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.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian NMR System spectrometer (500 MHz, 125 MHz) in DMSO-d_6 with calibration on the residual peak 2.50 ppm and 39.5 ppm, for ^{1}H NMR and ^{13}C 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/HF 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 Al_2O_3 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

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[1] M. Bystrzejewski, O. Łabędź, W. Kaszuwara, A. Huczko and H. Lange, *Powder Technol.*, 2013, **246**, 7-15.

completely from the surface. To eliminate the electrical noise the electrochemical cell was placed in a Faraday cage.

S2. Chemical structure of β-cyclodextrin

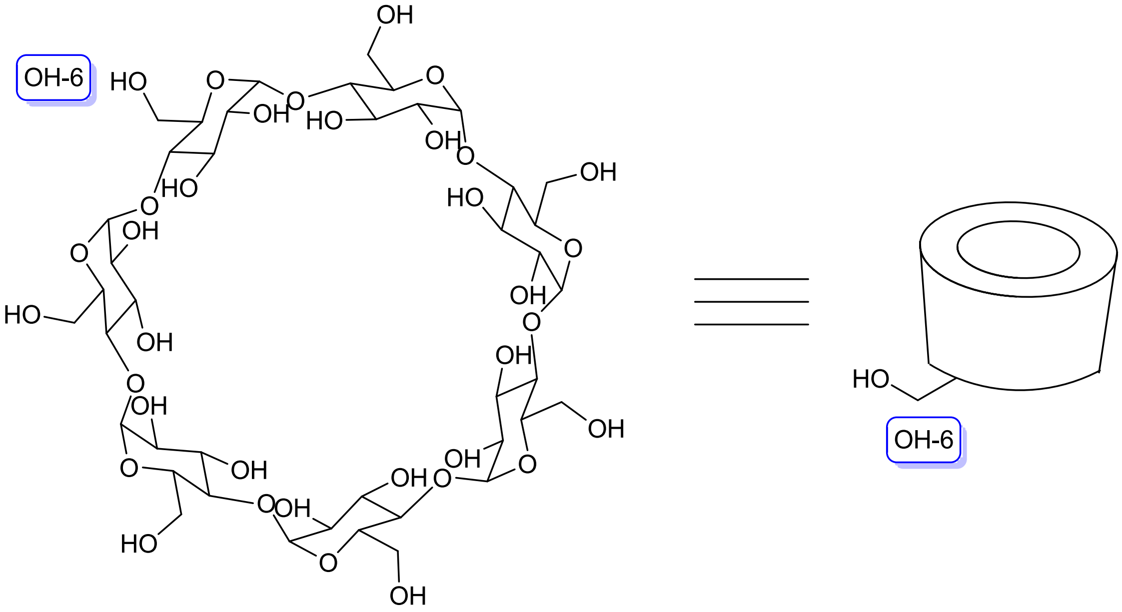
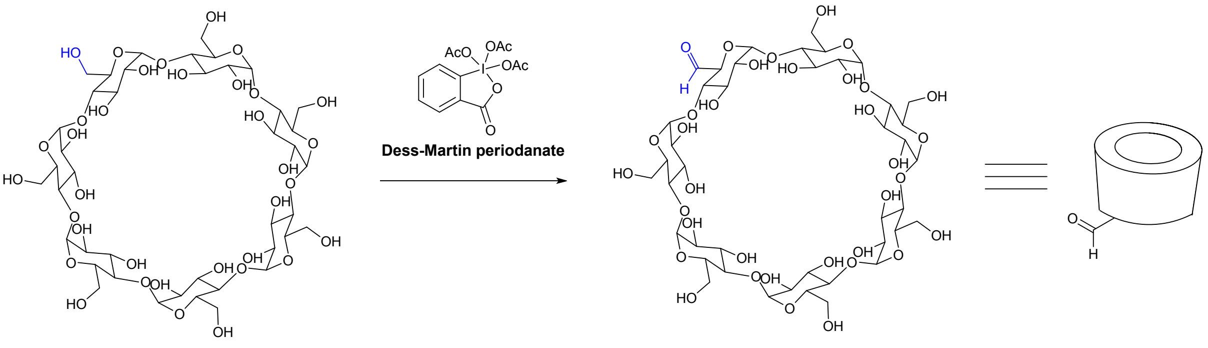


Fig. S1 Chemical structure of β-cyclodextrin

S3. Experimental section

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



β-cyclodextrin β-cyclodextrin monoaldehyde (7)

Synthesis of β-cyclodextrin monoaldehyde (**7**) was based on the literature method.[2] 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 δ_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 δ_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): υ = 1720, 1640, 1410, 1335, 1295, 1155, 1090, 1045, 940, 705 cm^{-1}

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[2] M. J. Cornwell, J. B. Huff and C. Bieniarz, *Tetrahedron Lett.,* 1995, **36**, 8371–8374.

[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:

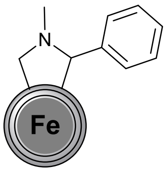
- **11** from the reaction with 4-hydroxybenzaldehyde): 23.0 mg,

- **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.

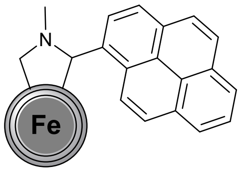
Material 8 (from the reaction with benzaldehyde):



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

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

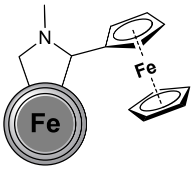
Material 9 (from the reaction with 1-pyrenecarboxaldehyde)



FT-IR (KBr): υ = 1585, 1510, 1460, 1390, 1270, 1155, 960, 820, 685, 460 cm-1

TGA (content of the organic moiety): 13.3 wt. %

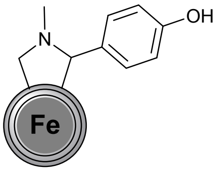
Material 10 (from the reaction with ferrocenecarboxaldehyde)



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

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

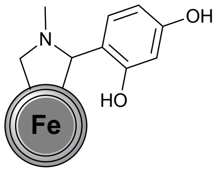
Material 11 (from the reaction with 4-hydroxybenzaldehyde)



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

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

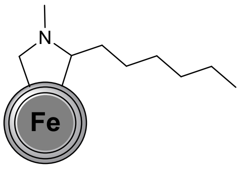
Material 12 (from the reaction with 2,4-dihydroxybenzaldehyde)



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

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

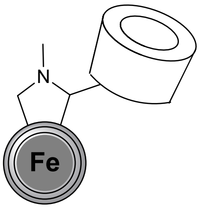
Material 13 (from the reaction with heptanal)



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

TGA (content of the organic moiety): 12.0 wt. %

Material 14 (from the reaction with β-cyclodextrin monoaldehyde):



FT-IR (KBr): υ = 1635, 1505, 1455, 1410, 1340, 1240, 1150, 1020, 1025, 675 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

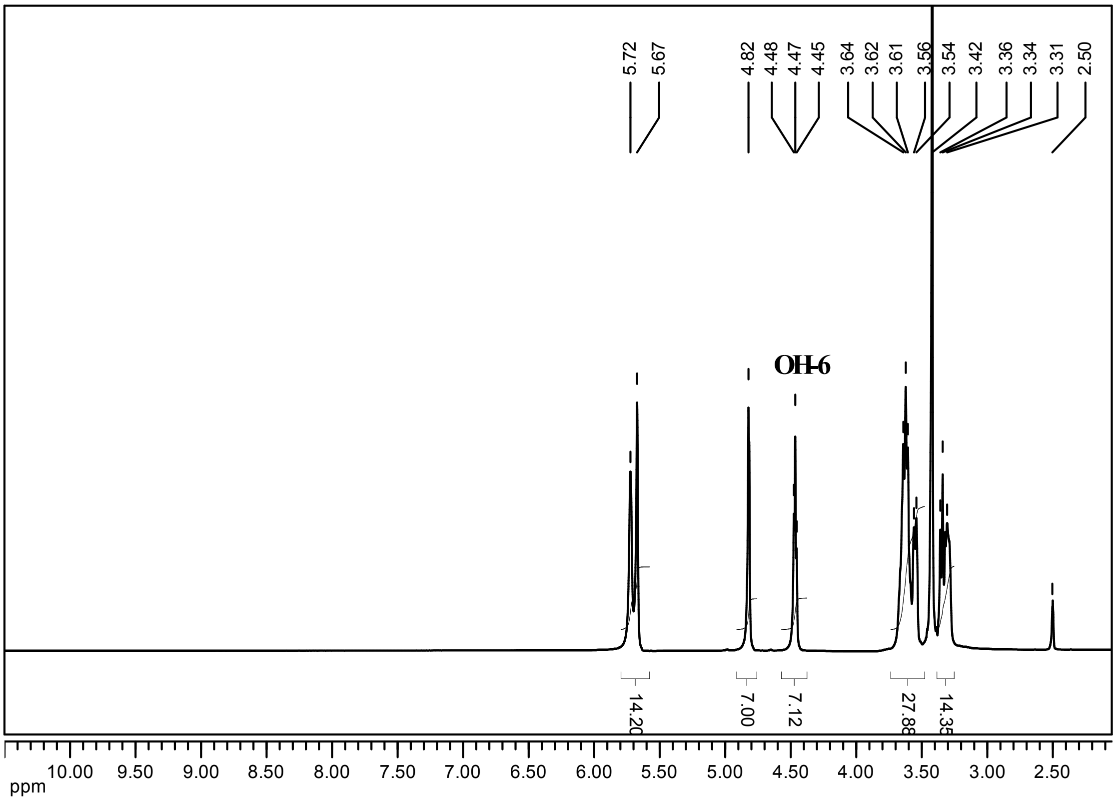


Fig. S2 ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of β-cyclodextrin

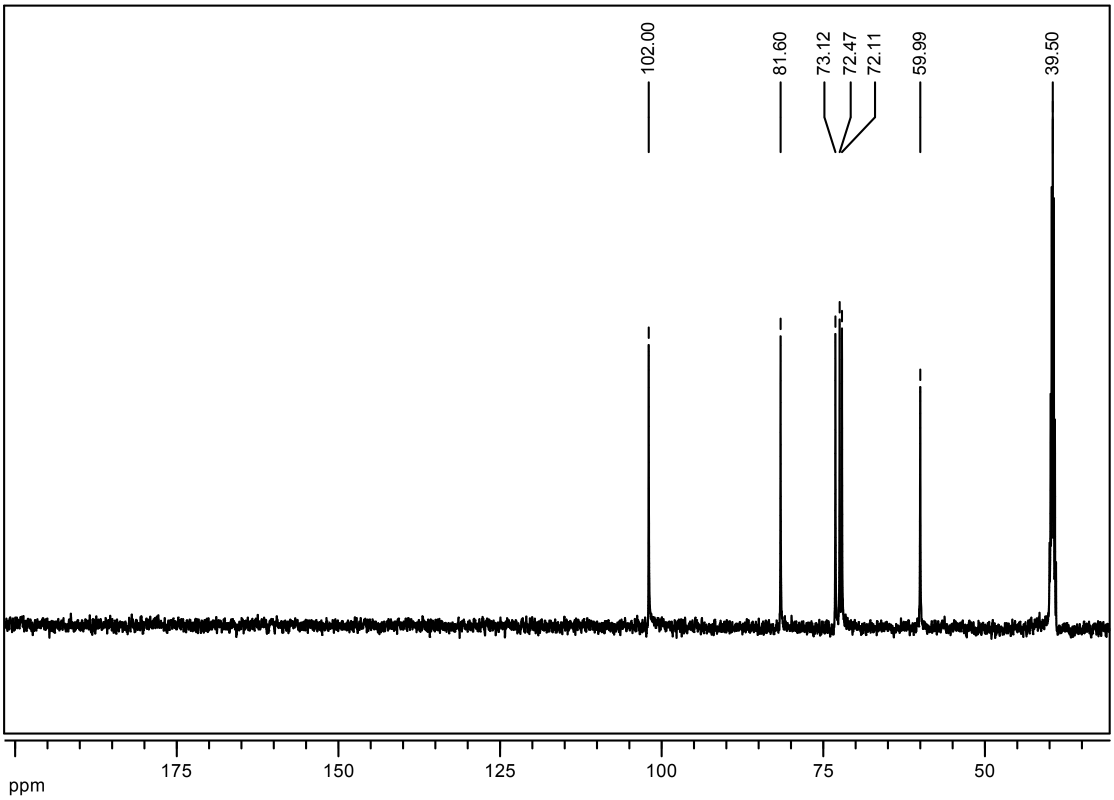


Fig. S3 ^{13}C NMR spectrum (125 MHz, DMSO-d_6) of β-cyclodextrin

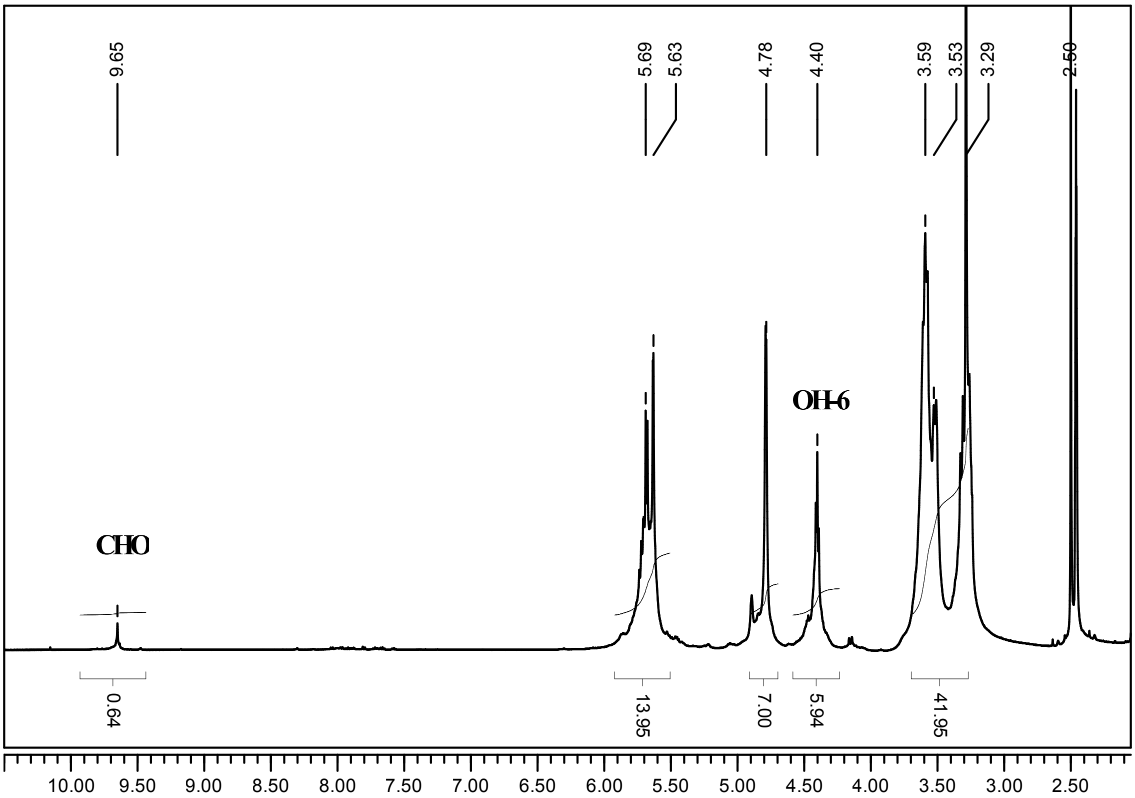


Fig. S4 ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of β-cyclodextrin monoaldehyde (**7**)

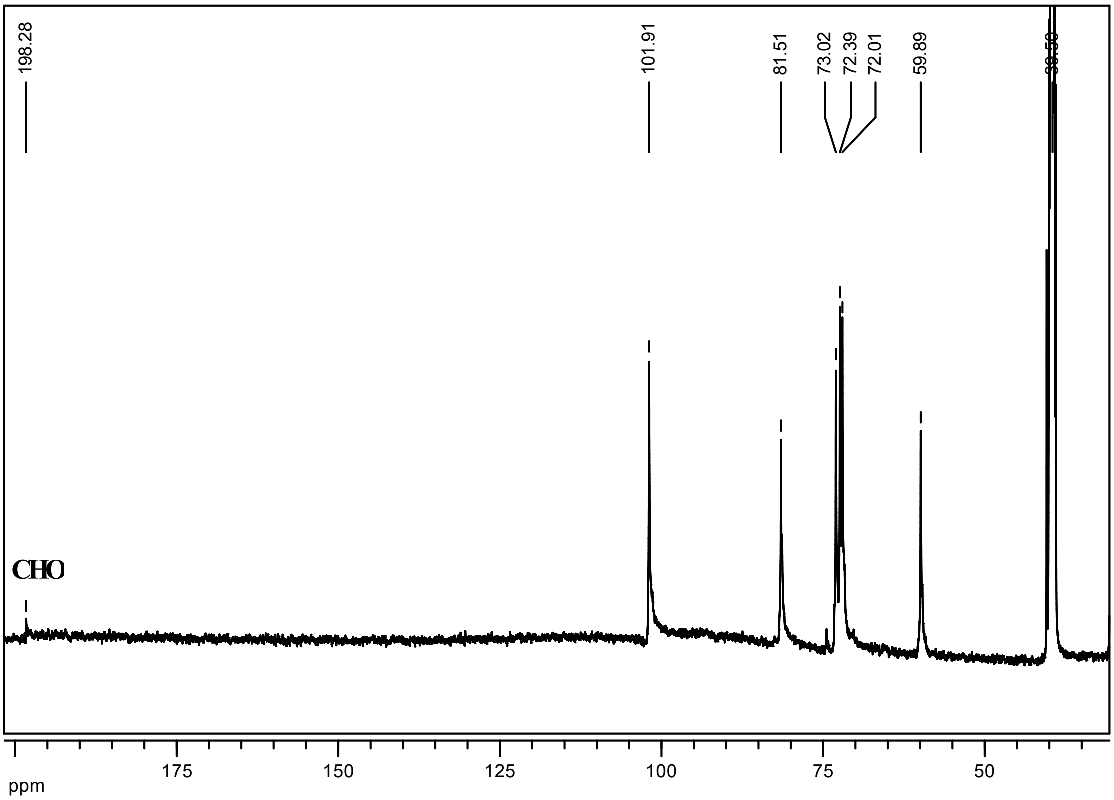


Fig. S5 ^{13}C NMR spectrum (125 MHz, DMSO-d_6) of β-cyclodextrin monoaldehyde (**7**)

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)

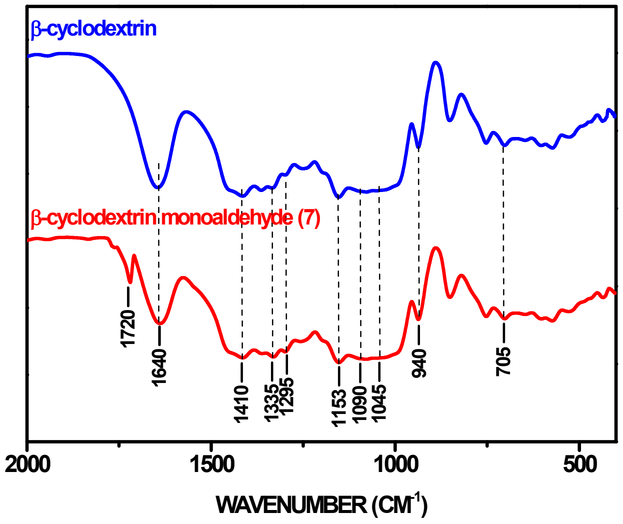


Fig. S6 FT-IR spectrum of β-cyclodextrin monoaldehyde (**7**). FT-IR spectrum of β-cyclodextrin is also presented

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[4] See for example: T. Yun, et al. *Angew. Chem. Int. Ed.*, 2014, **127**, 1594 – 1597.

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

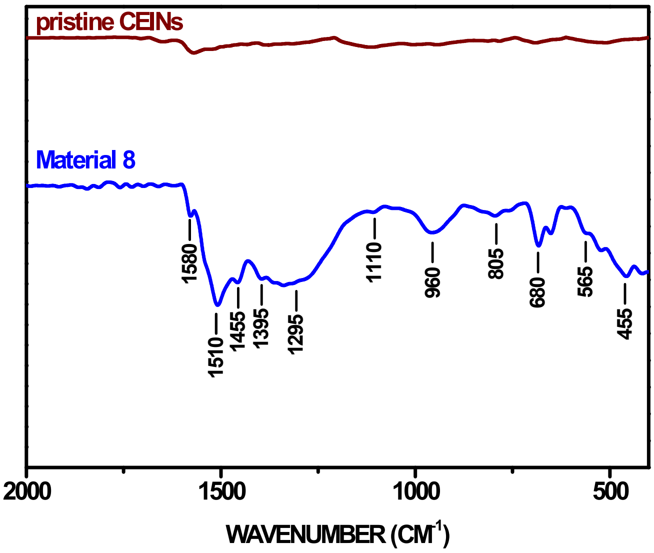

Fig. S7 FT-IR spectrum of carbon material **8**. FT-IR spectrum of pristine CEINs is also presented. For legends, see subsection 3.2 in ESI. For starting reactant, benzaldehyde (**1**), strong absorption band arising from C=O is located at 1710 cm^{-1}, based on literature data[5]

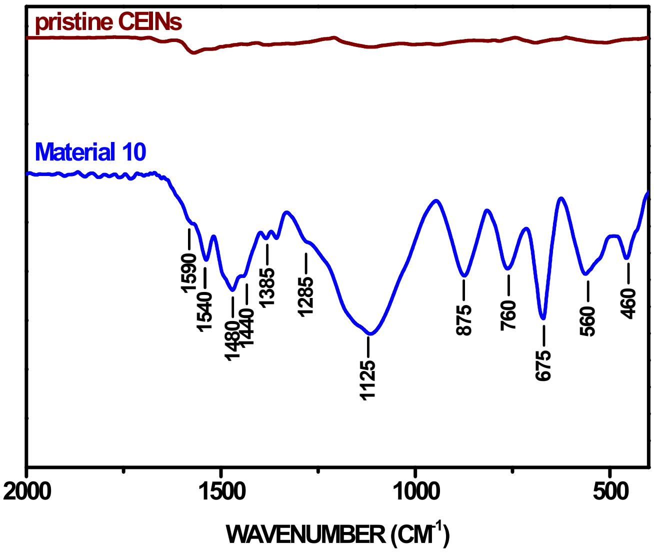

Fig. S8 FT-IR spectrum of carbon material **10**. FT-IR spectrum of pristine CEINs is also presented. For legends, see subsection 3.2 in ESI. For starting reactant, ferrocene carboxaldehyde (**3**), strong absorption band arising from C=O is located at 1690 cm^{-1}, based on literature data[6]

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[5] J. Niu, et al. *Inorg. Chem.*, 2014, **53**, 6107–6112.

[6] C. J. Richards, et al. *Chem. Eu. J.*, 2016, **22**, 3065 – 3072.

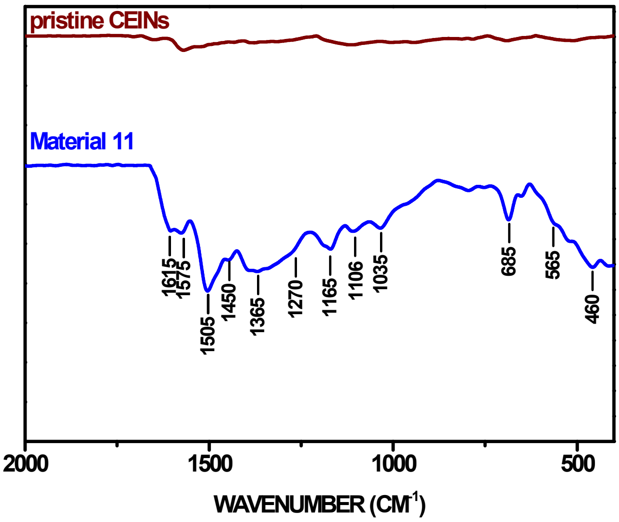

Fig. S9 FT-IR spectrum of carbon material **11**. FT-IR spectrum of pristine CEINs is also presented. For legends, see subsection 3.2 in ESI. For starting reactant, 4-hydroxybenzaldehyde (**4**), strong absorption band arising from C=O is located at 1720 cm^{-1}, based on literature data[7]

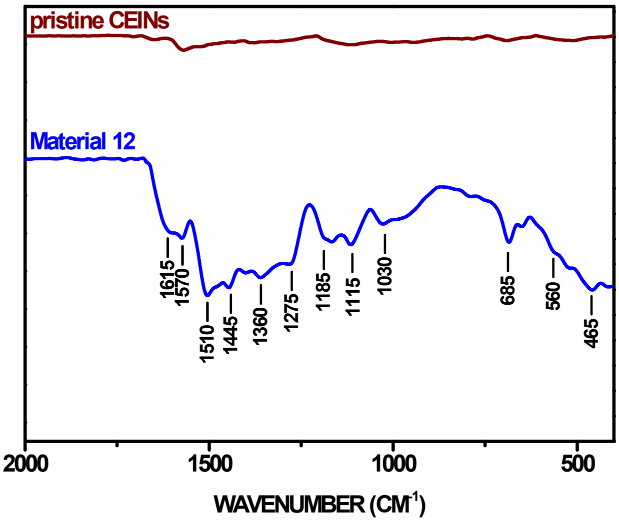

Fig. S10 FT-IR spectrum of carbon material **12**. FT-IR spectrum of pristine CEINs is also presented. For legends, see subsection 3.2 in ESI. For starting reactant, 2,4-dihydroxybenzaldehyde (**5**), strong absorption band arising from C=O is located at1690 cm^{-1}, based on literature data[8]

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[7] A. Naseem, et al. *Green Chem*, 2016, **18**, 648-656.

[8] N. M. Raghavendra, et al. *Bioorg. Chem.*, 2015, **59**, 97-105.

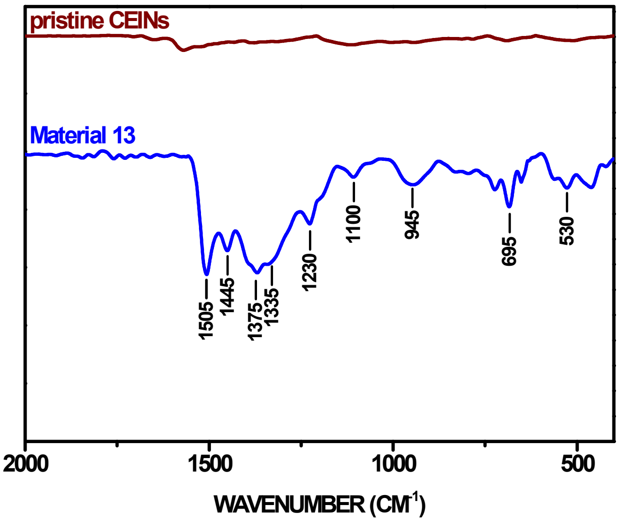

Fig. S11 FT-IR spectrum of carbon material **13**. FT-IR spectrum of pristine CEINs is also presented. For the legends, see subsection 3.2 in ESI. For starting reactant, heptanal (**6**), strong absorption band arising from C=O is located at 1730 cm^{-1}, based on literature data[9]

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[9] W. Zhiyong, *Synlett*, 2010, **13**, 1915-1918.

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

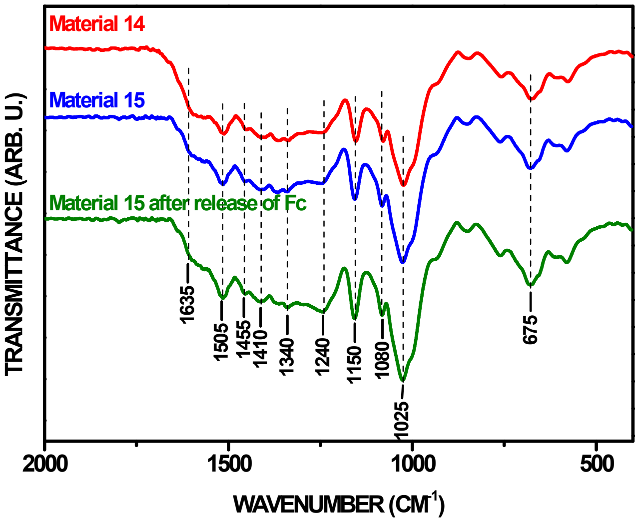

Fig. S12 FT-IR spectra of native carbon material **15** and material **15** recovered after release experiment. FT-IR spectrum of material **14** is also presented. For legends, see subsections 3.2 and 3.4 in ESI. See discussion below

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" and are actually not observed in the infrared spectrum of the inclusion complex with β-cyclodextrin.[10] 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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[10] See for example: (**a**) D. Riegel, et al. *Vib. Spectrosc.* 2010, **53**, 19–23 (*important conclusions about sensitivity of infrared spectroscopy for the analyses of βCD inclusion complexes*); (**b**) Y. Tian, et al. *Thermochimica Acta*, 2012, **541**, 62-69; (c) C. Yuan, et al. *Carbohdr. Polym.*, 2012, **89**, 492-496; (**d**) A. A. Hincal, et al. *AAPS PharmSciTech*, 2006, **7**, article 28.

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[11] and β-cyclodextrin[12], respectively)

The functionalization yield for the materials **10** and **14**, was calculated as follows: $C_F = (WL_{550}\text{-}M)\cdot(100\%\text{-}CH)$, 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.[13] For the materials **8**, **9**, **11**, **12**, **13**, the content of the introduced ligand was calculated as follows: $C_F = (WL_{550}\text{-}M)$, 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.

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[11] J.-H. Chai and Q.-S. Wu, *Beilstein J. Nanotechnol.*, 2013, **4**, 189–197.

[12] P. Subramaniam, S. Mohamad and Y. Alias, *Int. J. Mol. Sci.* 2010, **11**, 3675-3685

[13] (a) A. Kasprzak, M. Bystrzejewski, M. Koszytkowska-Stawinska and M. Poplawska, *Green Chem.*, 2017, DOI:10.1039/C7GC00282C; (b) A. Kasprzak, M. Poplawska, M. Bystrzejewski and I. P. Grudzinski, *J. Mater. Chem. B*, 2016, **4**, 5593; (c) M. Poplawska, M. Bystrzejewski, I. P. Grudzinski, M. A. Cywinska, J. Ostapko and A. Cieszanowski, *Carbon*, 2014, 74, 180-194.

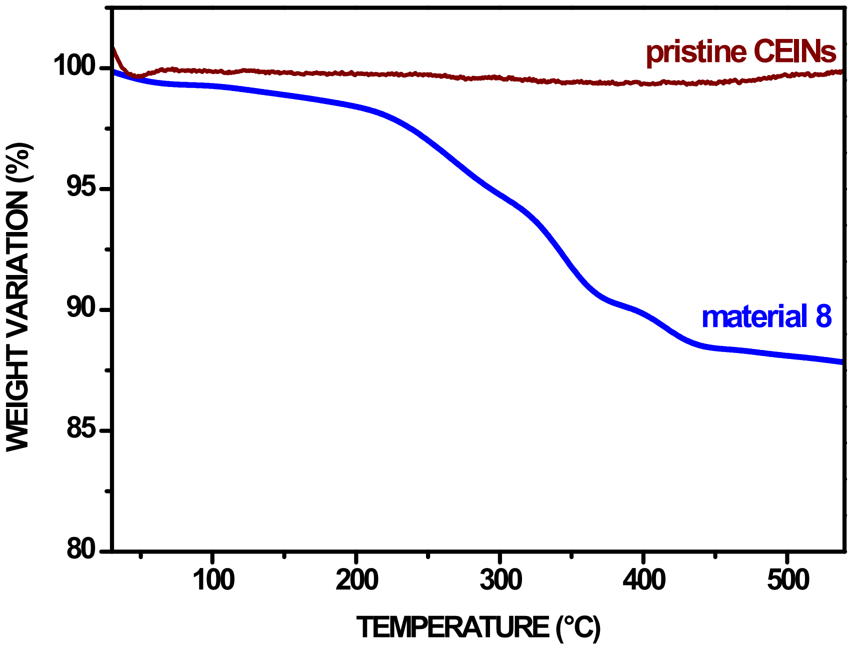

Fig. S13 TGA curve (in nitrogen) of carbon material **8**. TGA curve of pristine CEINs is also presented. For the legends, see subsection 3.2 in ESI

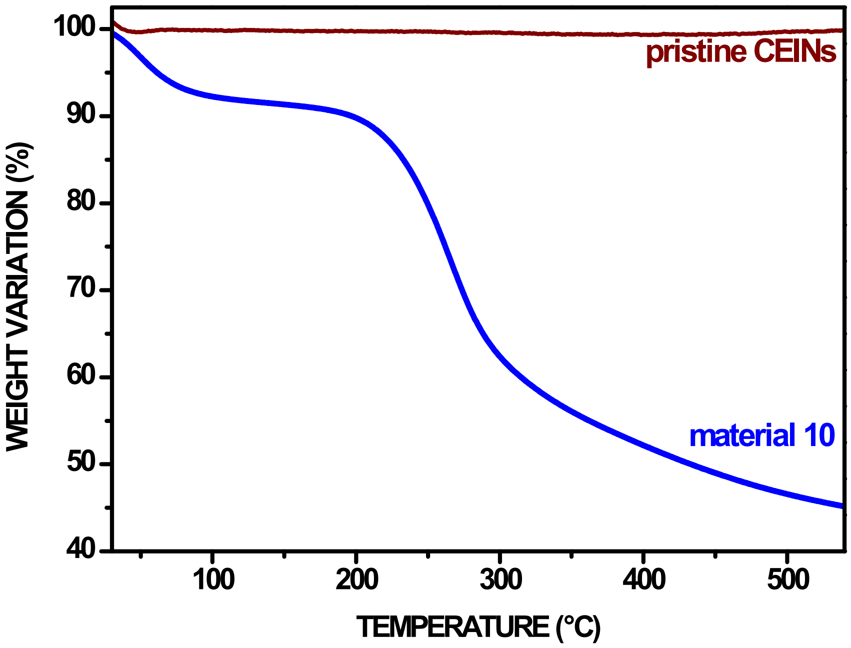

Fig. S14 TGA curve (in nitrogen) of carbon material **10**. TGA curve of pristine CEINs is also presented. For the legends, see subsection 3.2 in ESI

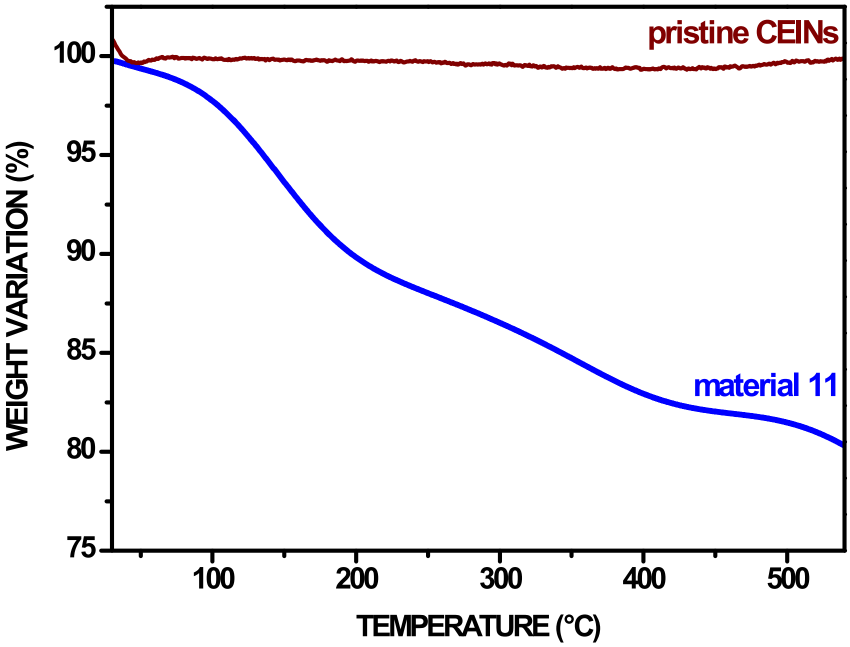

Fig. S15 TGA curve (in nitrogen) of carbon material **11**. TGA curve of pristine CEINs is also presented. For the legends, see subsection 3.2 in ESI

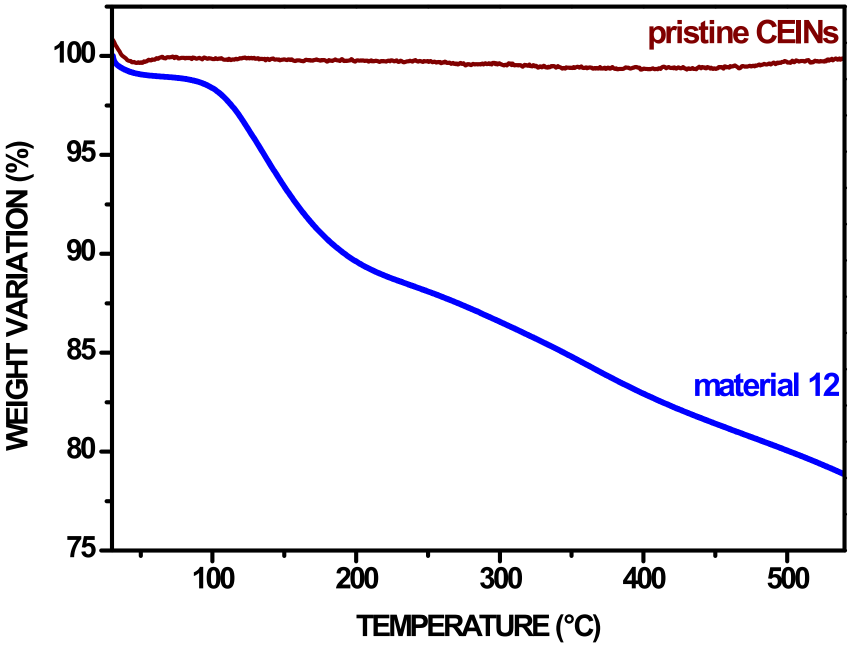

Fig. S16 TGA curve (in nitrogen) of carbon material **12**. TGA curve of pristine CEINs is also presented. For the legends, see subsection 3.2 in ESI

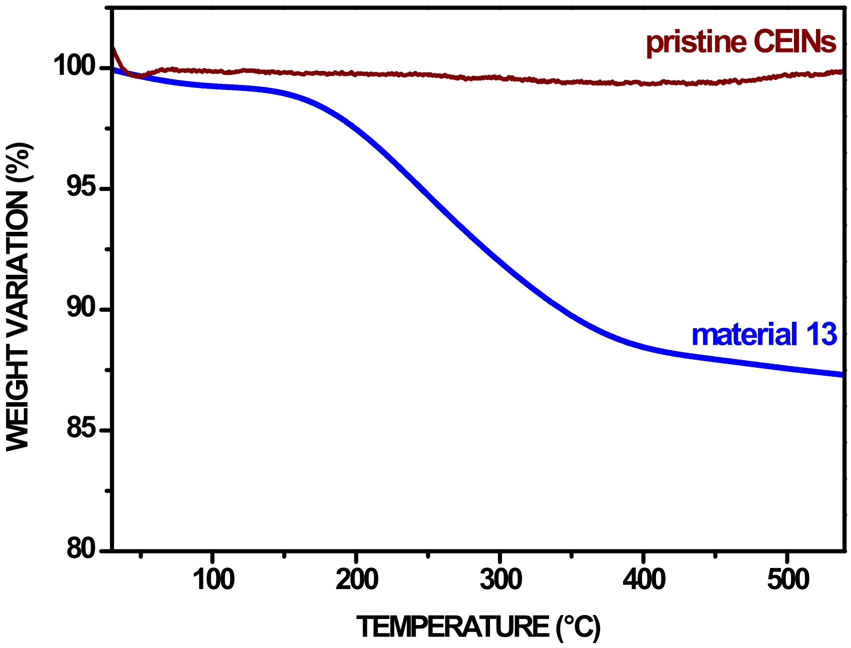

Fig. S17 TGA curve (in nitrogen) of carbon material **13**. TGA curve of pristine CEINs is also presented. For the legends, see subsection 3.2 in ESI

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-dihydroxynebenzaldehyde (**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.

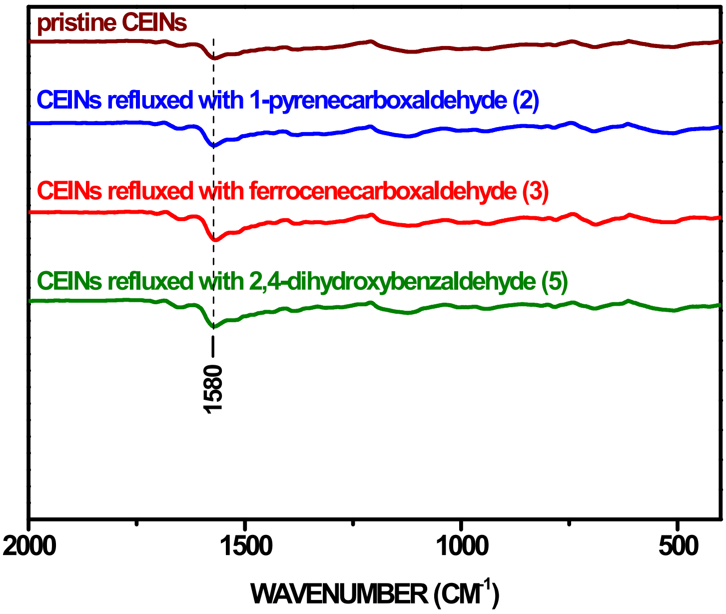

Fig. S18 FT-IR spectrum of CEINs after refluxing with 1-pyrenecarboxaldehyde (**2**), ferrocenecarboxaldehyde (**3**) and 2,4-dihydroxybenzaldehyde (**5**). FT-IR spectrum of pristine CEINs is also presented

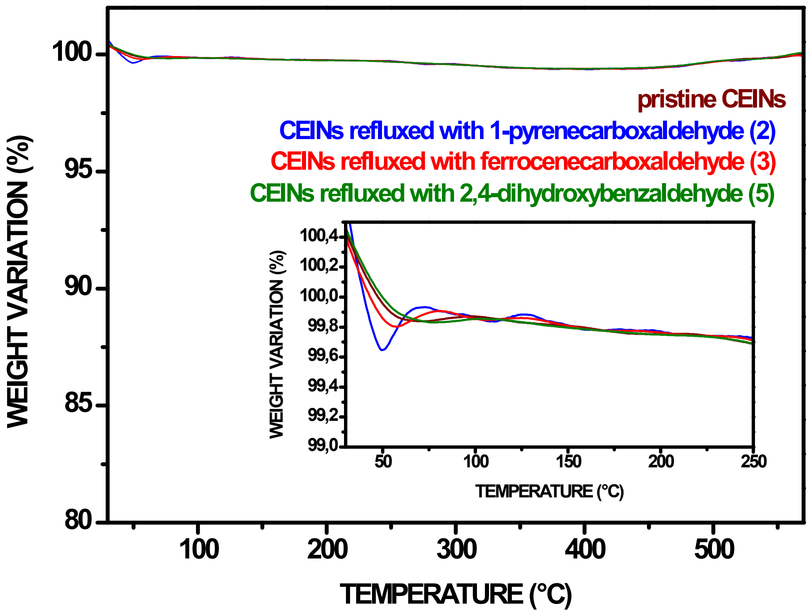

Fig. S19 TGA curve (in nitrogen) of CEINs after refluxing with 1-pyrenecarboxaldehyde (**2**), ferrocenecarboxaldehyde (**3**) and 2,4-dihydroxybenzaldehyde (**5**). TGA curve of pristine CEINs is also presented

S8. Electrochemical characterization of material 10

The voltametric 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 Fe$^{2+/3+}$ 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).

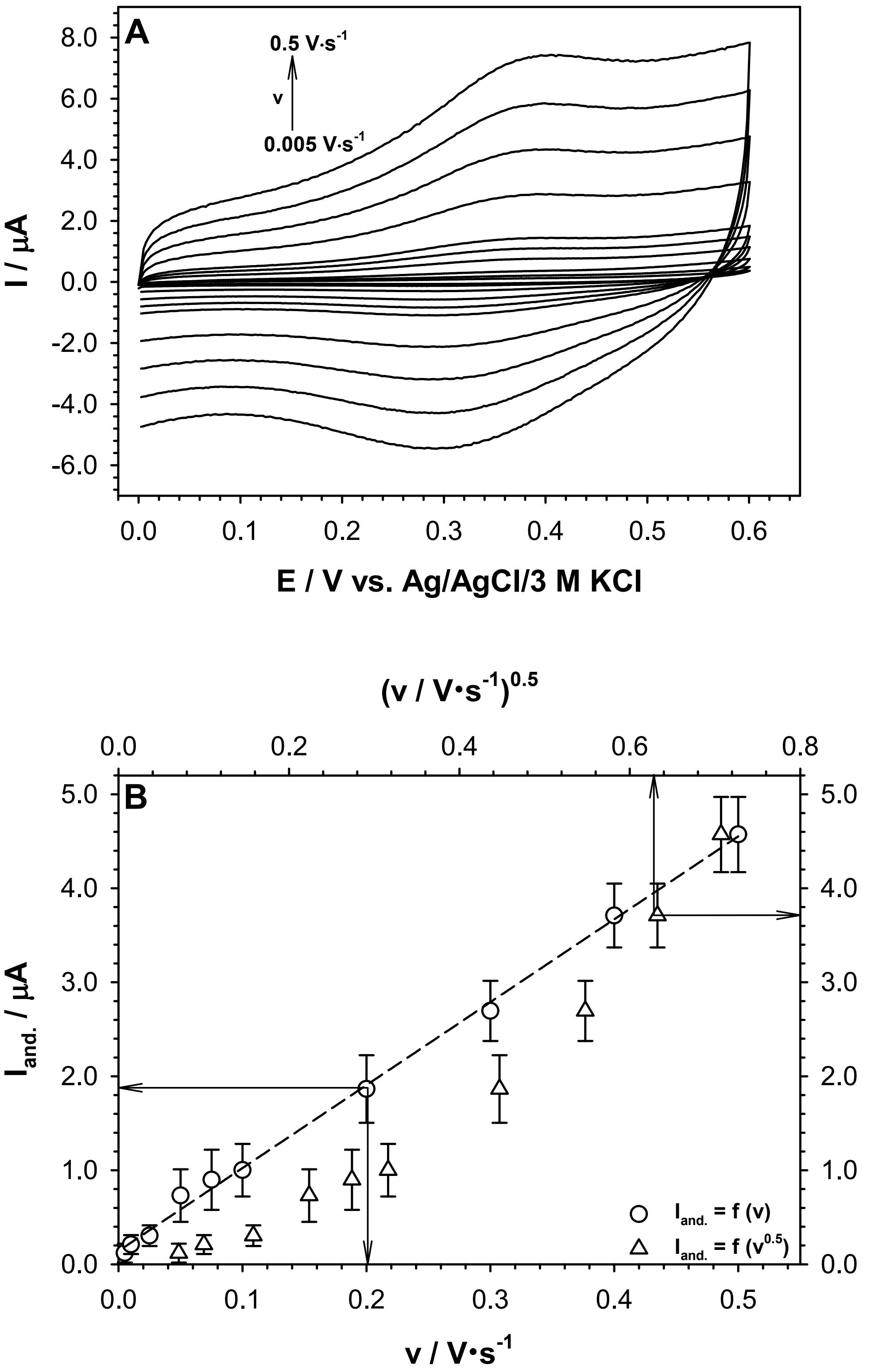

Fig. S20 **A)** Cyclic voltammograms of material **10** adsorbed on glassy carbon surface in 0.02 M PB buffer containing 0.15 M K_2SO_4, pH 7.40 for scan rates in range 0.005÷0.5 $V{\cdot}s^{-1}$. **B)** plots of anodic peak currents vs. scan rate and square root of scan rate

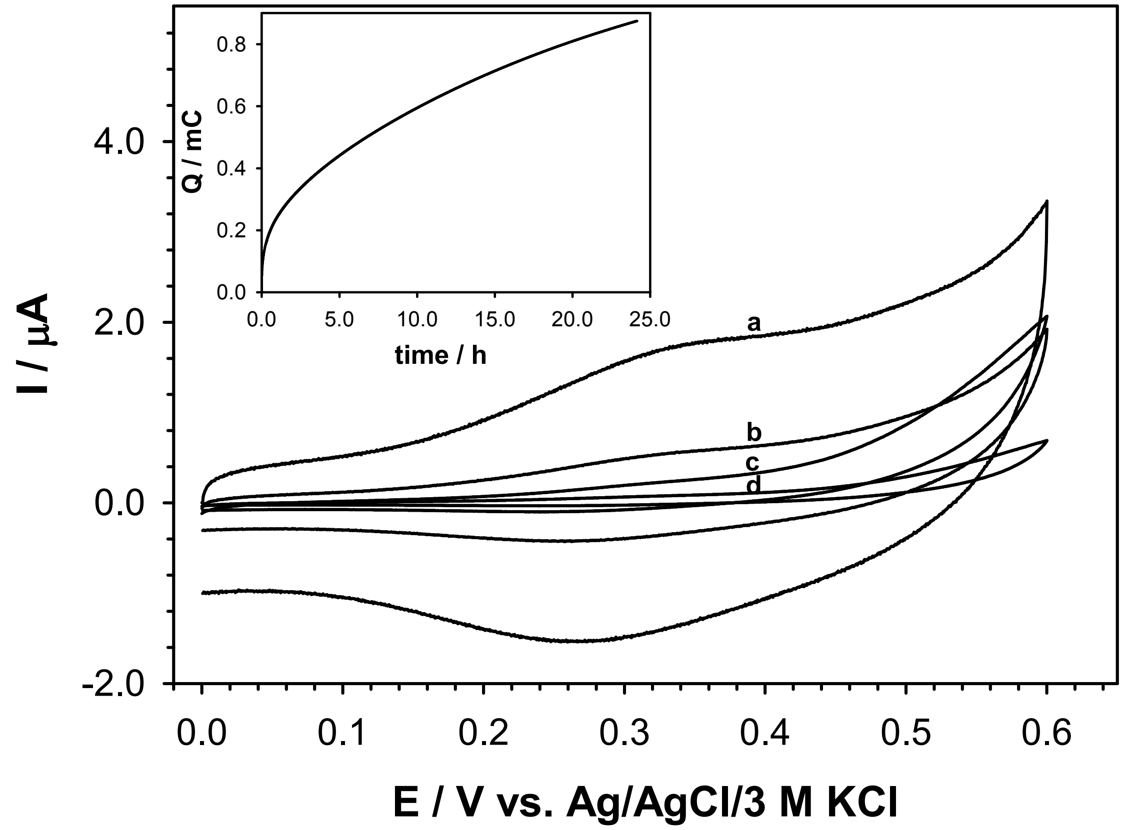

Fig. S21 Cyclic voltammograms of material **10** adsorbed on a glassy carbon surface after electrolysis process: 0 h (a), 3 h (b), 7 h (c) and 24 h (d). Inset: Change of charge during electrolysis process. Experimental conditions: $E_{\mathrm{app.}}$ = 0.5 V; 0.02 M PB buffer containing 0.15 M K_2SO_4, pH 7.40; T = 21 ^{o}C; ϕGC 3 mm