Electronic supplementary information (ESI)

## Water-Soluble Platinum Nanoparticles Stabilized by Sulfonated N-Heterocyclic Carbenes: Influence of the Synthetic Approach

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Figure S1. <sup>1</sup>H- (300 MHz) and <sup>13</sup>C-NMR (75 MHz) spectra for <sup>13</sup>C-C2c in DMSO- $d_6$ .

#### 2. TEM images of the Pt nanoparticles



Figure S2. TEM image with the corresponding size distribution obtained for PtNPs NP1b<sup>CO</sup>  $(1.3 \pm 0.4 \text{ nm}).$ 



Figure S3. TEM image with the corresponding size distribution obtained for PtNPs NP1c<sup>CO</sup>  $(1.0 \pm 0.3 \text{ nm}).$ 



Figure S4. TEM image with the corresponding size distribution obtained for PtNPs  ${}^{13}$ C-NP1c<sup>CO</sup> (1.1 ± 0.4 nm).



Figure S5. TEM image with the corresponding size distribution obtained for PtNPs  ${}^{13}$ CO-NP1c<sup>CO</sup> (1.0 ± 0.3 nm).



Figure S6. TEM image with the corresponding size distribution obtained for PtNPs  $NP2c^{H2}$  (3 ± 2 nm).



Figure S7. TEM image with the corresponding size distribution obtained for PtNPs NP2e<sup>H2</sup>  $(4.0 \pm 0.8 \text{ nm}).$ 



Figure S8. TEM image with the corresponding size distribution obtained for PtNPs  ${}^{13}$ C-NP2c ${}^{H2}$  (3 ± 2 nm).

#### 3. X-Ray diffractograms of the Pt nanoparticles



Figure S9. X-Ray Diffractogram of NP1a<sup>CO</sup> (Crystallite size 1.3 nm).



Figure S10. X-Ray Diffractogram of NP1b<sup>CO</sup> (Crystallite size 1.5 nm).



Figure S11. X-Ray Diffractogram of NP1c<sup>CO</sup> (Crystallite size 1.2 nm).



Figure S12. X-Ray Diffractogram of <sup>13</sup>C-NP1c<sup>CO</sup> (Crystallite size 1.2 nm).



Figure S13. X-Ray Diffractogram of <sup>13</sup>CO-NP1c<sup>CO</sup> (Crystallite size 1.3 nm).



Figure S14. X-Ray Diffractogram of NP2a<sup>H2</sup> (Crystallite size 1.8 nm).



**Figure S15**. X-Ray Diffractogram of **NP2c<sup>H2</sup>** (Crystallite size 3.2 nm).



Figure S16. X-Ray Diffractogram of NP2e<sup>H2</sup> (Crystallite size 3.8 nm).



Figure S17. X-Ray Diffractogram of <sup>13</sup>C-NP2c<sup>H2</sup> (Crystallite size 2.6 nm).



4. ATR-FTIR spectra of the imidazolium salts, Pt complexes and Pt nanoparticles

Figure S18. ATR-FTIR spectra for aH (black), C1a (red) and NP1a<sup>CO</sup> (blue).



Figure S19. ATR-FTIR spectra for bH (black), C1b (red) and NP1b<sup>CO</sup> (blue).



Figure S20. ATR-FTIR spectra for cH (black), C1c (red) and NP1c<sup>CO</sup> (blue).



Figure S21. ATR-FTIR spectra for <sup>13</sup>C-cH (black), <sup>13</sup>C-C1c (red) and <sup>13</sup>C-NP1c<sup>CO</sup> (blue).



Figure S22. ATR-FTIR spectra for aH (black), C2a (red) and NP2a<sup>H2</sup> (blue).



Figure S23. ATR-FTIR spectra for cH (black), C2c (red) and NP2c<sup>H2</sup> (blue).



Figure S24. ATR-FTIR spectra for eH (black), C2e (red) and NP2e<sup>H2</sup> (blue).



Figure S25. ATR-FTIR spectra for <sup>13</sup>C-cH (black), <sup>13</sup>C-C2c (red) and <sup>13</sup>C-NP2c<sup>H2</sup> (blue).

## 5. <sup>1</sup>H-NMR spectra of the Pt nanoparticles



**Figure S26**. <sup>1</sup>H-NMR (300 MHz) for PtNPs **NP1a**<sup>CO</sup> (*i.e.*, pair **NP1a**<sup>CO</sup>/**C3a**) in D<sub>2</sub>O. Resonances marked with an asterisk correspond to the bis(carbene) complex **C3a**, which is located in a second coordination sphere around NPs **NP1a**<sup>CO</sup>.



Figure S27. <sup>1</sup>H-NMR (300 MHz) for PtNPs NP1b<sup>CO</sup> in D<sub>2</sub>O.



**Figure S28**. <sup>1</sup>H-NMR (300 MHz) for PtNPs  $NP1c^{CO}$  in D<sub>2</sub>O.



Figure S29. <sup>1</sup>H-NMR (500 MHz) for PtNPs  $NP2a^{H2}$  in  $D_2O$ .



Figure S30. <sup>1</sup>H-NMR (500 MHz) for PtNPs  $NP2c^{H2}$  in D<sub>2</sub>O.



Figure S31. <sup>1</sup>H-NMR (500 MHz) for PtNPs  $NP2e^{H2}$  in D<sub>2</sub>O.

# 6. <sup>1</sup>H-<sup>13</sup>C CP-MAS NMR spectra of the imidazolium salts, Pt complexes and PtNPs



**Figure S32**. <sup>1</sup>H–<sup>13</sup>C CP-MAS and <sup>13</sup>C MAS NMR spectra for **NP1a**<sup>co</sup>. Resonance (I) corresponds to the carbenic <sup>13</sup>C resonance. This resonance is not observed in the MAS experiment probably due to a long  $T_1$  relaxation time associated to restricted motions and remoteness to <sup>1</sup>H nuclei (H atoms of the ligands or residual water).



Figure S33. <sup>1</sup>H-<sup>13</sup>C CP-MAS NMR spectra for **bH**, C1b and NP1b<sup>CO</sup>. Resonances (I) and (II) correspond to  $C^{2}_{Imz}$ -H and Pt- $C^{2}_{NHC}$  carbons, respectively.



**Figure S34**. <sup>1</sup>H-<sup>13</sup>C CP-MAS NMR spectra for **cH**, **C1c** and **NP1c**<sup>CO</sup>. Resonances (I) and (II) correspond to  $C^{2}_{Imz}$ -H and Pt- $C^{2}_{NHC}$  carbons, respectively.



Figure S35. <sup>1</sup>H-<sup>13</sup>C CP-MAS NMR spectra for <sup>13</sup>C-cH, <sup>13</sup>C-C1c and <sup>13</sup>C-NP1c<sup>CO</sup>. Resonances (I) and (II) correspond to  ${}^{13}C^{2}_{Imz}$ -H and Pt- ${}^{13}C^{2}_{NHC}$  carbons, respectively.



**Figure S36**. a) <sup>1</sup>H-<sup>13</sup>C CP-MAS NMR spectra for NP1c<sup>CO</sup>, b) <sup>1</sup>H-<sup>13</sup>C CP-MAS NMR spectra for <sup>13</sup>CO-NP1c<sup>CO</sup> and c) direct polarization <sup>13</sup>C MAS NMR for <sup>13</sup>CO-NP1c<sup>CO</sup>. Resonances (I), (II), and (III) correspond to Pt- $C^{2}_{NHC}$ , Pt-<sup>13</sup>CO in terminal mode, and Pt-<sup>13</sup>CO in multiterminal mode, respectively.



Figure S37. <sup>1</sup>H-<sup>13</sup>C CP-MAS NMR spectra for **cH**, C2c and NP2c<sup>H2</sup>. Resonances (I) and (II) correspond to  $C^{2}_{Imz}$ -H and Pt- $C^{2}_{NHC}$  carbons, respectively.



Figure S38. <sup>1</sup>H-<sup>13</sup>C CP-MAS NMR spectra for eH, C2e and NP2e<sup>H2</sup>. Resonances (I) and (II) correspond to  $C^{2}_{Imz}$ -H and Pt- $C^{2}_{NHC}$  carbons, respectively.



**Figure S39**. <sup>1</sup>H-<sup>13</sup>C CP-MAS NMR spectra for <sup>13</sup>C-cH, <sup>13</sup>C-C2c and <sup>13</sup>C-NP2c<sup>H2</sup>. Resonances (I) and (II) correspond to <sup>13</sup>C<sup>2</sup><sub>Imz</sub>–H and Pt-<sup>13</sup>C<sup>2</sup><sub>NHC</sub> carbons, respectively. The assignation of the carbonic carbon for <sup>13</sup>C-NP2c<sup>H2</sup> was based on the signal with the <sup>195</sup>Pt satellite (176 ppm).



**Figure S40.** <sup>1</sup>H-<sup>13</sup>C CP-MAS NMR spectrum for <sup>13</sup>C-NP2c<sup>H2</sup>, displaying its corresponding deconvolution curves. The estimated <sup>13</sup>C-<sup>195</sup>Pt coupling constant for the resonance signal of the carbonic carbon (176 ppm) is  $1050 \pm 50$  Hz. This is a rough estimation because of the presence of an overlapped resonance at 165 ppm.

7. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of the intermediates C4a-c and <sup>13</sup>C-C4c



**Figure S41**. <sup>1</sup>H-NMR (500 MHz) for intermediate **C4a** in D<sub>2</sub>O.



Figure S42. <sup>13</sup>C-NMR (125 MHz) for intermediate C4a in D<sub>2</sub>O.







Figure S44. <sup>13</sup>C-NMR (125 MHz) for intermediate C4b in D<sub>2</sub>O.



Figure S45. <sup>1</sup>H-NMR (500 MHz) for intermediate C4c in D<sub>2</sub>O.



Figure S46. <sup>13</sup>C-NMR (125 MHz) for intermediate C4c in D<sub>2</sub>O.



**Figure S47**. <sup>1</sup>H-NMR (500 MHz) for intermediate  ${}^{13}$ C-C4c in D<sub>2</sub>O.



Figure S48. <sup>13</sup>C-NMR (125 MHz) for intermediate <sup>13</sup>C-C4c in  $D_2O$ .



Figure S49. <sup>1</sup>H-<sup>13</sup>C HSQC for Pt–CH<sub>3</sub> moieties in intermediate <sup>13</sup>C-C4c in D<sub>2</sub>O.



Figure S50. TEM images taken from solutions of C1a (left) and C1c (right) in D<sub>2</sub>O after 1 h of reaction with <sup>13</sup>CO (3 bar).



**Figure S51**. <sup>1</sup>H-<sup>13</sup>C HMBC in the region of Pt–CH<sub>3</sub> moiety for byproduct C5c.

## 8. Characterization of the nano-object NP1a<sup>CO</sup>/C3a

The complex C3a was found in a second coordination sphere in PtNPs NP1a<sup>CO</sup> (resonances marked with an asterisk in Figure S27). The solution of PtNPs NP1a<sup>CO</sup> was analyzed by NMR spectroscopy and ESI mass spectrometry of samples of the nanoparticles after 36 and 60 h of dialysis, showing that complex C3a is still associated to the nanoparticle.



Trisodium*trans*-carbonylmethylbis[1,3-bis(3-sulfo-natepropyl)imidazol-2-ylidene]platinate(3–)(C3a): <sup>1</sup>H-NMR(300 MHz, D<sub>2</sub>O):  $\delta$  7.31 (s, 4H, Imz), 4.30 (m, 8H, NCH<sub>2</sub>), 2.87(t, <sup>3</sup>J<sub>HH</sub> = 8.4, 8H, CH<sub>2</sub>S), 2.31 (m, 8H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 0.22 (s with<sup>195</sup>Pt satellites, <sup>2</sup>J(<sup>1</sup>H-<sup>195</sup>Pt) = 63.0, 3H, PtMe). ESI-MS (negative

ion, H<sub>2</sub>O): m/z 904.0237 [C3a - Na]<sup>-</sup> (calcd 904.0215) 6%; 503.9850 [C3a - CO - NHC - 3Na - CH<sub>4</sub>]<sup>-</sup> (calcd 503.9868) 100%.



**Figure S52**. ROESY spectral region showing the cross peaks between Pt–CH<sub>3</sub> and methylene groups of the propylsulfonate chain in nano-object NP1a<sup>CO</sup>/C3a.



Figure S53. Calculated and experimental isotopic distributions of the molecular fragment [C3a – Na]<sup>-</sup> detected in the ESI mass spectra of NP1a<sup>CO</sup>/C3a.