

## SUPPORTING INFORMATION

### Optimizing the silanization of thermally-decomposed iron oxide nanoparticles for efficient aqueous phase transfer and MRI applications

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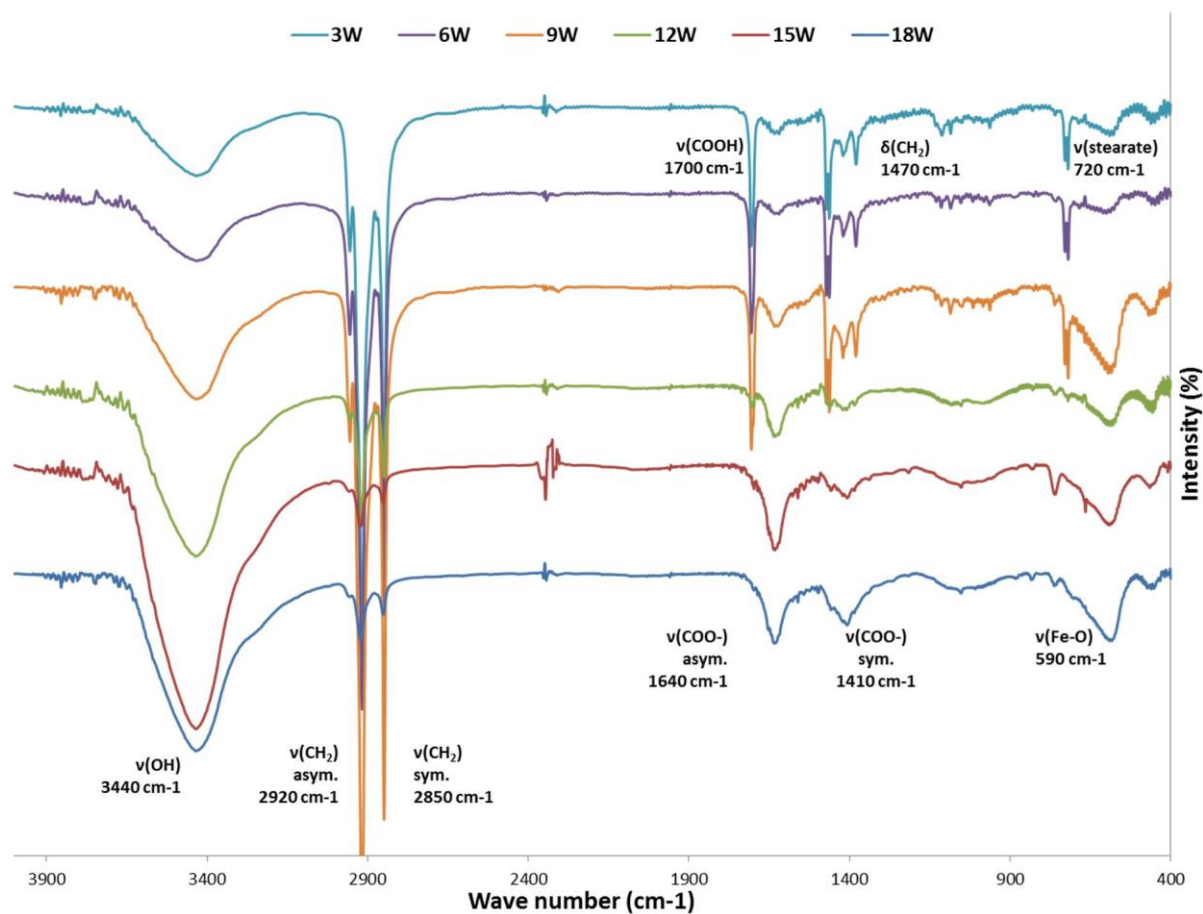
**Table S1.A.** Summary table of the reaction parameters of IO NPs silanization used for the *starting conditions*: 2 mL IO NPs, incubated with 5.6 mL EtOH and 240  $\mu\text{L}$  acetic acid (25% in water) at a stoichiometry 1101 silanes/ $\text{nm}^2$ .

Features	APTS	TPED	TPDT	TPEDTA
Stoichiometry/ $\text{nm}^2$	1101:1	1101:1	1101:1	1101:1
Volume ( $\mu\text{L}$ )	183	172	197	628 (45% wt in water)
Reaction time (h)	4 and 24	24	24	4 and 24
Dispersant medium	Acidified water	Acidified water	Acidified water	Water
after washing steps	pH=3.5	pH=3.5	pH=3.5	pH=7.5

**Table S1.B.** Summary table of the silane volume used for the study of IO NPs silanization by varying the stoichiometry from 6020 to 100 silanes/ $\text{nm}^2$ .

Stoichiometry/ $\text{nm}^2$	V(APTS) $\mu\text{L}$	V(TPED) $\mu\text{L}$	V(TPDT) $\mu\text{L}$	V(TPEDTA <sub>45% water</sub> ) $\mu\text{L}$
6020:1	1000	940	1080	n/a
1101:1	183	172	197	628
350:1	58	n/a	n/a	200
100:1	17	n/a	n/a	57

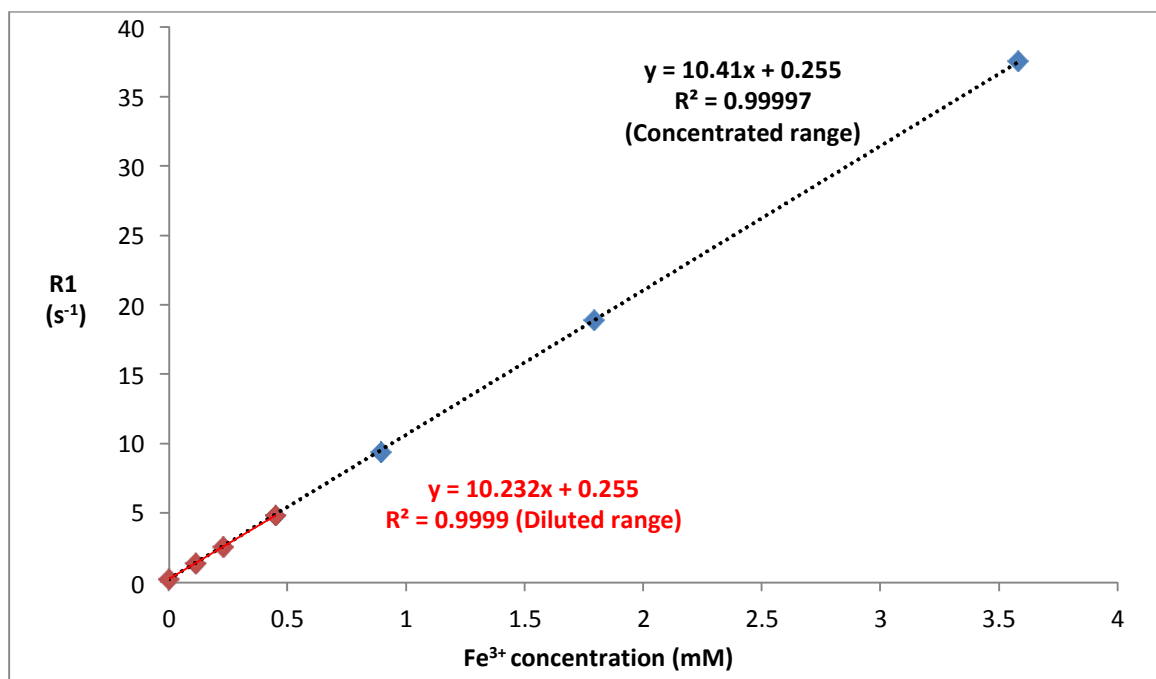
## S1. FTIR follow-up of the purification of oleic acid-coated IONPs



**Figure S1.** FTIR follow-up of the purification of oleic acid-coated IONPs with the number of washing steps.

IR spectra of the IO NPs were acquired after various washing steps to follow the purification of the IO NPs. The two peaks at 2920 and 2850 cm<sup>-1</sup> are the characteristic bands of the asymmetric and symmetric stretching of CH<sub>2</sub> from the oleic acid and stearate chains. The band at 1700 cm<sup>-1</sup> corresponds to the C=O bond (COOH) of the free oleic acid in suspension while the bands at 1640 and 1410 cm<sup>-1</sup> correspond to asymmetric and symmetric bands (COO<sup>-</sup>) of the oleic acid grafted at the surface of the IO NPs. The peak at 590 cm<sup>-1</sup> corresponds to the Fe-O bond of the iron oxide. The iron stearate residue was revealed by the peak at 720 cm<sup>-1</sup>. The efficacy of the purification of IONPs by washing was followed by the evolution of the ratio of the intensities of bands at 2920 cm<sup>-1</sup> and 590 cm<sup>-1</sup>. When the ratio is around 1.0, the NPs are empirically considered as cleaned (i.e.) assuming they are surrounded by one monolayer of oleic acid. Some studies have proved that when the ratio is too low, the oleic acid desorbs from the surface of IO and the IONPs may aggregate.

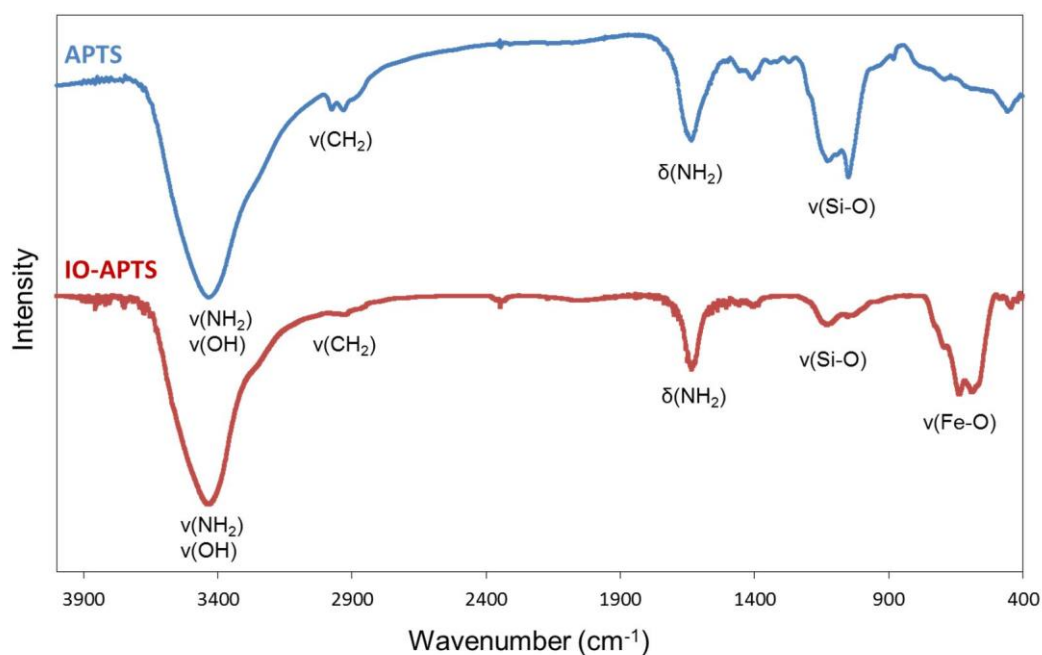
## S2. Dosage of Fe in IONPs by a relaxometric method



**Figure S2.** Etalon-curve of the longitudinal relaxation rate (R1) as a function of [Fe<sup>3+</sup>] concentration for the dosage of Fe by relaxometry at 37°C 1,41T in aqueous HNO<sub>3</sub> 2%.

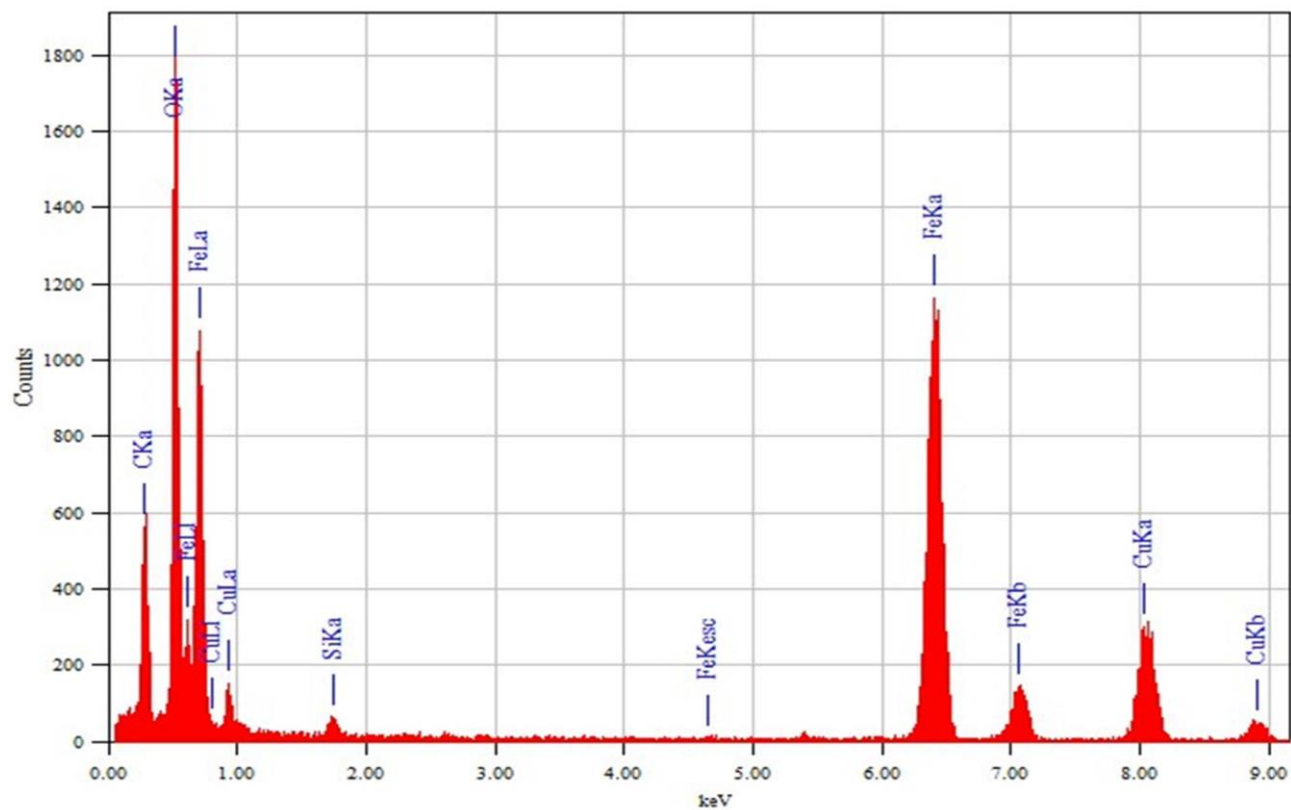
### S3. FTIR study of IO-APTS NPs

The spectrum of APTS was acquired as a reference. Compared with the FTIR spectrum of oleic acid stabilised IONPs shown in S1, several new bands were observed. First, the bands at 1040 and 1128  $\text{cm}^{-1}$  characteristic of the Si-O bonds indicate the efficient silane ligand exchange onto the IONPs surface. The complete disappearance of the  $\text{CH}_2$  band vibrations at 2920 and 2850 and of the symmetric  $\text{COO}^-$  of bound oleic acid at 1410  $\text{cm}^{-1}$  indicates that oleic acid was removed from the IONPs surface. Furthermore, the FTIR spectrum shows N-H bendings at 1633  $\text{cm}^{-1}$ , characteristic of the presence of  $\text{NH}_2$  groups from APTS.



**Figure S3.** FTIR spectra of APTS and IO-APTS NPs.

#### S4. Energy dispersive X rays (EDX) analysis of IO-APTS NPs.



**Figure S4.** EDX spectra performed on a zone containing thousands of IO –APTS NPs (magnitude 50000) confirming the simultaneous presence of Si and Fe elements.

**Table S2.** Summary table of the conditions used for the silanization of IONPs with APTS by varying the reaction time. \* corresponds to the results obtained by following the silanization procedure of the reference method.<sup>28</sup>

Amino-silane	Reaction time (h)	Reaction solvents	Stoichiometry silane/nm <sup>2</sup>	Dispersant medium	Hydrodynamic DLS size (nm)/ (PDI)	Zeta potential (mV)
APTS	72 *	Hexane	1204:1	Water pH=3.5	24 (94%) (0.52)	n/a
	72 *	Hexane	1204:1	Water pH=7.5	≥ 1000	n/a
	24	EtOH/CHCl <sub>3</sub> 3:1	1101:1	Water pH=3.5	26 (0.27)	+ 24
	24	EtOH/CHCl <sub>3</sub> 3:1	1101:1	Water pH=7.5	≥ 1000	n/a
	24	EtOH/CHCl <sub>3</sub> 3:1	1101:1	EtOH	19 (0.36)	n/a
	4	EtOH/CHCl <sub>3</sub> 3:1	1101:1	Water pH=3.5	22(0.40)	+ 18
	4	EtOH/CHCl <sub>3</sub> 3:1	1101:1	Water pH=7.5	≥ 1000	n/a
	4	EtOH/CHCl <sub>3</sub> 3:1	1101:1	EtOH	25 (0.39)	n/a

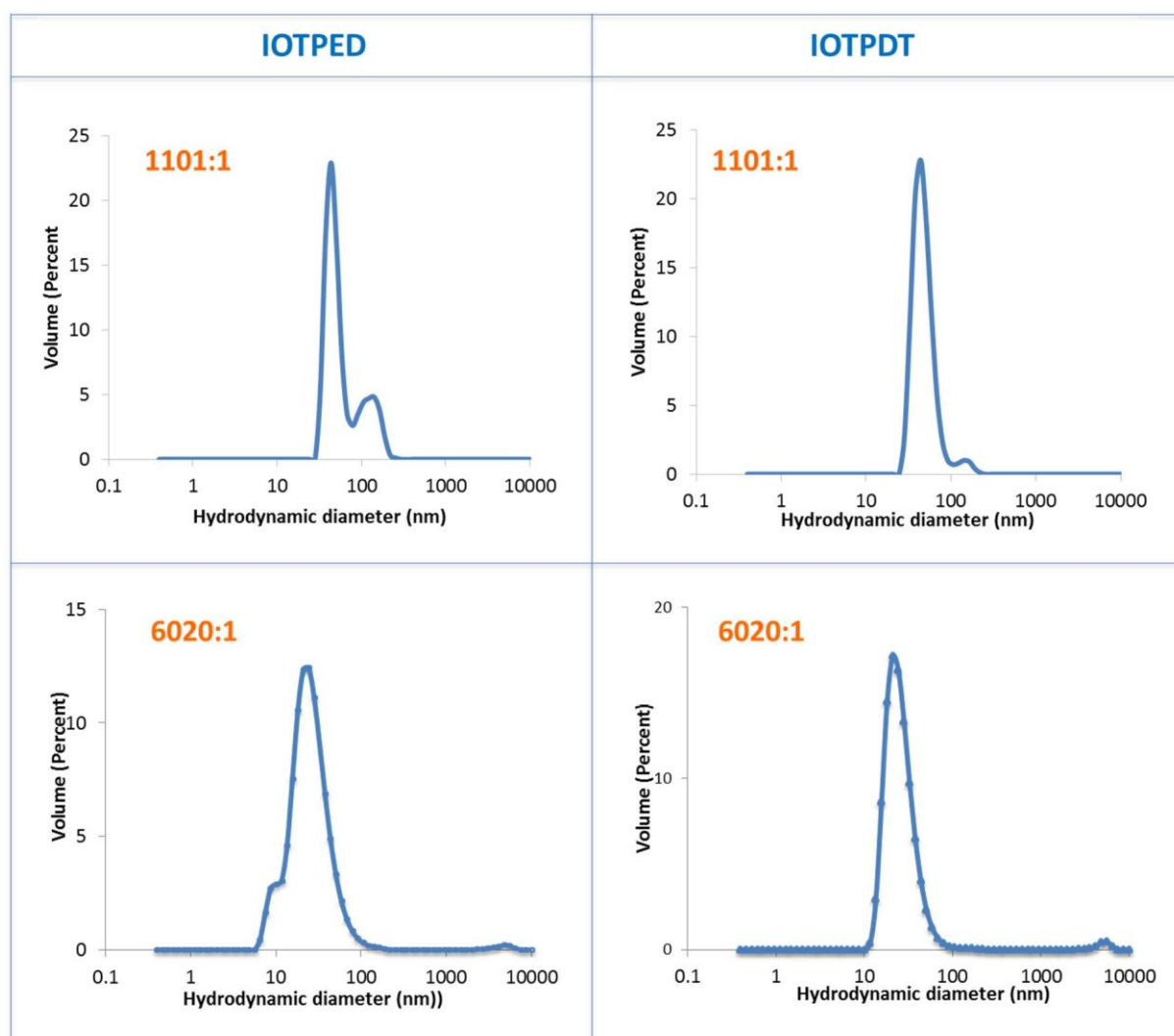
**Table S3.** Summary of the conditions used for the silanization of IONPs with APTS by varying the stoichiometry APTS/nm<sup>2</sup>.

Amino-silane	Reaction time (h)	Reaction solvents	Stoichiometry silane/nm <sup>2</sup>	Dispersant medium	Hydrodynamic DLS size (nm)	Zeta potential (mV)
APTS	24	EtOH/CHCl <sub>3</sub> 3:1	6020:1	Water pH=3.5	24 (0.45)	+ 22
	24	EtOH/CHCl <sub>3</sub> 3:1	1101:1	Water pH=3.5	26 (0.27)	+ 24
	24	EtOH/CHCl <sub>3</sub> 3:1	350:1	Water pH=3.5	48 (70%) (0.20)	+ 36
	24	EtOH/CHCl <sub>3</sub> 3:1	100:1	Water pH=3.5	78 (72%) (0.24)	+ 38

**Table S4.** Summary of the conditions used for the silanization of IONPs with TPED and TPDT. \* corresponds to results obtained following the silanization procedure of the reference method.<sup>28</sup>

Amino-silane	Reaction time (h)	Reaction solvents	Stoichiometry silane/nm <sup>2</sup>	Dispersant medium	Hydrodynamic DLS size (nm) (PDI)	Zeta potential (mV)
TPED	24	EtOH/CHCl <sub>3</sub> 3:1	6020:1	Water pH=3.5	28 (0.34)	+ 18.5
	24	EtOH/CHCl <sub>3</sub> 3:1	6020:1	Water pH =7.5	≥ 1000	+ 11
	24	EtOH/CHCl <sub>3</sub> 3:1	1101:1	Water pH=3.5	47 (75%) (0.20)	+30
	24	EtOH/CHCl <sub>3</sub> 3:1	1101:1	Water pH =7.5	≥ 1000	-4
	72 *	Hexane	1281:1	Water pH=3.5	125 (57%) (0.24)	n/a
	72 *	Hexane	1281:1	Water pH =7.5	≥ 1000	n/a
	TPDT	24	EtOH/CHCl <sub>3</sub> 3:1	6020:1	Water pH=3.5	27 (0.4)
24		EtOH/CHCl <sub>3</sub> 3:1	6020:1	Water pH =7.5	≥ 1000	+ 3.5
24		EtOH/CHCl <sub>3</sub> 3:1	1101:1	Water pH=3.5	42 (0.26)	+26
24		EtOH/CHCl <sub>3</sub> 3:1	1101:1	Water pH =7.5	≥ 1000	-2
72 *		Hexane	1115:1	Water pH=3.5	59 (0.24)	n/a
72 *		Hexane	1115:1	Water pH =7.5	≥ 1000	n/a

S5. DLS size distribution of IO-TPED and IO-TPDT NPs in acidified water (pH=3.5).



**Figure S5.** DLS size distribution of IO-TPED NPs (at the left) and IO-TPDT NPs (at the right) in acidified water (pH=3.5) obtained at 24h reaction, at stoichiometries of 1101 and 6020 silanes /nm<sup>2</sup> IO NPs.

### S6. FTIR spectra of TPED and TPDT grafted IO-NPs

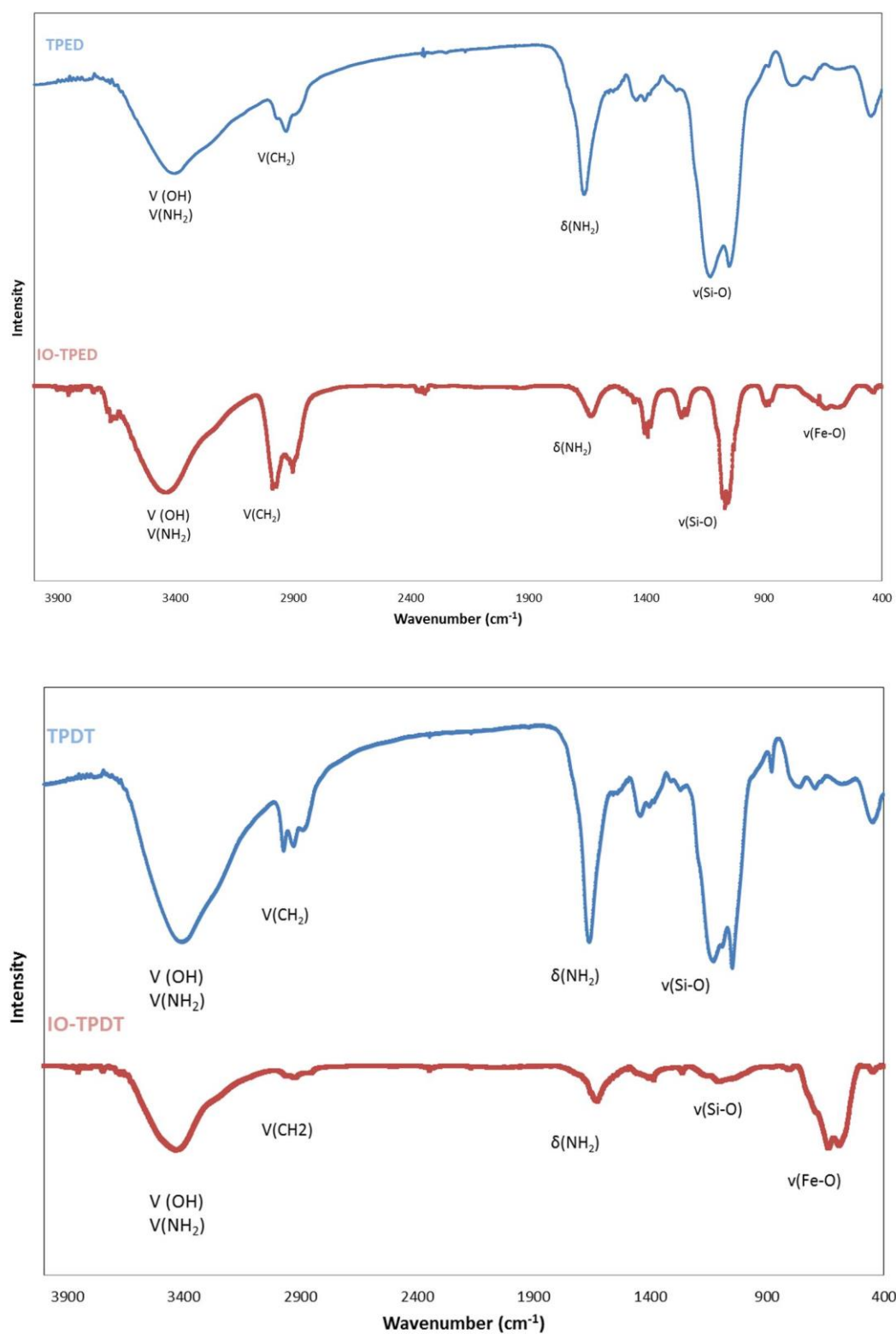
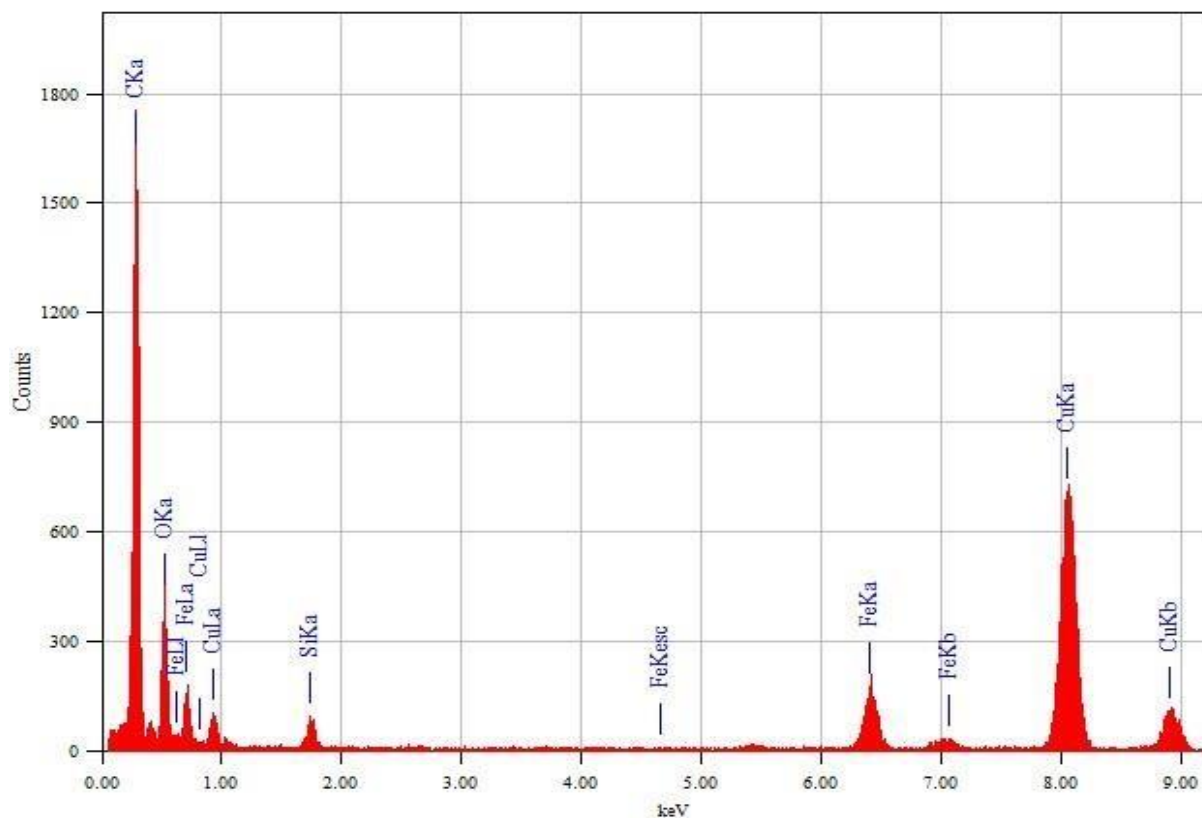


Figure S6. IR spectra of TPED silane, IO-TPED NPs, and TPDT silane, IO-TPDT NPs.



### S7. Energy dispersive X rays (EDX) analysis of IO –TPEDTA NPs



**Figure S7.** EDX spectra performed on a zone containing thousands of IO –TPEDTA NPs (magnitude 50000) confirming the simultaneous presence of Si and Fe elements.