Electronic Supplementary Material (ESI) for RSC Advances.
This journal is © The Royal Society of Chemistry 2015

# Conjugation of polyethylenimine and its derivatives to carbon-encapsulated iron nanoparticles

## Supplementary data

Artur Kasprzak,[a]* Magdalena Popławska,[a] Michał Bystrzejewski,[b] Olga Łabędź[b] and Ireneusz P. Grudziński[c]

[a] Faculty of Chemistry, Warsaw University of Technology, 00-664 Warsaw, Poland
[b] Faculty of Chemistry, University of Warsaw, 02-093 Warsaw, Poland
[c] Faculty of Pharmacy, Medical University of Warsaw, 02-097 Warsaw, Poland

### I. Structural modification of PEI – $^{1}$H and $^{13}$C NMR spectra

$^{1}$H NMR spectra were calibrated on the residual signal 4.79 ppm. **Fig. S1** shows $^{1}$H NMR spectra of PEI 0.8kDa (**spectrum 1**), $^{13}$C NMR spectra of PEI 0.8kDa (**spectrum 2**), $^{1}$H NMR spectra of PEI 25kDa (**spectrum 3**) and $^{1}$H NMR spectra of PEI 750kDa (**spectrum 4**). In **Fig. S2** are presented: $^{1}$H NMR spectra of PEI0.8k-SA (**spectrum 1**), $^{13}$C NMR spectra of PEI0.8k-SA (**spectrum 2**), $^{1}$H NMR spectra of PEI750k-SA (**spectrum 3**), $^{1}$H NMR spectra of PEI0.8k-pFBA (**spectrum 4**), $^{13}$C NMR spectrum of PEI0.8k-pFBA (**spectrum 5**) and $^{1}$H NMR spectrum of PEI750k-pFBA (**spectrum 5**). $^{13}$C NMR spectra of PEI 0.8kDa derivatives (PEI0.8k-SA and PEI0.8k-pFBA) were recorded overnight. Below, we present the assignment of new signals on the spectrum of PEI0.8k-pFBA (**spectrum 2** in **Fig. S2**):

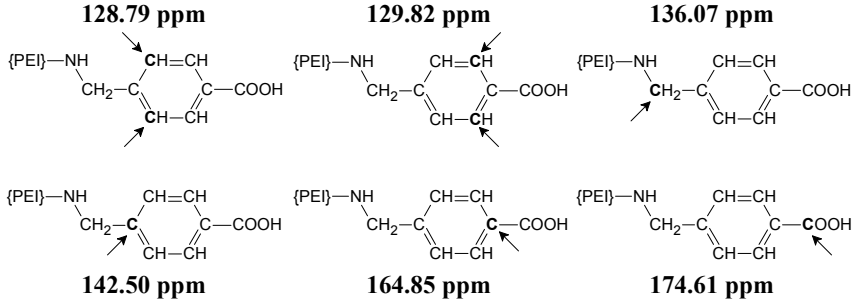
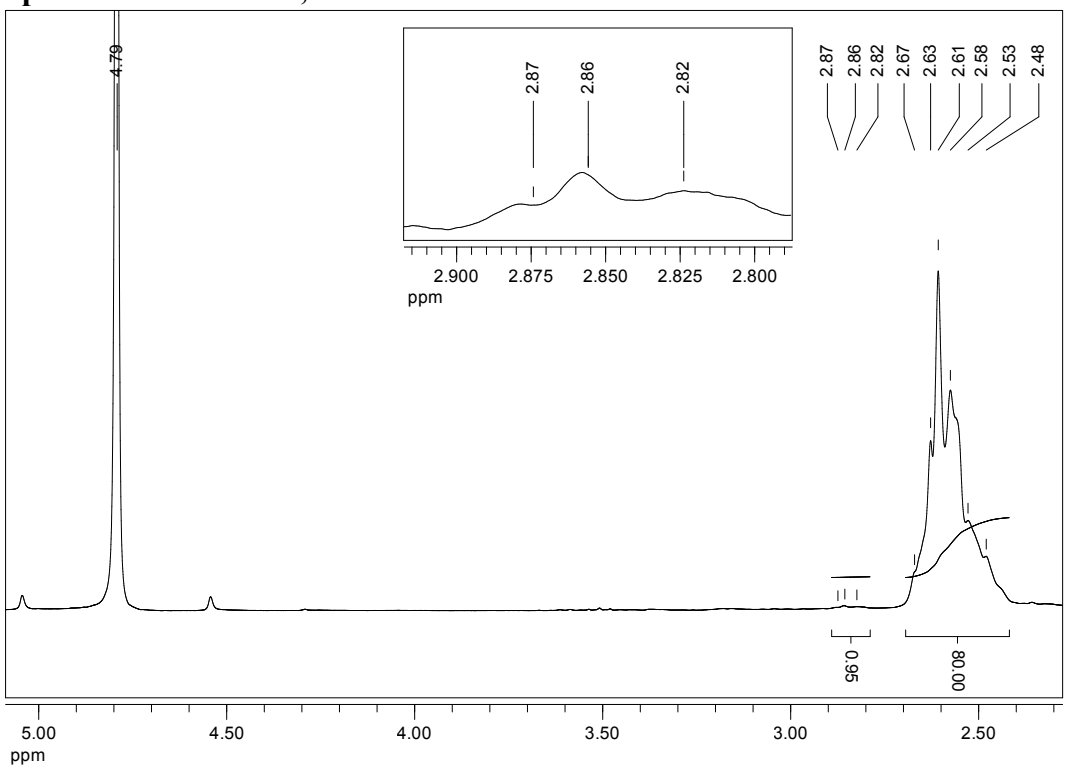
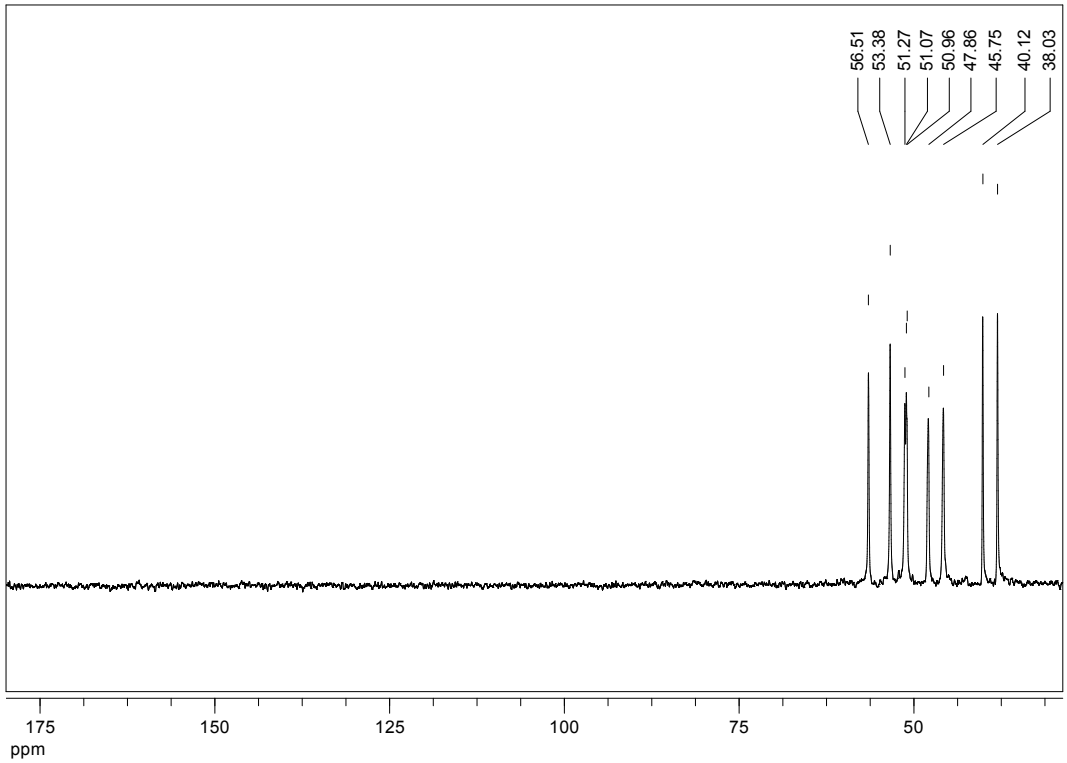


***Fig. S1.*** $^{1}$H NMR spectra of pristine PEIs and $^{13}$C NMR spectrum of PEI 0.8kDa

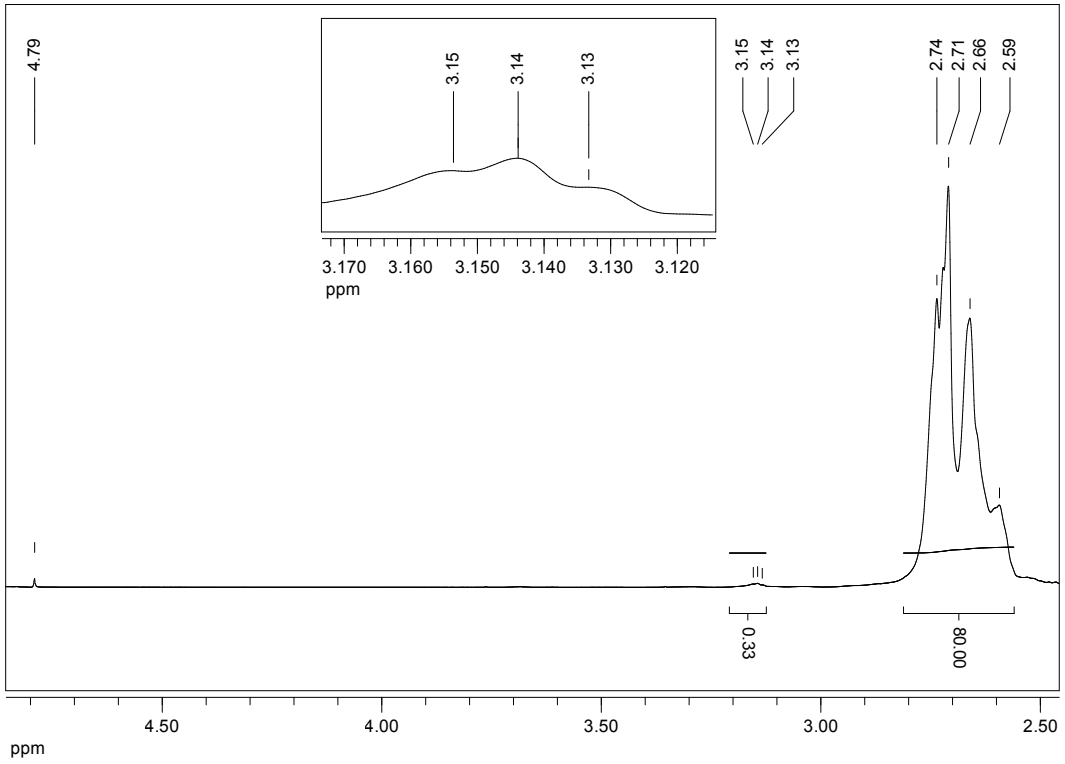
**Spectrum 1: $^{1}$H NMR, PEI 0.8kDa**




**Spectrum 2: $^{13}$C NMR, PEI 0.8kDa**



**Spectrum 3: $^{1}$H NMR, PEI 25kDa**




**Spectrum 4: $^{1}$H NMR, PEI 750kDa**

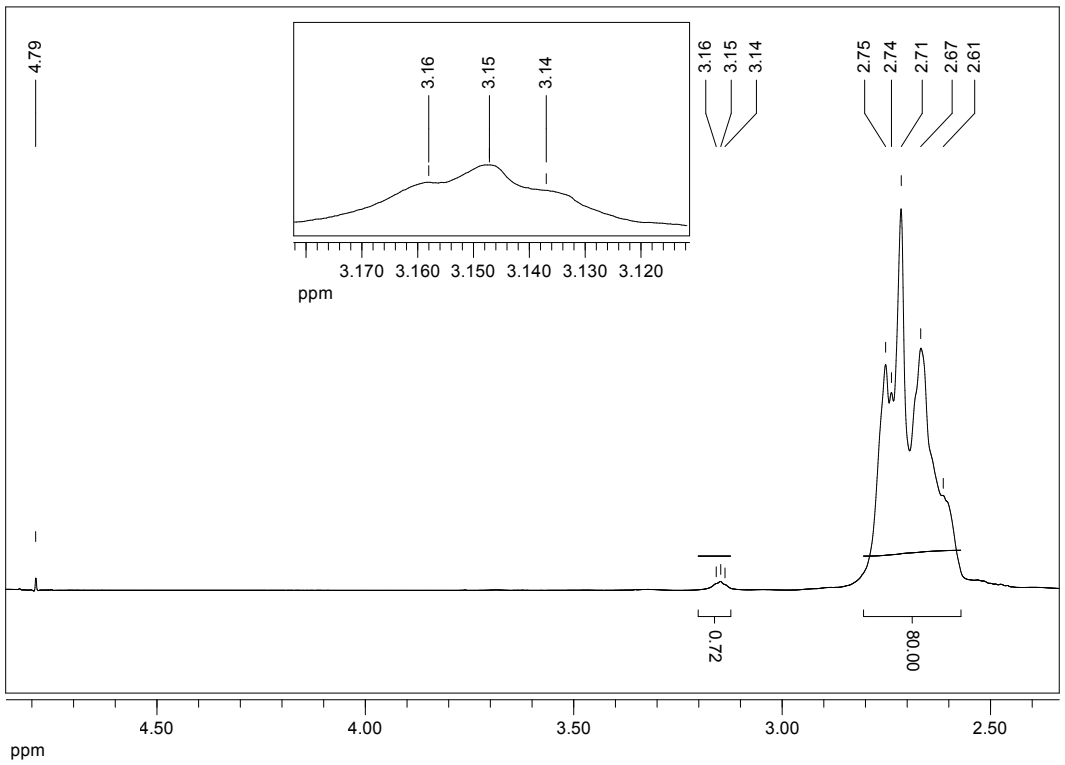
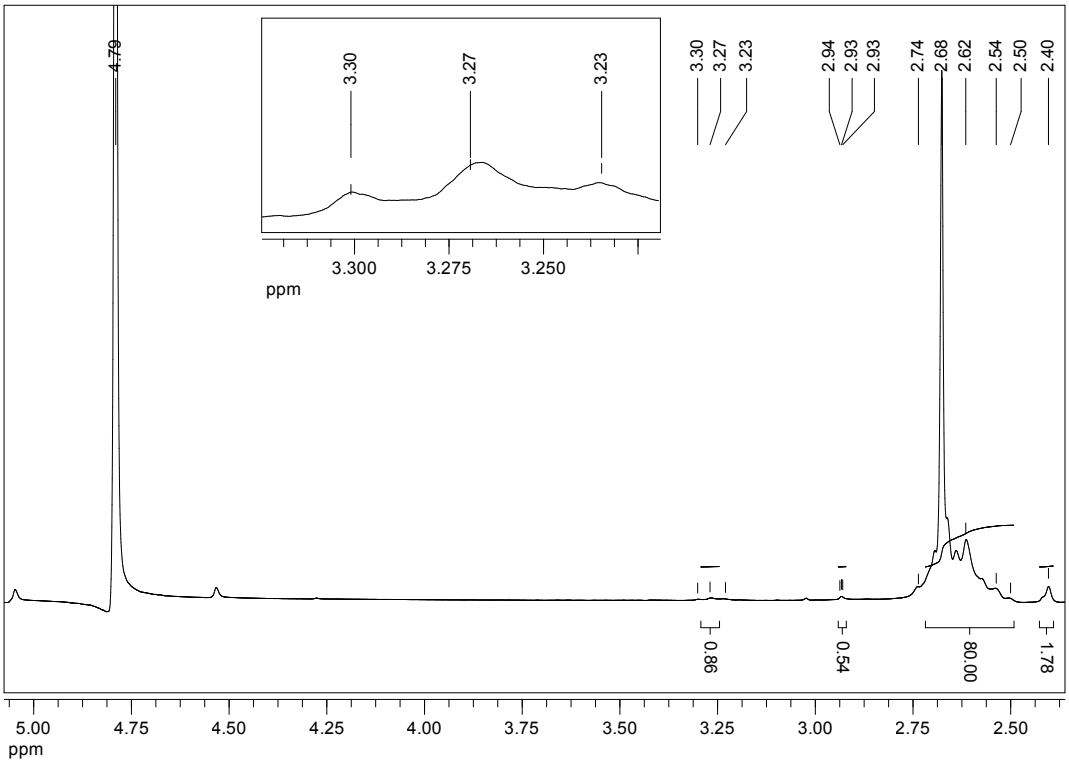
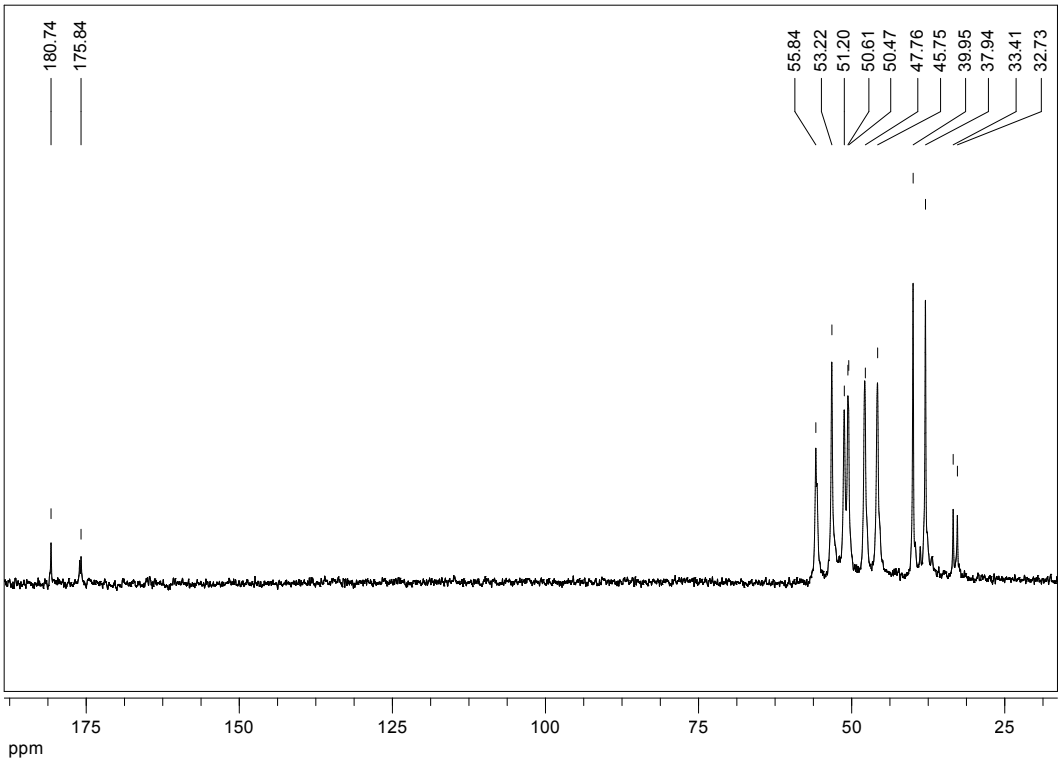


***Fig. S2.*** $^{1}$H NMR spectra of PEI derivatives and $^{13}$C NMR spectra of PEI 0.8kDa derivatives

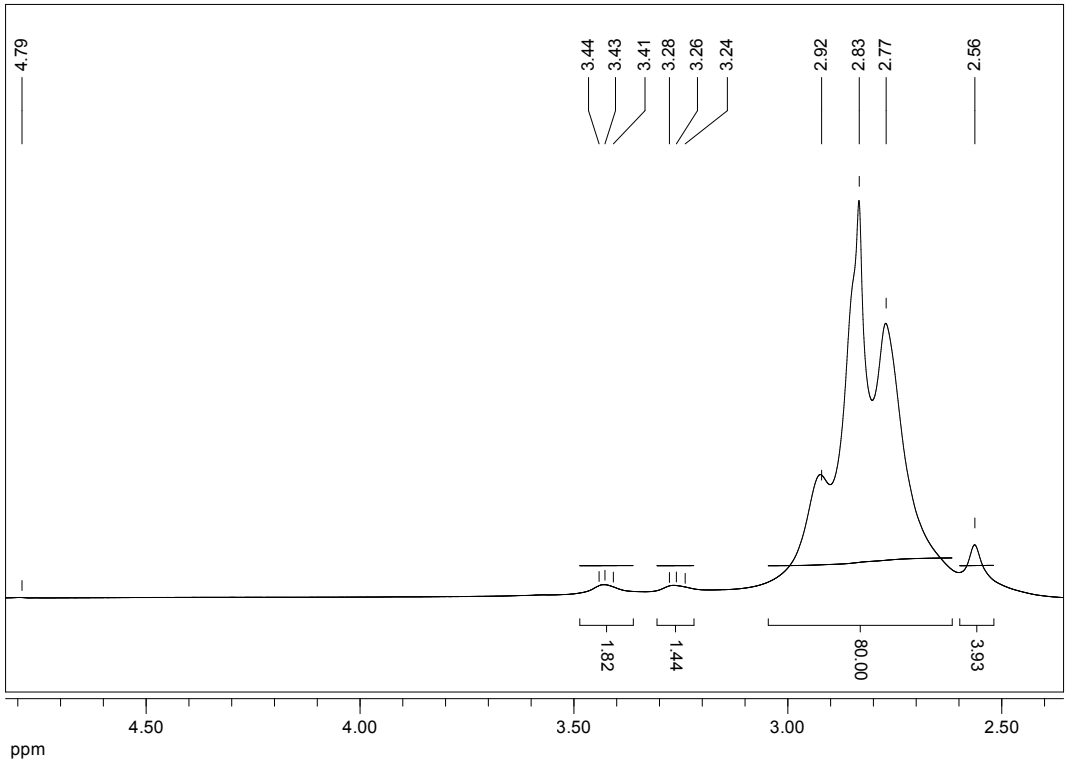
**Spectrum 1: $^{1}$H NMR, PEI0.8k-SA**



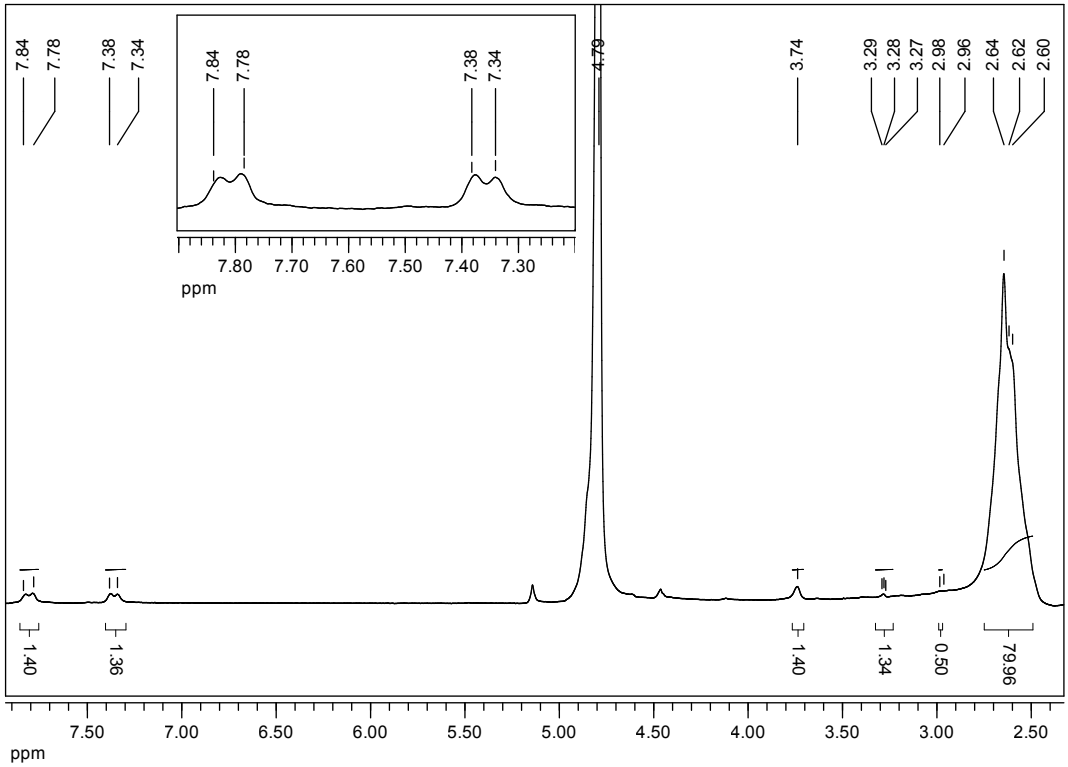

**Spectrum 2: $^{13}$C NMR, PEI 0.8k-SA**



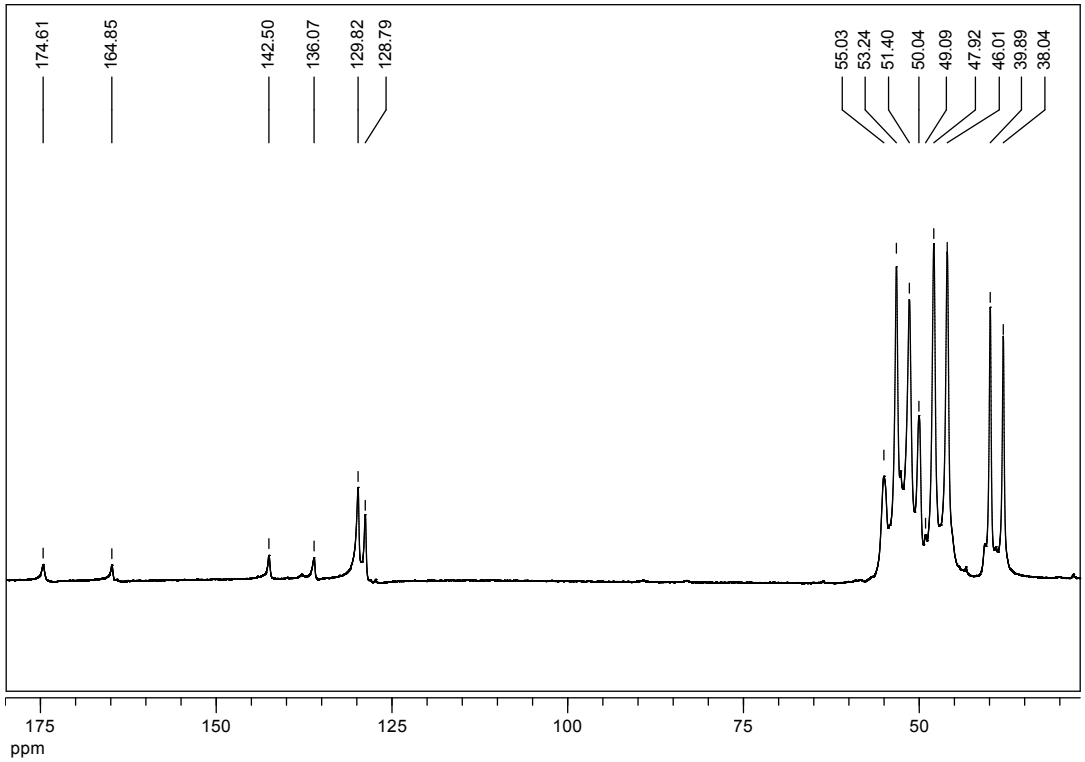
**Spectrum 3: $^{1}$H NMR, PEI750k-SA**



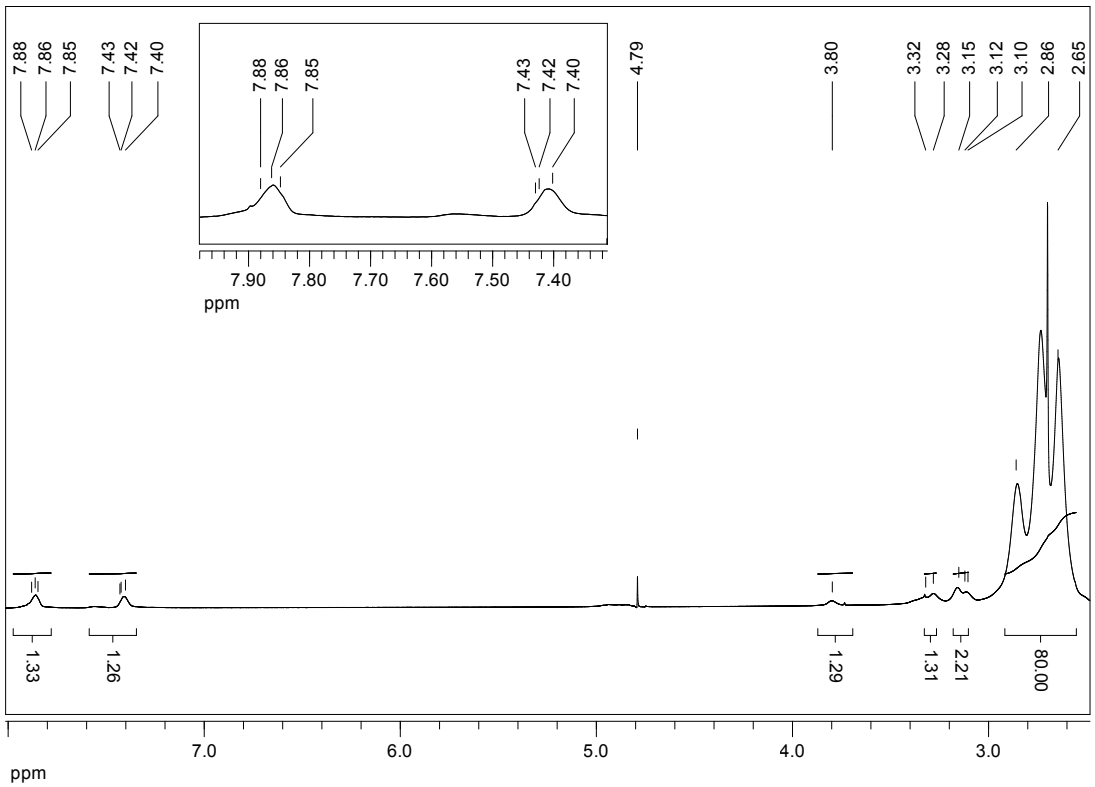

**Spectrum 4: $^{1}$H NMR, PEI0.8k-pFBA**



**Spectrum 5: $^{13}$C NMR, PEI 0.8k-pFBA**




**Spectrum 6: $^{1}$H NMR, PEI750k-pFBA**

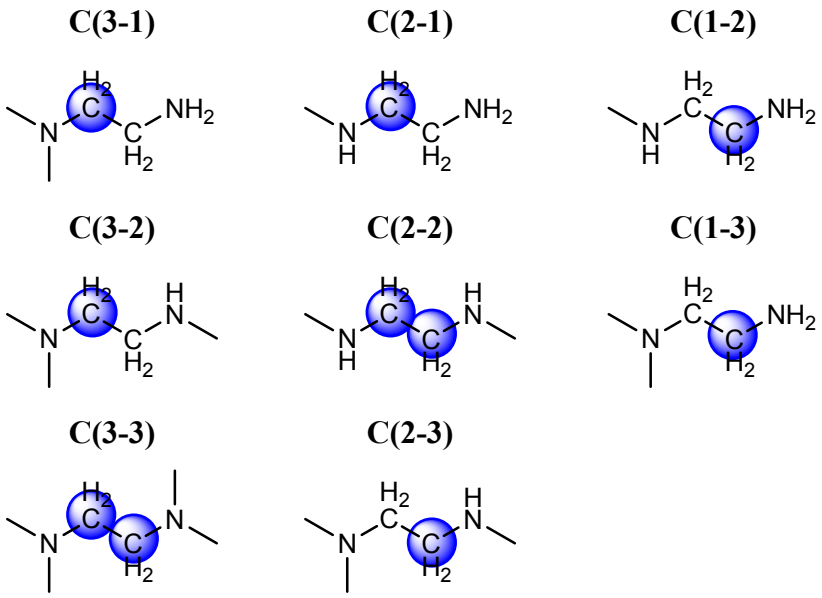


II. Inverted-gate $^{13}C$ NMR analysis

The ratio $NH_2$ : NH : N was calculated according to the equation (please see designations below):

$$NH_2 : NH : N = I(C_{1\text{-}2} + C_{1\text{-}3}) : I(C_{2\text{-}1} + C_{2\text{-}2} + C_{2\text{-}3})/2 : I(C_{3\text{-}1} + C_{3\text{-}2} + C_{3\text{-}3})/3$$

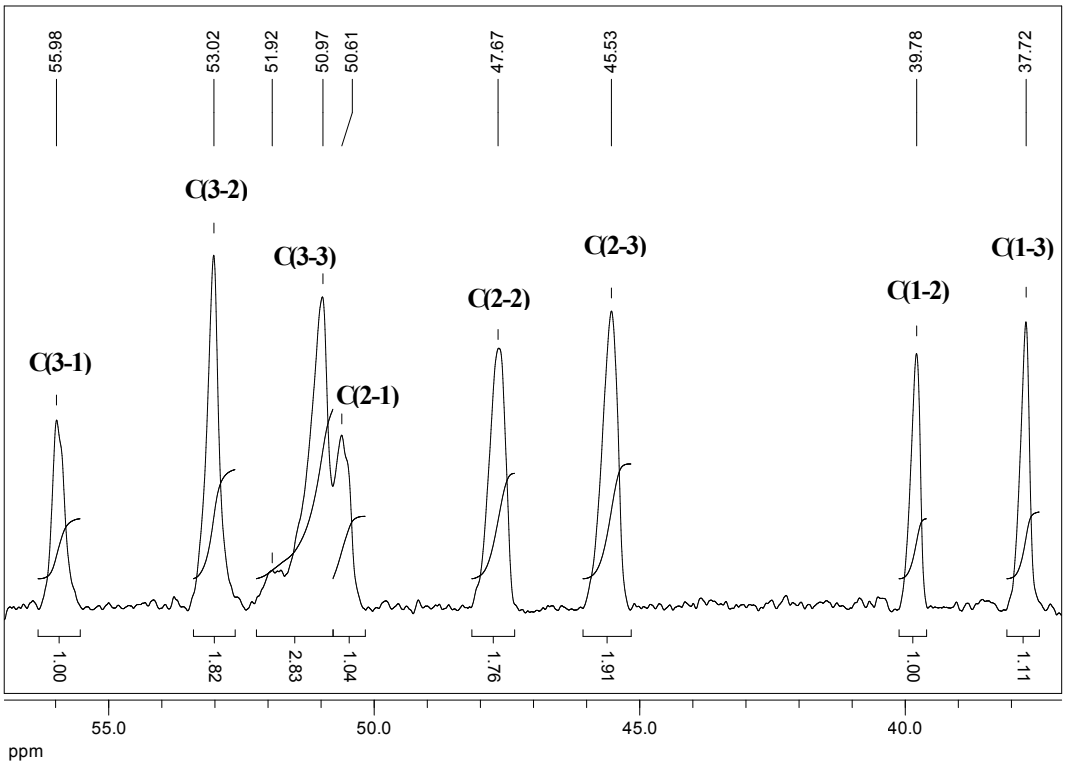
where: $I$ – signal integration.



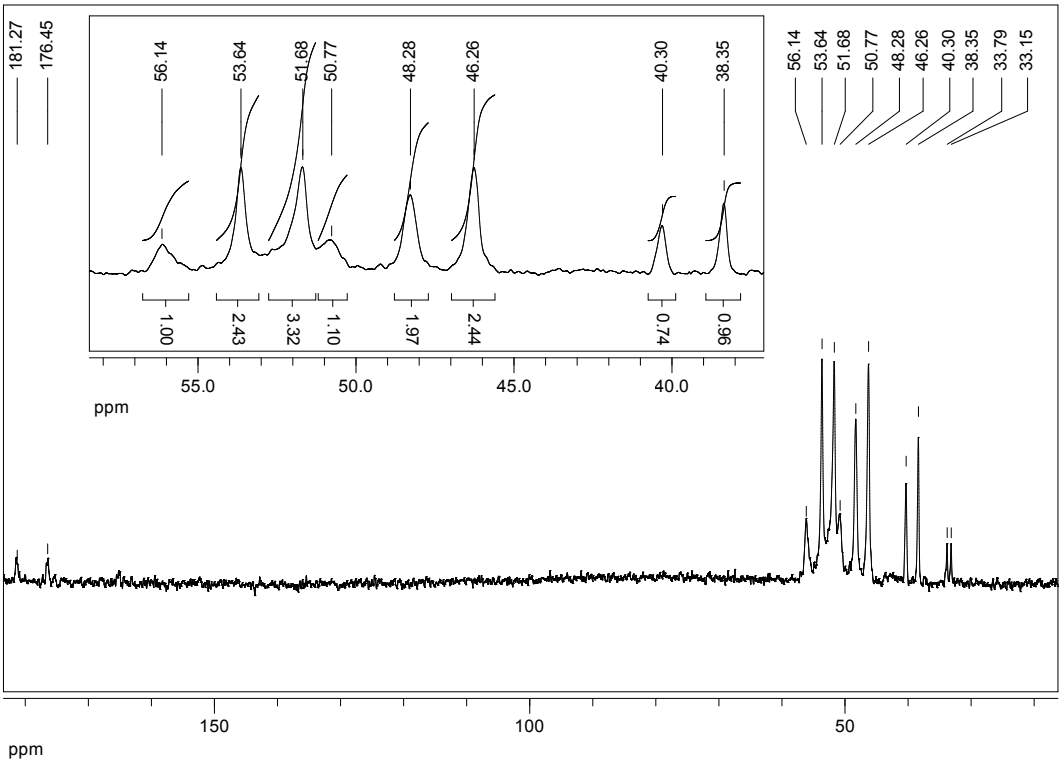

In **Fig. S3** inverted-gate $^{13}C$ NMR spectra are shown: pristine PEI 25kDa (**spectrum 1**), PEI25k-SA (**spectrum 2**), PEI25k-pFBA (**spectrum 3**). All the spectra were recorded in deuterium oxide, overnight. Please note, that peaks from substituents do not coincide with peaks from methylene groups of PEI. Hence, substituents location on the spectra do not interfere in the inverted-gate $^{13}C$ NMR analysis.

***Fig. S3.*** Inverted-gate $^{13}C$ NMR spectra of PEI 25kDa and its derivatives

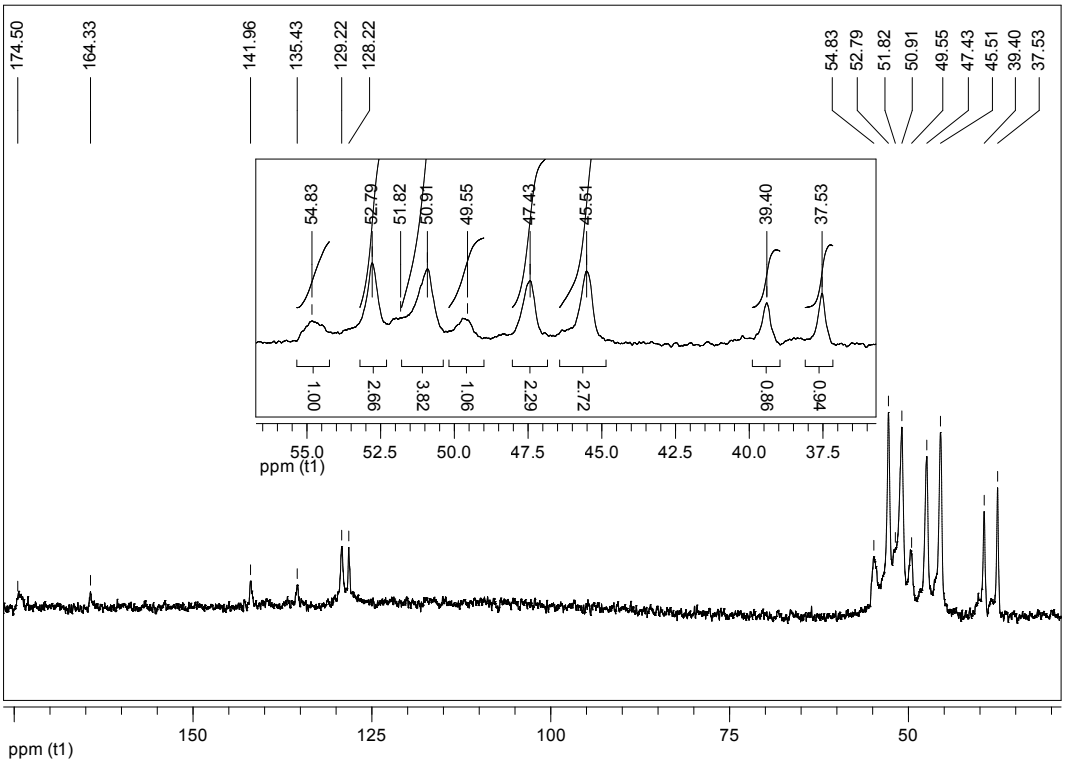
**Spectrum 1: inverted-gate $^{13}C$ NMR, PEI 25kDa; $NH_2$ : NH : N** ratio is **1 : 1.12 : 0.89**




**Spectrum 2: inverted-gate $^{13}C$ NMR, PEI25k-SA; $NH_2$ : NH : N** ratio is **1 : 1.62 : 1.32**



**Spectrum 3: inverted-gate $^{13}C$ NMR, PEI25k-pFBA; $NH_2$ : NH : N** ratio is **1 : 1.69 : 1.39**



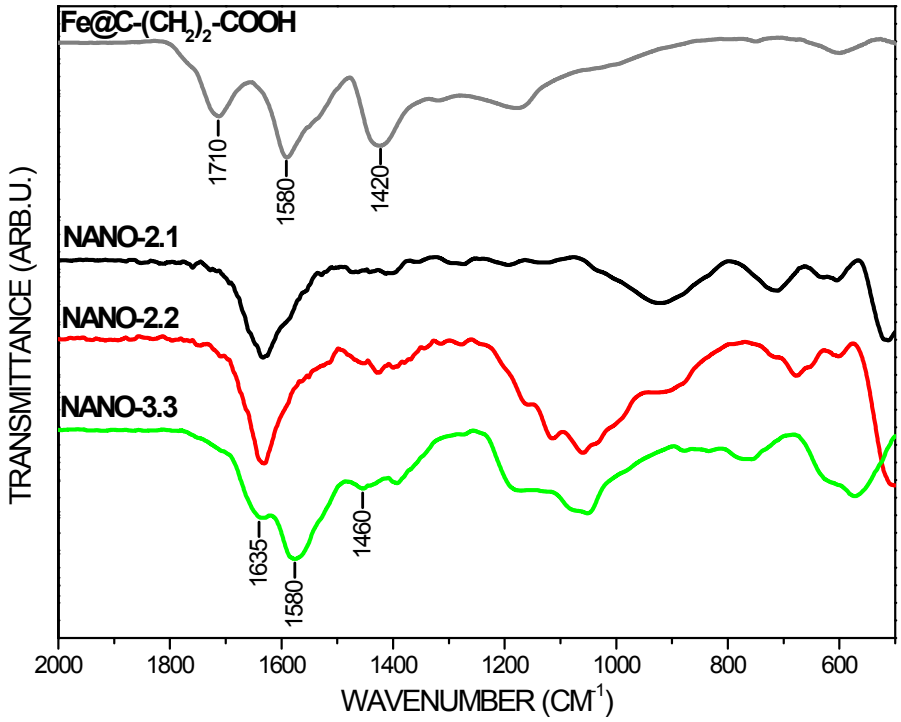

III. Quantitative analysis of PEI-CEINs conjugates

FT-IR spectra of other PEI-CEINs conjugates are presented in **Fig. S4**: Fe@C-$(CH_2)_2$-CONH-PEI (NANO-2.1-2.2) (**spectrum 1**), Fe@C-CONH-PEI-SA (NANO-3.1-3.3) (**spectrum 2**), Fe@C-$(CH_2)_2$-CONH-PEI-SA (NANO-4.1-4.2) (**spectrum 3**) and Fe@C-CONH-PEI-pFBA (NANO-5.1-5.3) (**spectrum 4**).

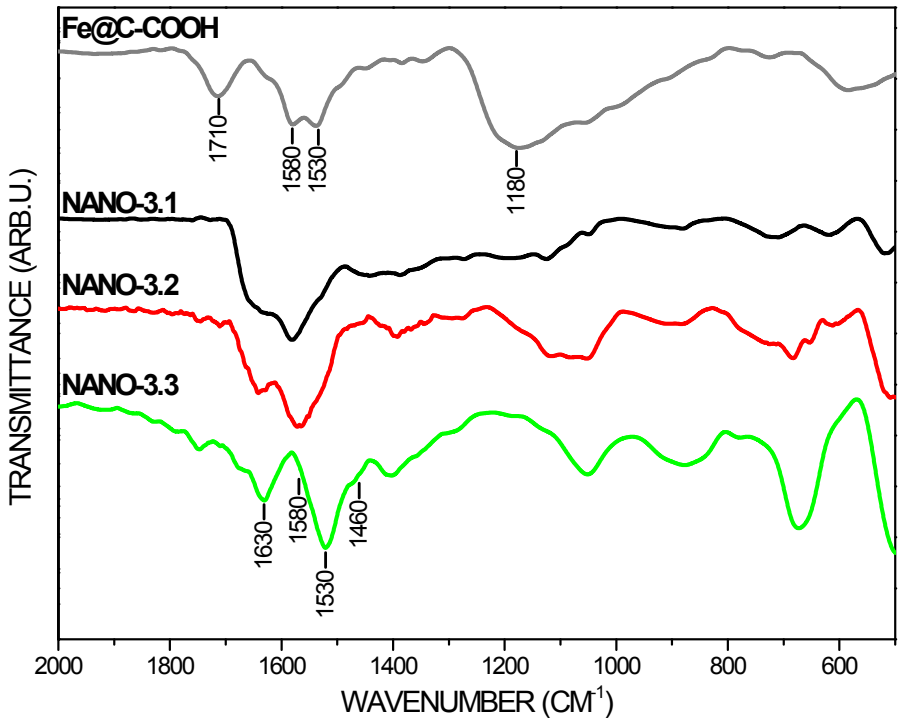
In **Fig. S5** C-H stretching vibrations in the $CH_2$ moiety of PEI, founded on PEI-CEINs conjugates spectra, is presented.

**Fig. S4**. FT-IR spectra of PEI-CEINs conjugates

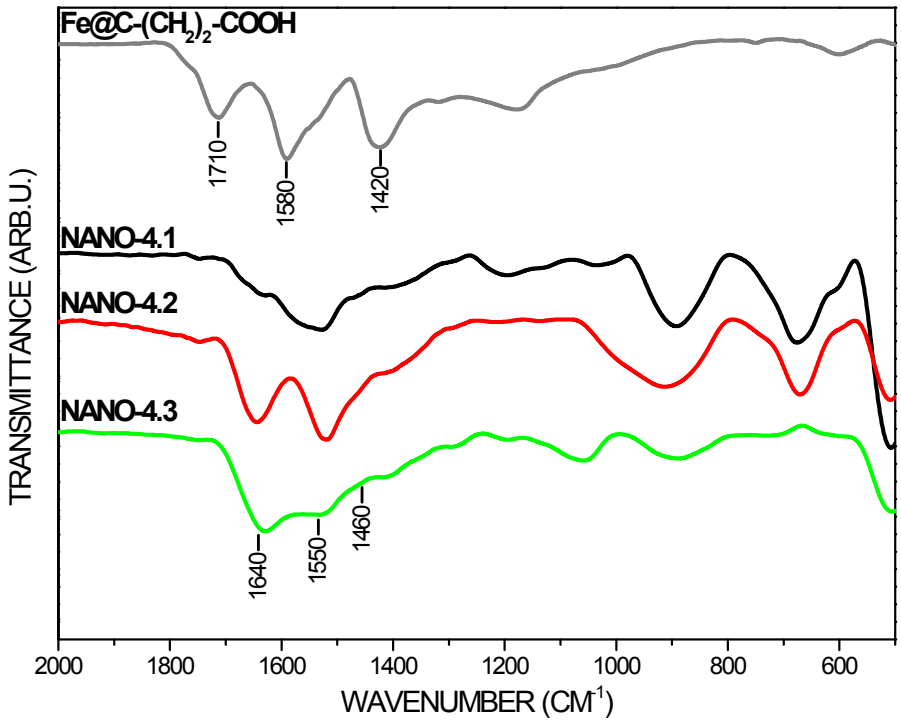
**Spectrum 1:** Fe@C-$(CH_2)_2$-CONH-PEI (NANO-2.1-2.2)



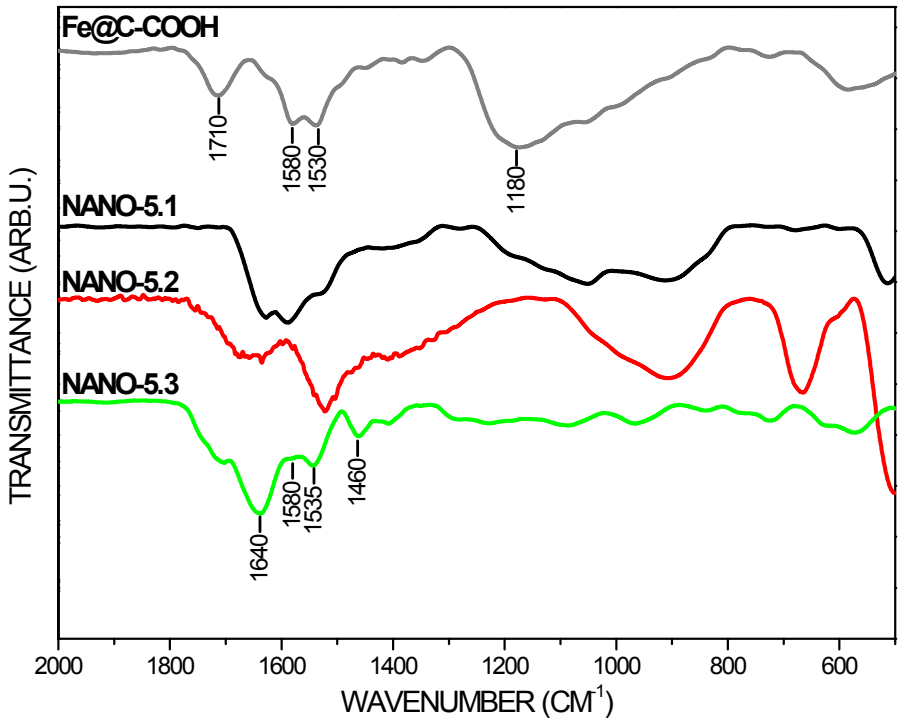

**Spectrum 2:** Fe@C-CONH-PEI-SA (NANO-3.1-3.3)



**Spectrum 3:** Fe@C-$(CH_2)_2$-CONH-PEI-SA (NANO-4.1-4.2)




**Spectrum 4:** Fe@C-CONH-PEI-pFBA (NANO-5.1-5.3)



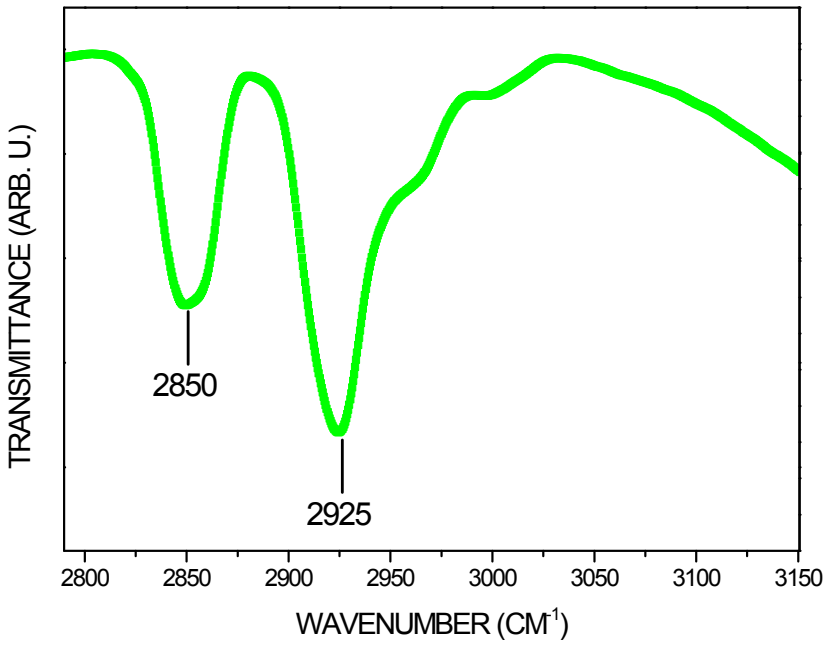



***Fig. S5.*** C-H stretching vibrations in the $CH_2$ moiety of PEI, founded on PEI-CEINs conjugates spectra

IV. PEI content

In **Fig. S6** TGA curves of pristine PEIs of various molecular weight are shown. TGA curves of other PEI-CEINs conjugates are presented in **Fig. S7**: Fe@C-$(CH_2)_2$-CONH-PEI (NANO-2.1-2.2) (**section 1**), Fe@C-CONH-PEI-SA (NANO-3.1-3.3) (**section 2**), Fe@C-$(CH_2)_2$-CONH-PEI-SA (NANO-4.1-4.2) (**section 3**) and Fe@C-CONH-PEI-pFBA (NANO-5.1-5.3) (**section 4**). DTG curves of two representative samples: PEI 750kDa (**curve 1**) and Fe@C-CONH-PEI750k (**curve 2**) are shown in **Fig. S8**.

The relative CEINs fraction ($F_{CEINs}$) in each conjugate, was approximated as follows: $F_{CEINs}$ [%] = 100% - $W_{200\text{-}530}$ – $LP_{nano}$, where: $W_{200\text{-}530}$ – weight loss in temperature range between 200 °C – 530 °C, $LP_{nano}$ – weight loss for linker-modified CEINs (3.5% and 5.1% for Fe@C-COOH and Fe@C-$(CH_2)_2$-COOH, respectively).

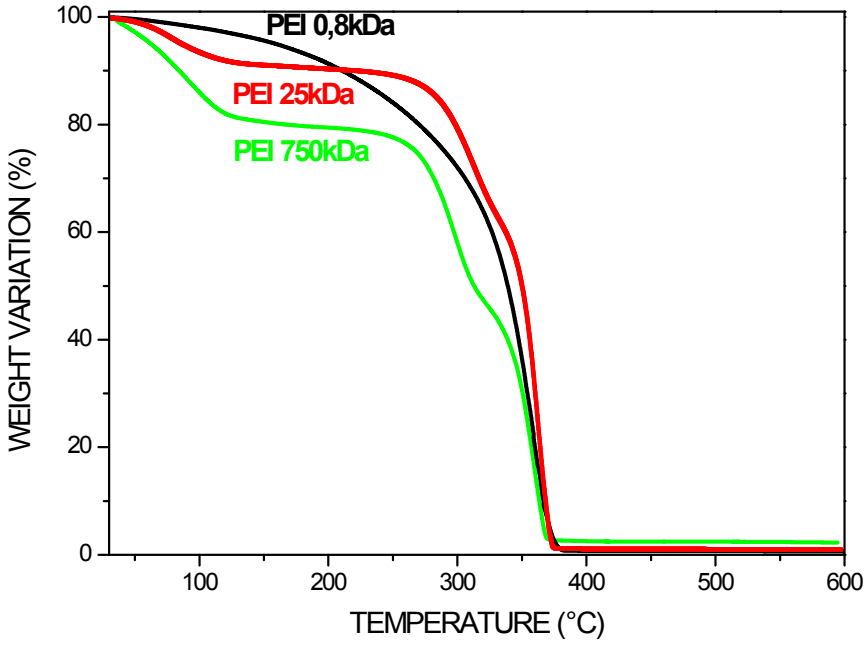
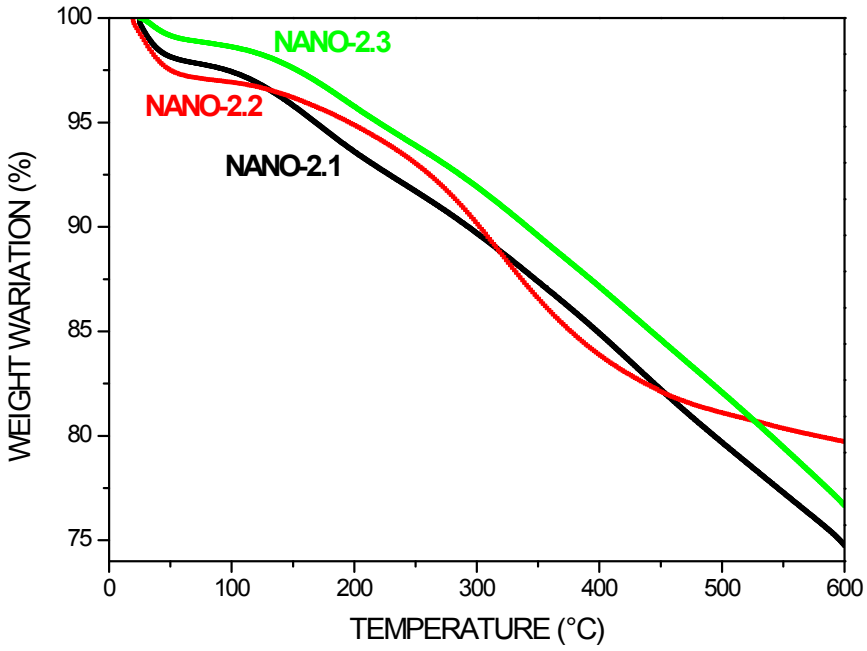


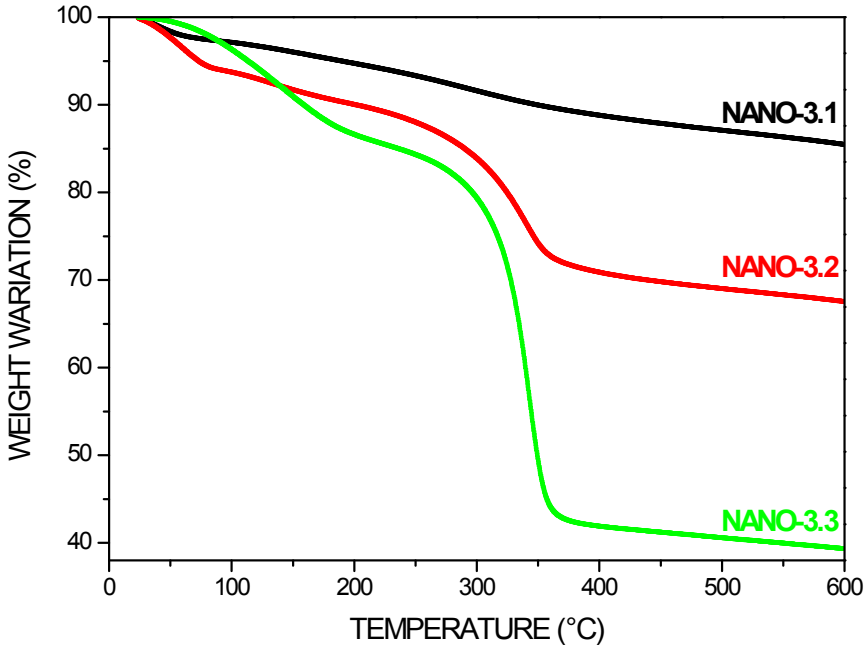

**Fig. S6**. TGA curves (in nitrogen) of pristine PEIs

**Fig. S7**. TGA curves (in nitrogen) of PEI-CEINs conjugates

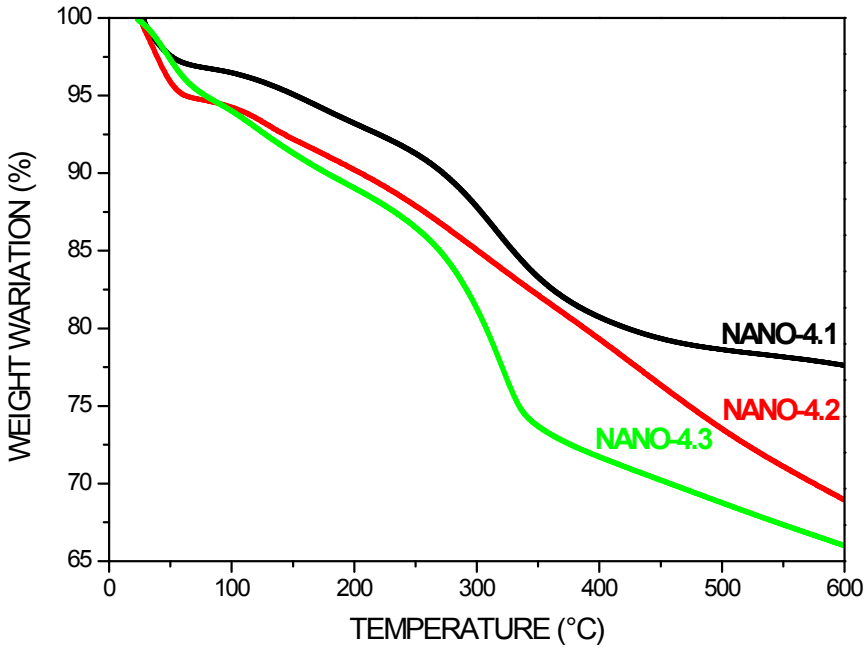
**Graph 1:** Fe@C-$(CH_2)_2$-CONH-PEI (NANO-2.1-2.2)



**Graph 2:** Fe@C-CONH-CONH-PEI-SA (NANO-3.1-3.3)




**Graph 3:** Fe@C-$(CH_2)_2$-CONH-PEI-SA (NANO-4.1-4.2)



**Graph 4:** Fe@C-CONH-PEI-pFBA (NANO-5.1-5.3)

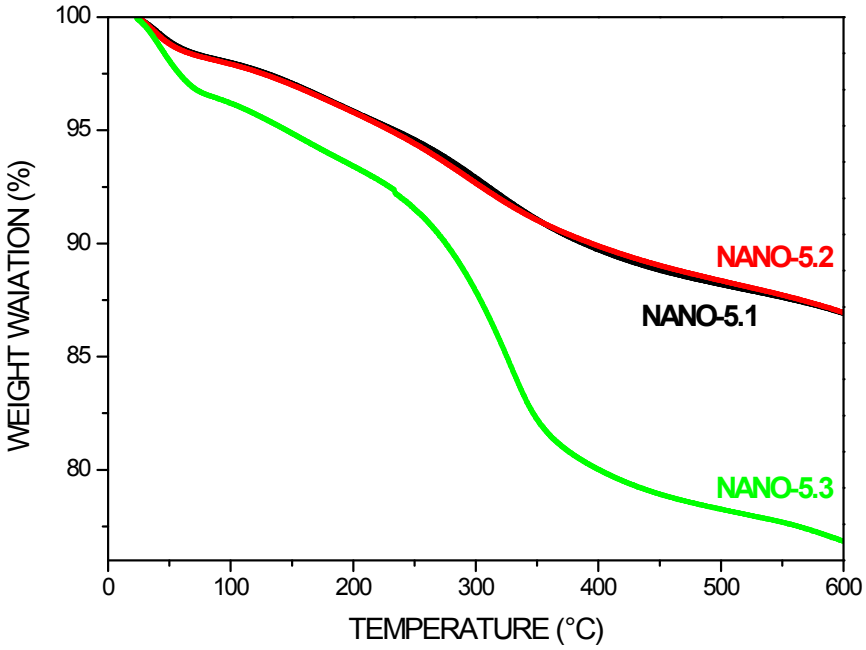
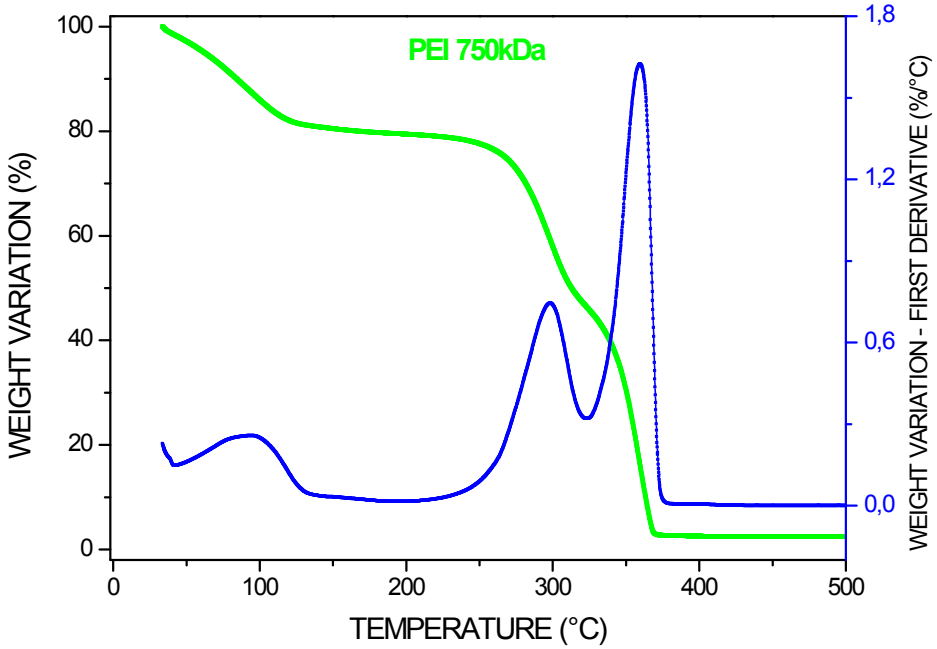
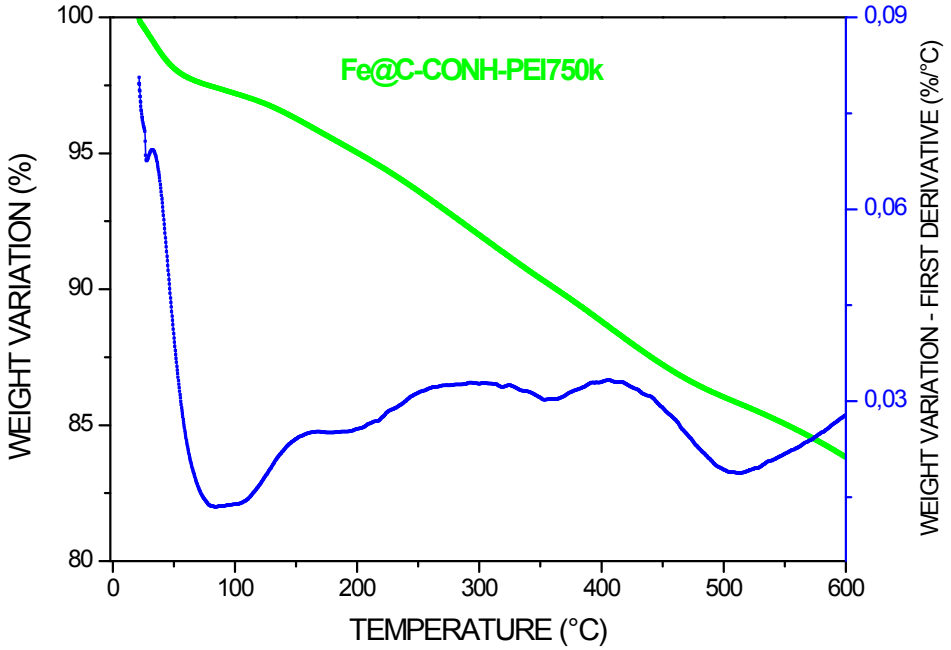



**Fig. S8**. TGA and DTG curves (in nitrogen) of PEI 750kDa and Fe@C-CONH-PEI750k

**Graph 1:** PEI 750kDa



**Graph 2:** Fe@C-CONH-PEI750k




V. Study on the physical adsorption of PEI onto CEINs

FT-IR spectra of samples of the non-covalent PEI adsorption onto CEINs are presented in **Fig. S9**. The assignment of the characteristic absorption bands of CEINs and PEI, was presented in the earlier parts of the text. The weak absorption band at 1650 $cm^{-1}$ may occur due to the electrostatic interactions between primary amine groups of PEI and carboxylic groups on the surface of the surface-modified CEINs. The absorption band located at 1745 $cm^{-1}$ comes from C=O moieties and is upshifted, due to the physical adsorption of PEI (compare with Fe@C-$(CH_2)_2$-COOH spectrum presented earlier i.e. **spectrum 1** in **Fig. S4**).

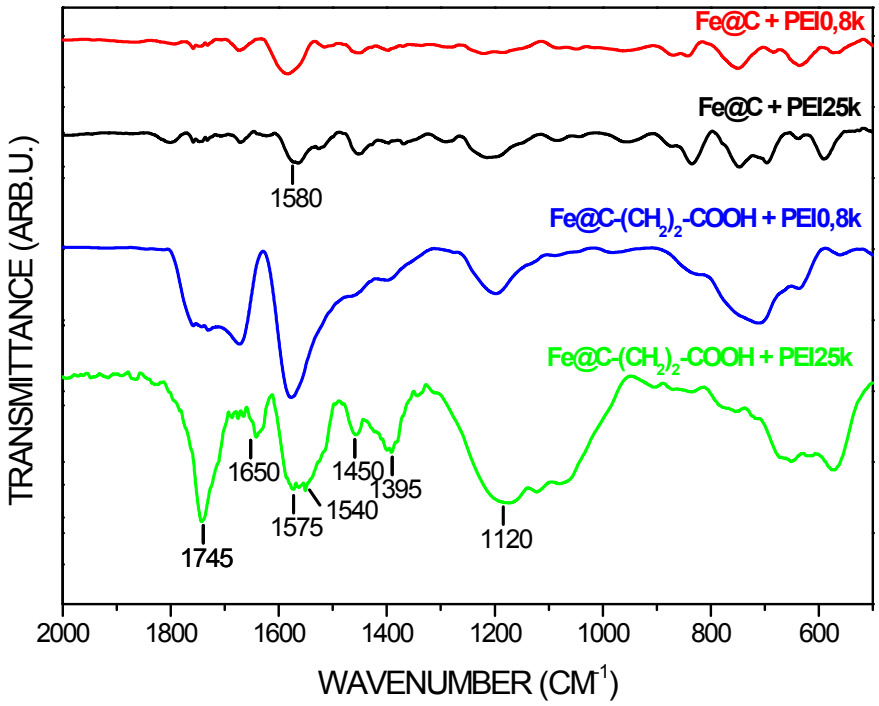



***Fig. S9.*** FT-IR spectra of samples of the non-covalent attachment of PEI onto CEINs surface (discussion above)