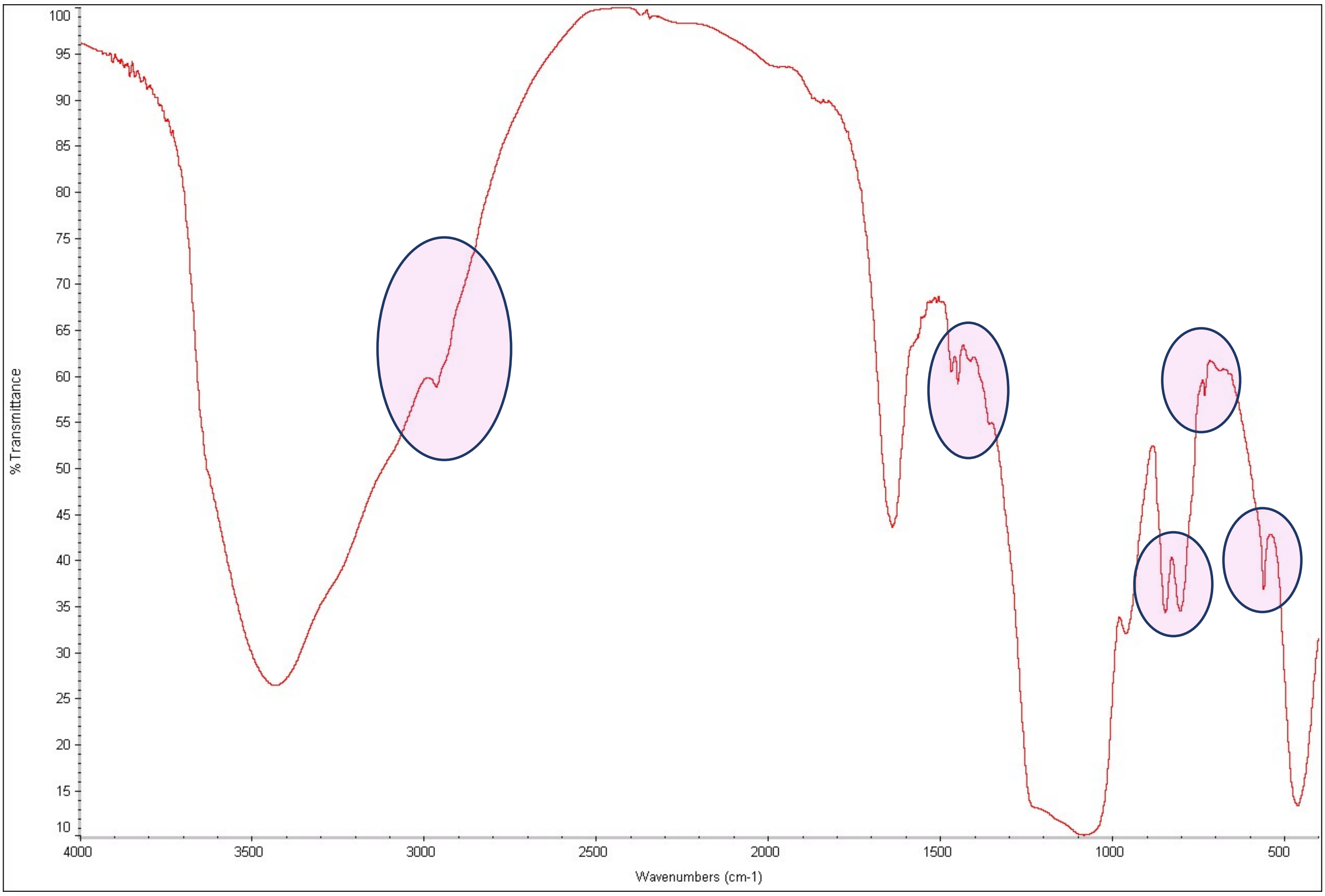


Figure S7. FT-IR spectrum of MSN-CNO-Ru in a very concentrated KBr pellet.

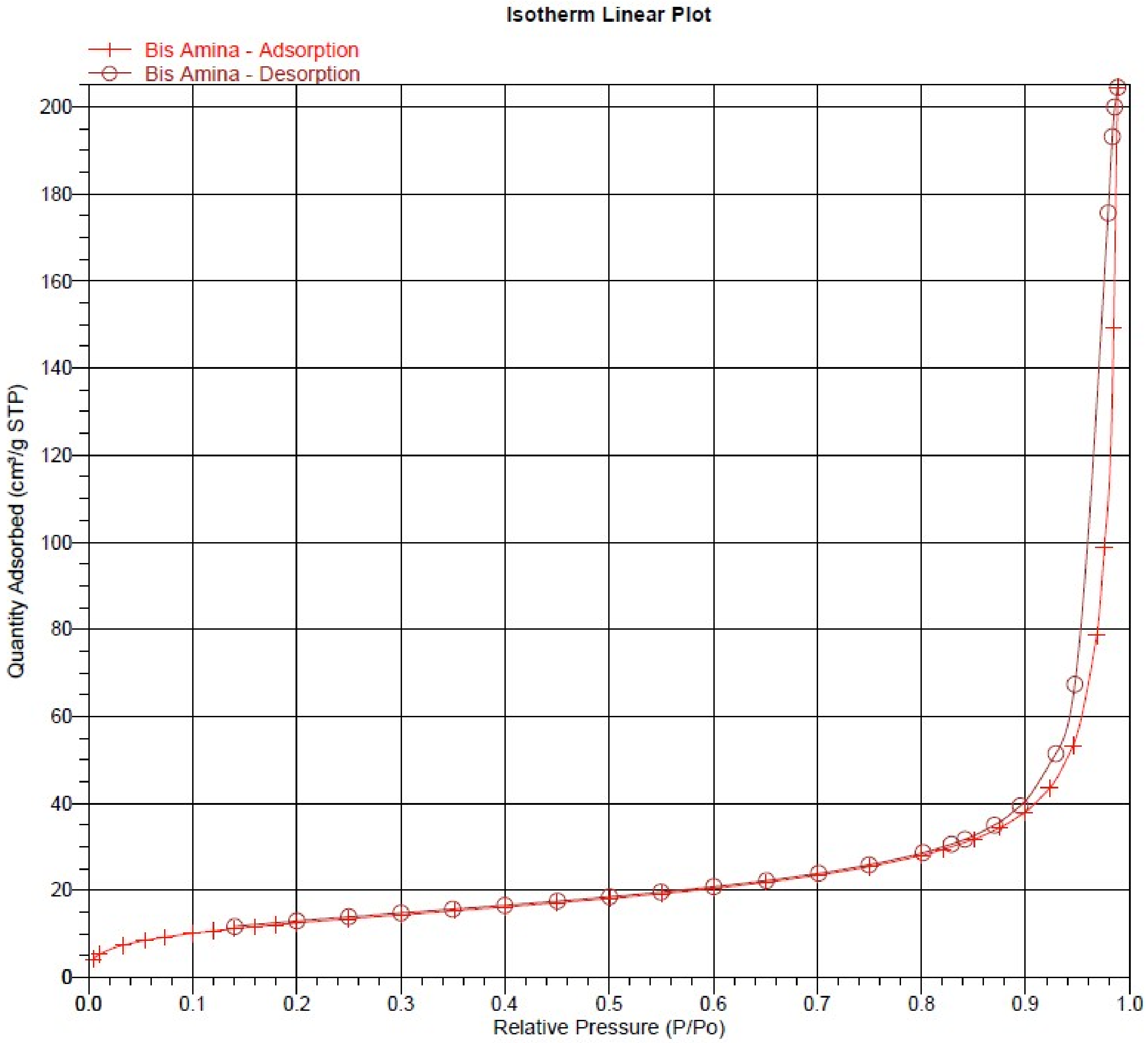


Figure S8. Nitrogen adsorption-desorption isotherm of material MSN-TRI

Table S1. Comparison of physical parameters of **MSN**, **MSN-TRI** and **MSN-TRI-Ru** measured by N_2 adsorption-desorption isotherm

Material	**S_{BET} (m^2/g)**	**Total pore volume (cm^3/g)**	**D_P (BJH)[1] (nm)**
MSN	853	0.728	2.54
MSN-TRI	47	0.122	<2.0
MSN-TRI-Ru	7	0.022	<2.0

[1] Barrett, Joyner and Halenda.

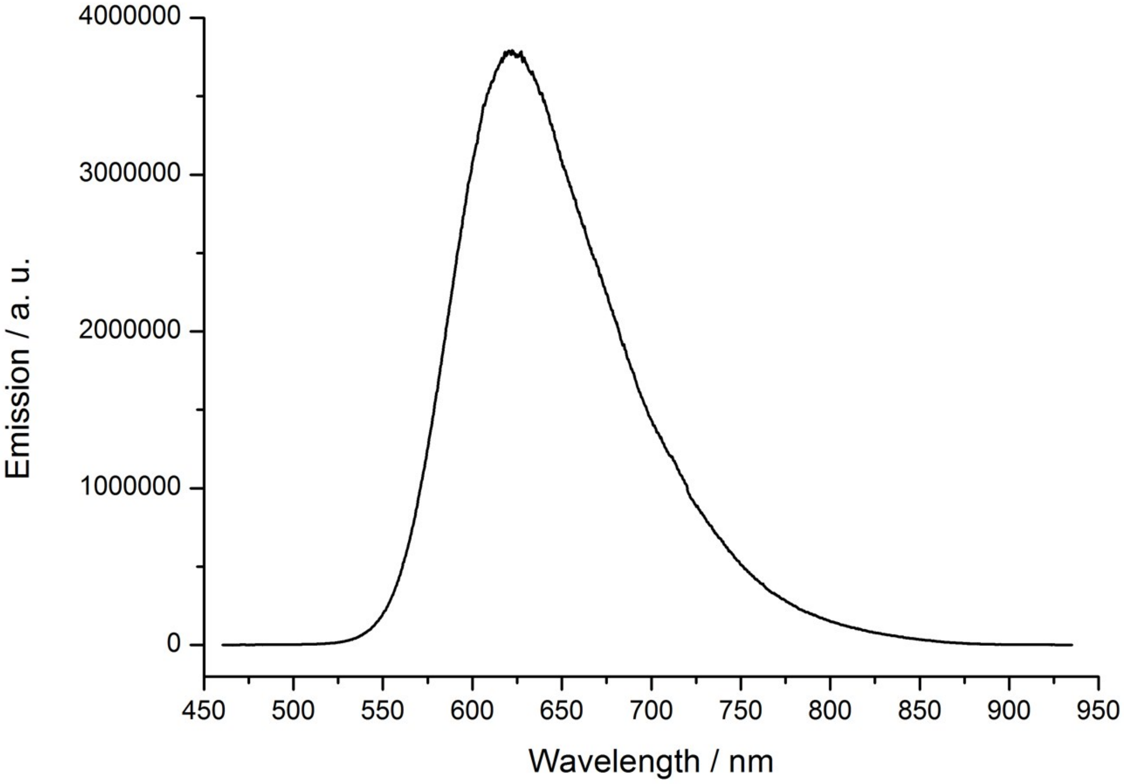


Figure S9. Emission spectrum of **MSN-TRI-Ru** in CH_3CN.

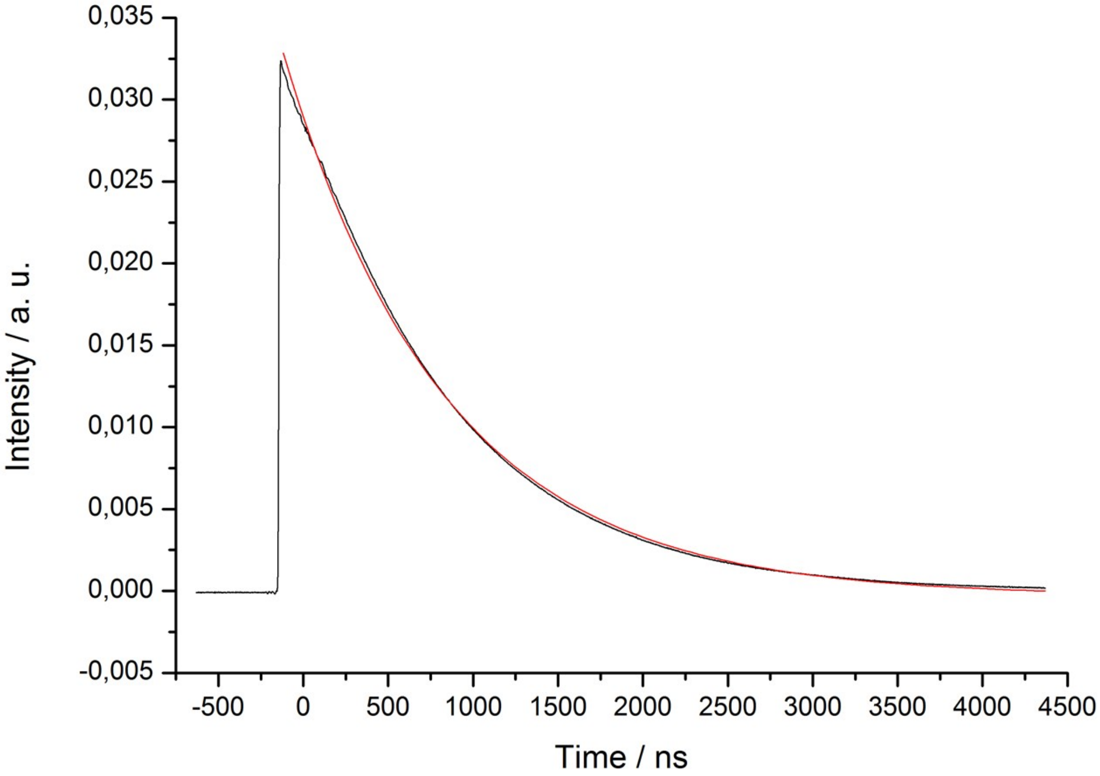


Figure S10. Lifetime spectrum of **MSN-TRI-Ru** in degassed CH_3CN.

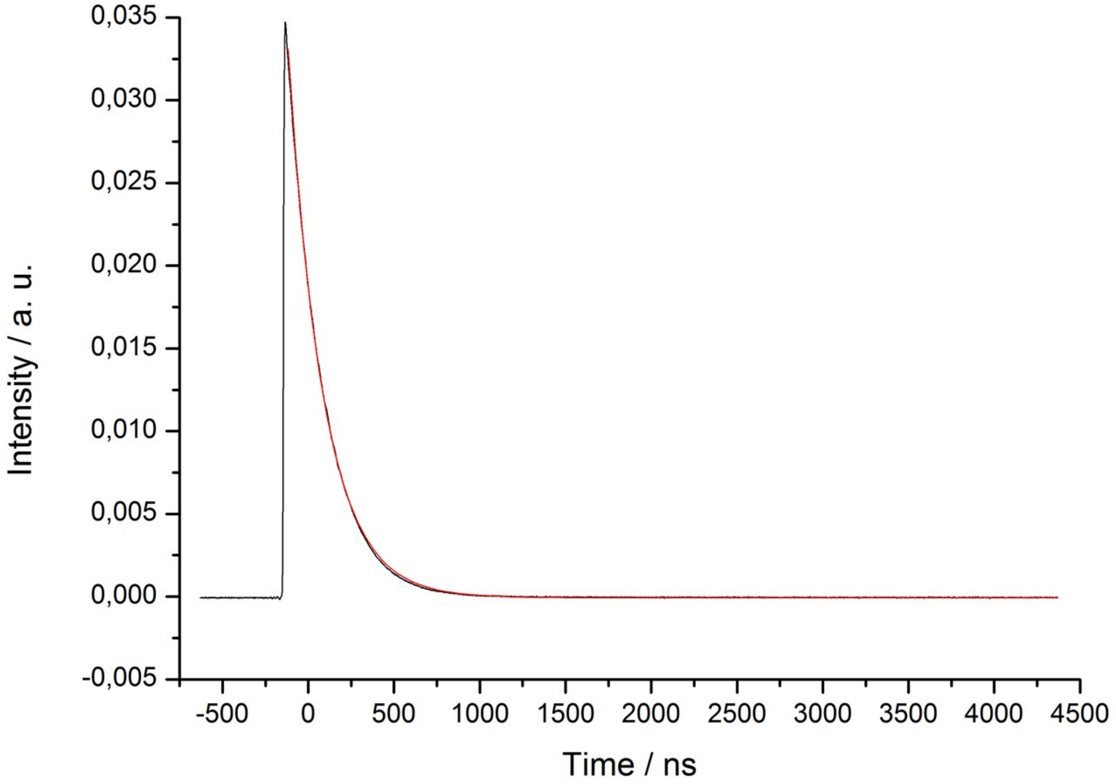


Figure S11. Lifetime spectrum of **MSN-TRI-Ru** in air saturated CH_3CN.