Addition of azomethine ylides to carbon-encapsulated iron nanoparticles

Electronic Supplementary Information (ESI)

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S1. Materials and methods

Carbon-encapsulated iron nanoparticles (CEINs) were synthesized by the carbon-arc route. The protocol is described in detail elsewhere.¹

Ferrocenecarboxaldehyde (98%), ferrocene (98%), 4-hydroxybenzaldehyde (98%), 1-pyrenecarboxaldehyde (99%), heptanal (95%), sarcosine (98%), β-cyclodextrin (>95%), iron (III) chloride hexahydrate (>99%) were purchased from Sigma-Aldrich. 2,4-Dihydroxybenzaldehyde (>98%) was purchased from Fluka. Dess-Martin periodinane (95%) was purchased from Fluorochem. Benzaldehyde (99%) was purchased from Avantor Performance Materials Poland S.A. All reagents were used as received without further purification.

Thermogravimetric analysis (TGA) was performed with a TA Q-50 instrument under nitrogen atmosphere and the heating rate of 10 °C min⁻¹.

Fourier transformation infrared (FT-IR) spectra were recorded in a transmission mode with a Thermo Nicolet Avatar 370 spectrometer with the spectral resolution of 4 cm⁻¹ (150 scans). The samples were mixed with KBr and pressed in a form of pellets.

¹H NMR and ¹³C NMR spectra were recorded on a Varian NMR System spectrometer (500 MHz, 125 MHz) in DMSO-d₆ with calibration on the residual peak 2.50 ppm and 39.5 ppm, for ¹H NMR and ¹³C NMR, respectively. The MestRe-C 2.0 software was used for the simulation of NMR spectra (MestRe-C NMR Data Processing Made Easy 4.9.9.6, 1996–2006, courtesy F.J. Sardina, Universidad de Santiago de Compostela, Spain).

Sonication of carbon materials was performed using a Bandelin Sonorex RK 100 H ultrasonic probe (ultrasonic peak output/RF power: 320W/80W; 35 kHz). The suspensions were centrifuged on a MPW-260R centrifuge (14000 rpm, 14504 rcf).

Cyclic voltammetry (CV) was performed in a home-made 1-mL electrochemical cell using an Autolab (Eco Chemie B.V., Utrecht, Netherlands), model PGSTAT 12 potentiostat, controlled via the producer’s software. The three-electrode system, consisting of a disc glassy carbon electrode, GCE, (φ = 3 mm, BAS Instruments) used as the working electrode, an Ag/AgCl/3 M KCl reference electrode and a platinum wire used as the counter electrode were employed. Each time before the measurements the working electrode was briefly polished with 1-μm Al₂O₃ powder on a wet pad. After the polishing step, the electrode was rinsed with a direct stream of ultrapure water (Hydrolab, conductivity 0.056 μS·cm⁻¹). to remove alumina

completely from the surface. To eliminate the electrical noise the electrochemical cell was placed in a Faraday cage.
S2. Chemical structure of β-cyclodextrin

Fig. S1 Chemical structure of β-cyclodextrin
S3. Experimental section

S3.1 Synthesis of β-cyclodextrin monoaldehyde (7)

Synthesis of β-cyclodextrin monoaldehyde (7) was based on the literature method. β-Cyclodextrin (567.5 mg, 0.5 mmol) was dissolved in DMSO (10 mL) and Dess-Martin periodinane (424.1 mg, 1.0 mmol) was added. The reaction mixture was stirred for 1 h at room temperature. The crude product was isolated via the addition of acetone (350 mL), followed by cooling at -28°C for 1 h and filtration over a nylon membrane (0.45 μm pore size). The as-obtained white solid was then dissolved in DMSO (5 mL) and precipitated with acetone (150 mL). The product was filtered off over a nylon membrane (0.45 μm pore size), washed with acetone (10 mL) and dried at 45°C for 24 h. 505.2 mg (89%) of the β-cyclodextrin monoaldehyde (7) was obtained.

$^1$H NMR $\delta_H$ (500 MHz, DMSO-$d_6$, ppm): 9.65 (s), 5.69-5.63 (m), 4.78-4.77 (m), 4.41-4.40 (t, J = 5.4 Hz), 3.59-3.53 (m), 3.33-3.26 (m)

$^{13}$C NMR $\delta_C$ (125 MHz, DMSO-$d_6$, ppm): 198.28 (s), 101.91 (s), 81.51 (s), 73.02 (s), 72.39 (s), 72.01 (s), 59.89 (s)

FT-IR$^3$ (KBr): $\nu = 1720, 1640, 1410, 1335, 1295, 1155, 1090, 1045, 940, 705$ cm$^{-1}$

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$^3$ In the wavenumber range of 2000–400 cm$^{-1}$
S3.2 Functionalization of CEINs

The reaction scheme is presented in Fig. 1 in the main text of the article.

**General method for the synthesis of carbon materials 8, 9, 10, 13**

Prior to the reaction, CEINs (20 mg) were sonicated in toluene (30 mL) for 1 h. Aldehyde (0.5 mmol) and sarcosine (0.4 mmol) were added to the dispersion of CEINs. The reaction mixture was sonicated for 5 min and refluxed for 24 h. Next, the content of the flask was once again sonicated for 20 min, the aldehyde (0.5 mmol) and sarcosine (0.4 mmol) were added and the reaction mixture was then refluxed for another 24 h. The obtained suspension was filtered off over a nylon membrane (0.22 µm pore size), washed with toluene (20 mL) and methanol (20 mL). The material was dispersed in methanol (40 mL), sonicated for 3 h, filtered off, washed with water (5 mL), acetone (15 mL) and finally dried in 45°C overnight. The amount of the product was as follows:

- 8 (from the reaction with benzaldehyde): 22.5 mg,
- 9 (from the reaction with 1-pyrenecarboxaldehyde): 23.1 mg,
- 10 (from the reaction with ferrocenecarboxaldehyde): 24.2 mg,
- 13 (from the reaction with heptanal): 22.5 mg.

**General method for the synthesis of carbon materials 11 and 12**

Prior to the reaction, CEINs (20 mg) were sonicated in toluene/DMSO solvent system (20 mL/10 mL) for 1 h. Aldehyde (0.5 mmol) and sarcosine (0.4 mmol) were added to a dispersion of CEINs. The reaction mixture was sonicated for 5 min and refluxed for 24 h. Next, the content of the flask was once again sonicated for 20 min, the aldehyde (0.5 mmol) and sarcosine (0.4 mmol) were added and the reaction mixture was then refluxed for another 24 h. The obtained suspension was filtered off over a nylon membrane (0.22 µm pore size), washed with toluene (20 mL) and methanol (20 mL). The material was dispersed in water (25 mL) and sonicated for 2 h to remove the traces of DMSO remaining, if any. Then, the dispersion was filtered off and washed with methanol (5 mL). The as-obtained carbon material was redispersed in methanol (40 mL), sonicated for 3 h, filtered off, washed with acetone (10 mL) and finally dried in 45°C overnight. The amount of the product was as follows:

- 11 (from the reaction with 4-hydroxybenzaldehyde): 23.0 mg,
• 12 from the reaction with 2,4-dihydroxybenzaldehyde: 22.8 mg,

**Synthesis of carbon material 14**

Prior to the reaction, CEINs (20 mg) were sonicated in the toluene/DMSO solvent system (20 mL/20 mL) for 1 h. β-Cyclodextrin monoaldehyde (7; 566.49 mg, 0.5 mmol) and sarcosine (35.6 mg, 0.4 mmol) were added to a dispersion of CEINs. The reaction mixture was sonicated for 5 min and refluxed for 24 h. Next, the content of the flask was once again sonicated for 20 min, β-cyclodextrin monoaldehyde (7; 566.49 mg, 0.5 mmol) and sarcosine (35.6 mg, 0.4 mmol) were added and the reaction mixture was then refluxed for another 24 h. The obtained suspension was filtered off over a nylon membrane (0.22 µm pore size) and washed with methanol (20 mL). The material was dispersed in water (80 mL) and sonicated for 3 h to remove the traces of DMSO remaining as well as the unreacted β-cyclodextrin monoaldehyde. Then, the dispersion was filtered off and washed with methanol (15 mL). The as-obtained carbon material was redispersed in acetone (40 mL) to remove the traces of complexed toluene, if any. Content of the flask was sonicated for 3 h, filtered off, washed with acetone (15 mL) and finally dried in 45°C overnight. 25.3 mg of material 14 was obtained.

**Material 8** (from the reaction with benzaldehyde):

![FeN](attachment:image.png)

**FT-IR** (KBr): \(\nu = 1580, 1510, 1455, 1395, 1295, 1110, 960, 805, 680, 565, 455 \text{ cm}^{-1}\)

**TGA** (content of the organic moiety): 11.8 wt. %

**Material 9** (from the reaction with 1-pyrenecarboxaldehyde)

![FeN](attachment:image.png)

**FT-IR** (KBr): \(\nu = 1585, 1510, 1460, 1390, 1270, 1155, 960, 820, 685, 460 \text{ cm}^{-1}\)

**TGA** (content of the organic moiety): 13.3 wt. %
**Material 10** (from the reaction with ferrocenecarboxaldehyde)

FT-IR (KBr): $\nu = 1590, 1540, 1480, 1440, 1385, 1285, 1125, 875, 760, 675, 560, 460 \text{ cm}^{-1}$

TGA (content of the organic moiety): 21.2 wt. %

**Material 11** (from the reaction with 4-hydroxybenzaldehyde)

FT-IR (KBr): $\nu = 1615, 1575, 1505, 1450, 1365, 1270, 1165, 1035, 685, 565, 460 \text{ cm}^{-1}$

TGA (content of the organic moiety): 17.0 wt. %

**Material 12** (from the reaction with 2,4-dihydroxybenzaldehyde)

FT-IR (KBr): $\nu = 1615, 1570, 1510, 1445, 1360, 1275, 1185, 1115, 1030, 685, 560, 465 \text{ cm}^{-1}$

TGA (content of the organic moiety): 18.2 wt. %

**Material 13** (from the reaction with heptanal)

FT-IR (KBr): $\nu = 1505, 1445, 1375, 1335, 1230, 1100, 945, 695, 530 \text{ cm}^{-1}$

TGA (content of the organic moiety): 12.0 wt. %
Material 14 (from the reaction with β-cyclodextrin monoaldehyde):

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**FT-IR (KBr):** \( \nu = 1635, 1505, 1455, 1410, 1340, 1240, 1150, 1020, 1025, 675 \text{ cm}^{-1} \)

**TGA (content of the organic moiety):** 20.8 wt. %

S3.3 Complexation of ferrocene in carbon material 14

The reaction scheme is presented in Fig. 5a in the main text of the article. The material 14 (10 mg) was sonicated for 6 h with the solution of ferrocene (15.0 mg) in ethanol (2 mL). The dispersion was then centrifuged (14000 rpm, 30 min, 22°C) and the supernatant was removed. The obtained carbon material was dried for 45°C overnight. 10.3 mg of the material 15 was obtained. In order to release the ferrocenium cation, the carbon material (15; 10.0 mg) was sonicated for 30 min with aqueous solution of iron (III) chloride hexahydrate (20 mg·mL\(^{-1}\); 2 mL). This dispersion was centrifuged (14000 rpm, 30 min, 22°C) and the supernatant was removed. The carbon material was redispersed in water (2 mL), sonicated for 1 h, centrifuged (using the same parameters as mentioned above) and finally dried in 45°C overnight. 9.8 mg of the material (14) was recovered.

See discussion in section S5.3 for the characterization of the material 15.
S4. NMR spectra

**Fig. S2** $^1$H NMR spectrum (500 MHz, DMSO-$d_6$) of $\beta$-cyclodextrin

**Fig. S3** $^{13}$C NMR spectrum (125 MHz, DMSO-$d_6$) of $\beta$-cyclodextrin
**Fig. S4** $^1$H NMR spectrum (500 MHz, DMSO-$d_6$) of β-cyclodextrin monoaldehyde (7)

**Fig. S5** $^{13}$C NMR spectrum (125 MHz, DMSO-$d_6$) of β-cyclodextrin monoaldehyde (7)
S5. FTIR spectra

FT-IR spectra of materials 9 and 14 are presented in Fig. 2 in the main text of the article. For the carbon material 9, the strong absorption band coming from C=O of the starting reactant (1-pyrenecarboxyaldehyde (2)) is located at 1700 cm⁻¹, based on the literature data.⁴ The FT-IR spectrum of β-cyclodextrin monoaldehyde (7; starting material for material 14) is presented in Fig. S6.

For other carbon materials (8, 10-14), the data for C=O absorption band of the respective starting reactant are given in the description of the respective figure.

S5.1 FT-IR spectrum of β-cyclodextrin monoaldehyde (7)

*Fig. S6* FT-IR spectrum of β-cyclodextrin monoaldehyde (7). FT-IR spectrum of β-cyclodextrin is also presented.

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S5.2 FT-IR spectra of materials 8, 10-13

**Fig. S7** FT-IR spectrum of carbon material 8. FT-IR spectrum of pristine CEINs is also presented. For legends, see subsection 3.2 in ESI. For starting reactant, benzaldehyde (1), strong absorption band arising from C=O is located at 1710 cm$^{-1}$, based on literature data.$^5$

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**Fig. S8** FT-IR spectrum of carbon material 10. FT-IR spectrum of pristine CEINs is also presented. For legends, see subsection 3.2 in ESI. For starting reactant, ferrocene carboxaldehyde (3), strong absorption band arising from C=O is located at 1690 cm$^{-1}$, based on literature data.$^6$


**Fig. S9** FT-IR spectrum of carbon material 11. FT-IR spectrum of pristine CEINs is also presented. For legends, see subsection 3.2 in ESI. For starting reactant, 4-hydroxybenzaldehyde (4), strong absorption band arising from C=O is located at 1720 cm$^{-1}$, based on literature data$^7$

**Fig. S10** FT-IR spectrum of carbon material 12. FT-IR spectrum of pristine CEINs is also presented. For legends, see subsection 3.2 in ESI. For starting reactant, 2,4-dihydroxybenzaldehyde (5), strong absorption band arising from C=O is located at 1690 cm$^{-1}$, based on literature data$^8$


Fig. S11 FT-IR spectrum of carbon material 13. FT-IR spectrum of pristine CEINs is also presented. For the legends, see subsection 3.2 in ESI. For starting reactant, heptanal (6), strong absorption band arising from C=O is located at 1730 cm\(^{-1}\), based on literature data\(^9\)

S5.3 FT-IR spectra and general comments for the complexation test

**Fig. S12** FT-IR spectra of native carbon material 15 and material 15 recovered after release experiment. FT-IR spectrum of material 14 is also presented. For legends, see subsections 3.2 and 3.4 in ESI. See discussion below

The spectra of the materials 14 and 15 are very consistent and no characteristic absorption bands for pristine ferrocene (Fc) are observed. The spectra of the materials 14 and 15 recovered after release of Fc are also very similar. This is because of a well-known fact that the characteristic absorption bands coming from the guest molecules are extinguished\(^\text{10}\) and are actually not observed in the infrared spectrum of the inclusion complex with β-cyclodextrin. The presence of Fc in native material 15 can be therefore proven indirectly via the release test (Fig. 5 in the main text, discussion in the main text and section S3.4 in ESI). What is more important, the direct comparison between the spectra of materials: **14, native 15** and 15 recovered after release of Fc (Fig. S14) brings a conclusion that Fc is not non-covalently adsorbed on material 15, because the characteristic signals for pristine Fc are not observed in the FT-IR spectrum of 15. In other words, if Fc were adsorbed on material 15, the spectrum would comprise of the absorption bands coming both from material 14 and pristine Fc. If so, these analyses support our theses (i) on the formation of the host-guest system between

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Fc and β-cyclodextrin immobilized onto CEINs and (ii) sequential release of ferrocenium cation via the treatment with aqueous solution of iron (III) chloride.
S6. TGA curves

The thermal decomposition (under nitrogen) of ferrocene and β-cyclodextrin results in the formation of metallic Fe and char, respectively. Hence, the char formation yields for ferrocene and β-cyclodextrin need to be known for the accurate calculation of the functionalization yield. Such data are reported in the literature (52% and 6% for ferrocene\textsuperscript{11} and β-cyclodextrin\textsuperscript{12}, respectively)

The functionalization yield for the materials 10 and 14, was calculated as follows: $C_F = (WL_{550} - M) \cdot (100\% - CH)$, where $C_F$ is the content of introduced ligand [%], WL$_{550}$ is the observed weight loss up to 550°C, M is a content of moisture in the sample (weight loss up to 110°C), and CH is the char formation yield coming from the introduced moiety.\textsuperscript{13} For the materials 8, 9, 11, 12, 13, the content of the introduced ligand was calculated as follows: $C_F = (WL_{550} - M)$, because no char formation is observed for the introduced organic moiety.

The TGA curves for materials 9 and 14 are presented in Fig. 2 in the main text of the article. The TGA curves of materials 8, 10, 11, 12 and 13 are shown in Fig. S13, S14, S15, S16 and S17, respectively.

**Fig. S13** TGA curve (in nitrogen) of carbon material 8. TGA curve of pristine CEINs is also presented. For the legends, see subsection 3.2 in ESI

**Fig. S14** TGA curve (in nitrogen) of carbon material 10. TGA curve of pristine CEINs is also presented. For the legends, see subsection 3.2 in ESI
Fig. S15 TGA curve (in nitrogen) of carbon material 11. TGA curve of pristine CEINs is also presented. For the legends, see subsection 3.2 in ESI

Fig. S16 TGA curve (in nitrogen) of carbon material 12. TGA curve of pristine CEINs is also presented. For the legends, see subsection 3.2 in ESI
**Fig. S17** TGA curve (in nitrogen) of carbon material 13. TGA curve of pristine CEINs is also presented. For the legends, see subsection 3.2 in ESI.
S7. Adsorption experiments

The adsorption experiments were performed analogously to the covalent functionalization process listed in the experimental section (section S3.2) with a difference that sarcosine was not added to the reaction flask. The amounts of the obtained carbon materials were as follows:

- CEINs (20 mg) refluxed with 1-pyrenecarboxaldehyde (2; 1.0 mmol): 18.7 mg,
- CEINs (20 mg) refluxed with ferrocenecarboxaldehyde (3; 1.0 mmol): 19.0 mg,
- CEINs (20 mg) refluxed with 2,4-dihydroxybenzaldehyde (5; 1.0 mmol): 18.2 mg.

FT-IR spectra of the obtained materials are presented in Fig. S18, whilst TGA curves (in nitrogen) are shown in Fig. S19.

![FT-IR spectrum](image)

**Fig. S18** FT-IR spectrum of CEINs after refluxing with 1-pyrenecarboxaldehyde (2), ferrocenecarboxaldehyde (3) and 2,4-dihydroxybenzaldehyde (5). FT-IR spectrum of pristine CEINs is also presented.
**Fig. S19** TGA curve (in nitrogen) of CEINs after refluxing with 1-pyrenecarboxaldehyde (2), ferrocenecarboxaldehyde (3) and 2,4-dihydroxybenzaldehyde (5). TGA curve of pristine CEINs is also presented.
S8. Electrochemical characterization of material 10

The voltammetric measurements were performed from the limited diffusion region, strictly speaking the redox probe was adsorbed at the electrode surface. A droplet (10 μL) of the suspension of material 10 (1 mg·mL⁻¹) was placed on the electrode surface and the electrode was left to dry at room temperature. The droplet volume was sufficient to completely cover the electrode surface. To prepare the uniform aqueous suspension of material 10 a highly-efficient ultrasound homogenizer was applied. In the first step the remnant magnetization of magnetic nanoparticles was eliminated by continuous and intensive (50 W) ultrasound irradiation of the suspension under slowly decaying magnetic field. The exact dispersion was obtained by application the alternating symmetric (1 second) ON-OFF ultrasound 80 W in peak pulses for 90 s.

Prior to investigating the usefulness of carbon material 10 as a redox mediator, the electrochemical characterization of this compound was performed. The typical cyclic voltammograms of 10 obtained at the scan rates from 1 to 500 mV/s are presented in Fig. S20. The voltammograms exhibit well-defined oxidation and reduction peaks corresponding to the Fe²⁺/³⁺ redox couple in the ferrocene molecule. The formal potential determined on the basis of the recorded CV curves is 0.345 V (vs. Ag/AgCl/ 3M KCl). The peak currents change linearly with the potential scan rate (Fig. S20), and this indicates the surface confined electrochemical response, as it is expected for redox probe adsorbed at the electrode surface.

To support the content data of the introduced Fc residues determined from TGA the controlled-potential electrolysis (chronoamperometric experiment) was performed. The measurements were carried out for 24 hours at constant potential of 0.5 V and the progress of electrolysis was monitored periodically by application of voltammetric technique. With the increase in electrolysis time, the intensity of current signals gradually decreased (Fig. S21). During oxidation process of Fc, one electron is exchanged. After 24 hours of electrolysis of carbon material 10 the maximum charge which was achieved equaled ca. 0.92 ± 0.09 mC (inset in Fig. S21). This number corresponds to the mass Fc units of 1.83 ± 0.2 μg and is ca. 18 wt. % of the total weight of the material 10 (the total amount of material 10 adsorbed at the electrode surface was 10 μg).
Fig. S20 A) Cyclic voltammograms of material 10 adsorbed on glassy carbon surface in 0.02 M PB buffer containing 0.15 M K₂SO₄, pH 7.40 for scan rates in range 0.005–0.5 V·s⁻¹. B) plots of anodic peak currents vs. scan rate and square root of scan rate.
Fig. S21 Cyclic voltammograms of material 10 adsorbed on a glassy carbon surface after electrolysis process: 0 h (a), 3 h (b), 7 h (c) and 24 h (d). Inset: Change of charge during electrolysis process. Experimental conditions: $E_{\text{app.}} = 0.5$ V; 0.02 M PB buffer containing 0.15 M K$_2$SO$_4$, pH 7.40; $T = 21$ °C; $\phi$ GC 3 mm