

Electronic Supplementary Information (ESI)

The Optoelectronic Behaviour of Carbon Nanoparticles: Evidence of the Importance of the Outer Carbon Shell†

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Synthesis and Characterization of the CNPs

Carbon nanoparticles were synthesized by mixing and further stirring for 1 h ethanolic solutions of citric acid (1g) and octadecan-1-amine (1.5g). The produced ammonium salt was filtered, washed several times with ethanol and finally calcinated in air at 300 °C for 2 h. The dark-brown solid product was ultrasonicated in dry tetrahydrofuran (THF) for 30 minutes; the solids were removed by filtration and washed with THF. The filtrate and washings were combined and vacuum-dried in a rotary evaporator at 45 °C to total dryness (yield 93%). The carbogenic extract was finally separated by column chromatography developed with dichloromethane.

Column chromatography used silica gel (Merck Millipore, 70-230 mesh ASTM, pretreated overnight at 200 °C) with an adsorbent to sample weight ratio greater than 100, prewashed with three column volumes of dichloromethane before the sample was charged. The dry carbogenic extract was slurried in dichloromethane; a small portion loaded in the column and eluted by gravity with dichloromethane until the eluate was pure solvent. Eluate volumes of 15 ml were collected, and samples of each were analyzed by UV-visible and fluorescence spectroscopy. From the spectroscopic analysis, a first fraction was clearly identified and separated for its study.

Photophysical Characterization

The absorption and fluorescence data were collected into quartz fluorometer cuvettes 1x1 cm on a Hewlett-Packard 8453 diode array spectrophotometer and a Spex FluoroMax fluorometer, respectively.

The quantum yield was measured by comparing the integrated photoluminescence intensities and the absorbance values of the samples with the reference 9,10-diphenyl-anthracene. The 9,10-diphenyl-anthracene ($\Phi=0.90$) was dissolved in cyclohexane (refractive index (η) of 1.427) and CNPs were dissolved in THF ($\eta=1.408$). All solutions were thoroughly deaerated by purging with N_2 . The protocol for quantum yield measurements follows references and the quantum yield was calculated using the following equation:¹

$$\Phi = \Phi_R \times \frac{I}{I_R} \times \frac{A_R}{A} \times \frac{\eta^2}{\eta_R^2} \quad (1)$$

where Φ is the quantum yield, I is the measured integrated emission intensity, η is the refractive index, and A is the optical density. The subscript R refers to the reference fluorophore of known quantum yield. In order to minimize re-absorption effects the optical densities in the 10 mm fluorescence cuvette were kept under 0.1 at the excitation wavelength. An excitation slit width of 2.5 nm and an emission slit width of 2.5 nm were used to excite the CNPs samples and to record their photoluminescence spectra.

HRTEM

High-resolution transmission electron microscopy (HRTEM) studies were carried out in a Philips CM200 UT microscope at 200 kV and room temperature. Careful inspection showed that under the experimental conditions neither the CNPs morphology nor their crystallinity was affected. In other words, no changes were detected due to electron irradiation.

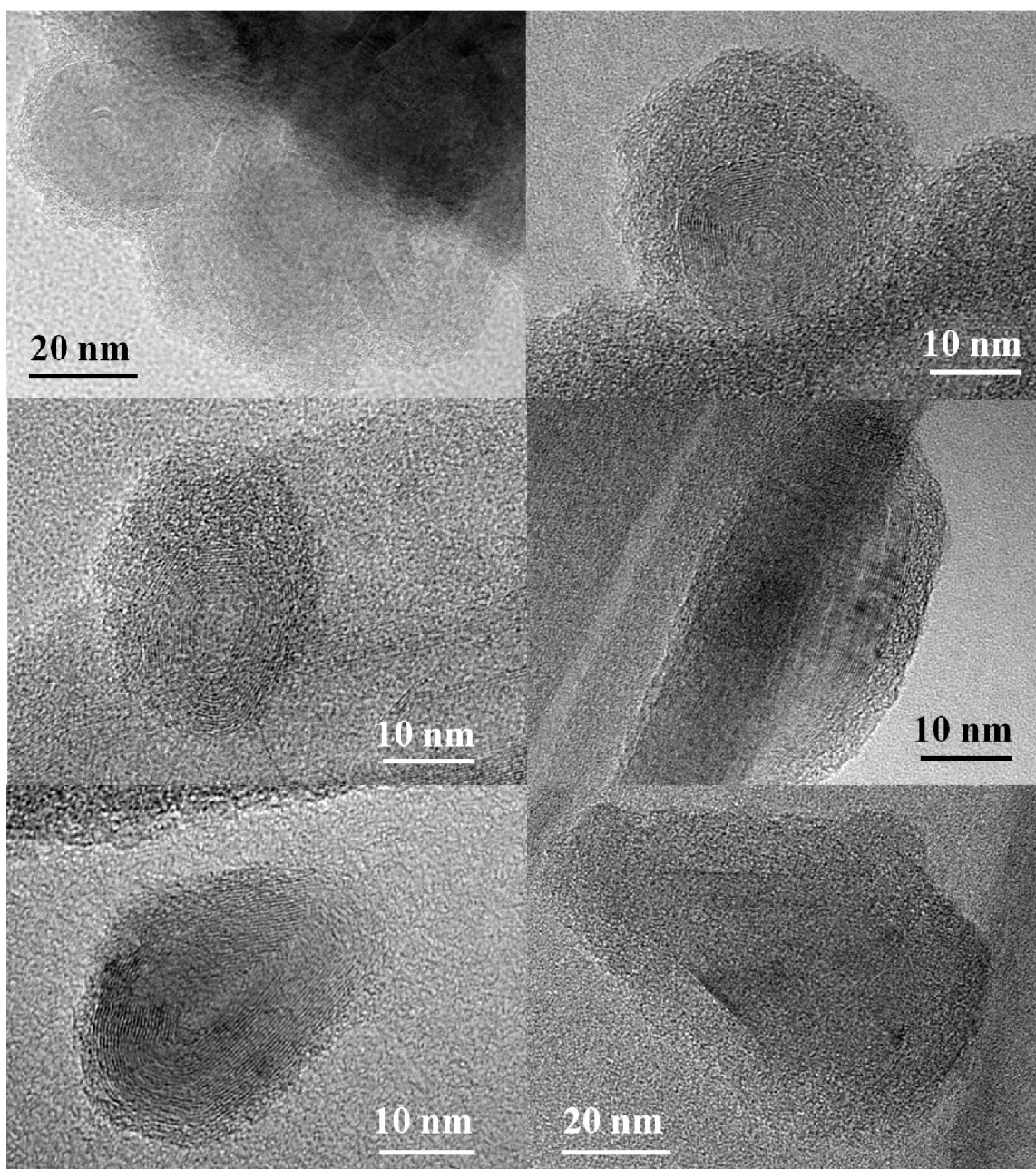


Figure 1S. Selected HRTEM images showing shapes and sizes distribution of the synthesized CNPs, and variations within a particular morphology.

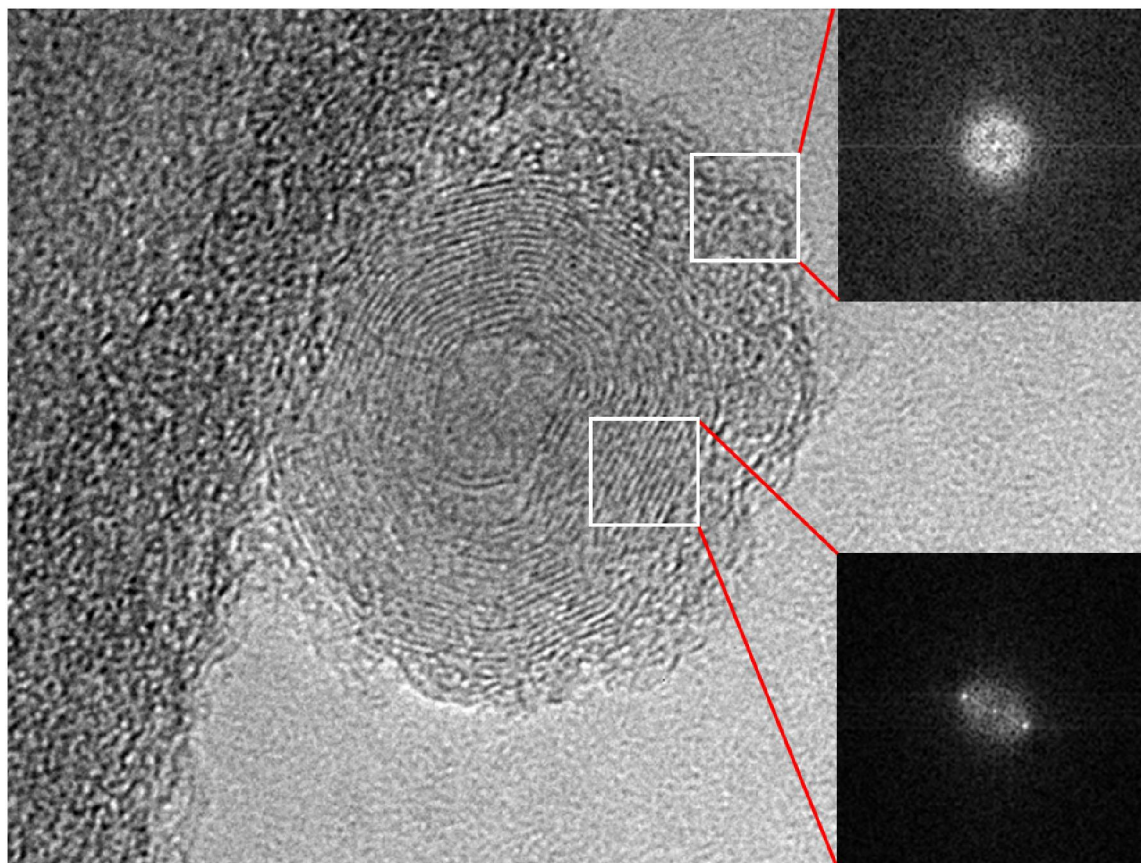


Figure S2. HRTEM image of a carbon nanoparticle. The inset shows the power spectrum of the regions marked by white squares.

Spectroscopic Characterization

FT-IR

FTIR measurements were performed using a Bruker Tensor 27 spectrometer equipped with a DTGS detector. Spectra were collected in a spectral range from 700 cm^{-1} to 3750 cm^{-1} with a resolution of 4 cm^{-1} and 400 scans to improve the signal-to-noise ratio. The samples were analyzed by transmission through a thin film of the carbonaceous materials on a silicon window.

Sample preparation: A thin layer composed of the ammonium salt precursor was prepared by depositing a droplet from an ethanolic suspension of the precursor onto an optical silicon substrate dried under vacuum and analyzed by FTIR spectroscopy. Then, the precursor layer was treated by consecutively heating and further analysis by FTIR at 100°C

for 2 hours, at 200°C for 2 hours and 300°C during 2 hours (Figure 3S).

The resulting spectra, absorbance as a function of frequency, were analyzed as follows. First, the raw absorption spectra were subtracted by the absorption spectrum of the silicon substrate itself and baseline corrected. This was done in order to highlight the principal absorption features and to suppress continuum absorption by the carbonaceous materials, which is primarily due to scattering and interference from the carbonaceous material/silicon interface and the exposed surfaces.

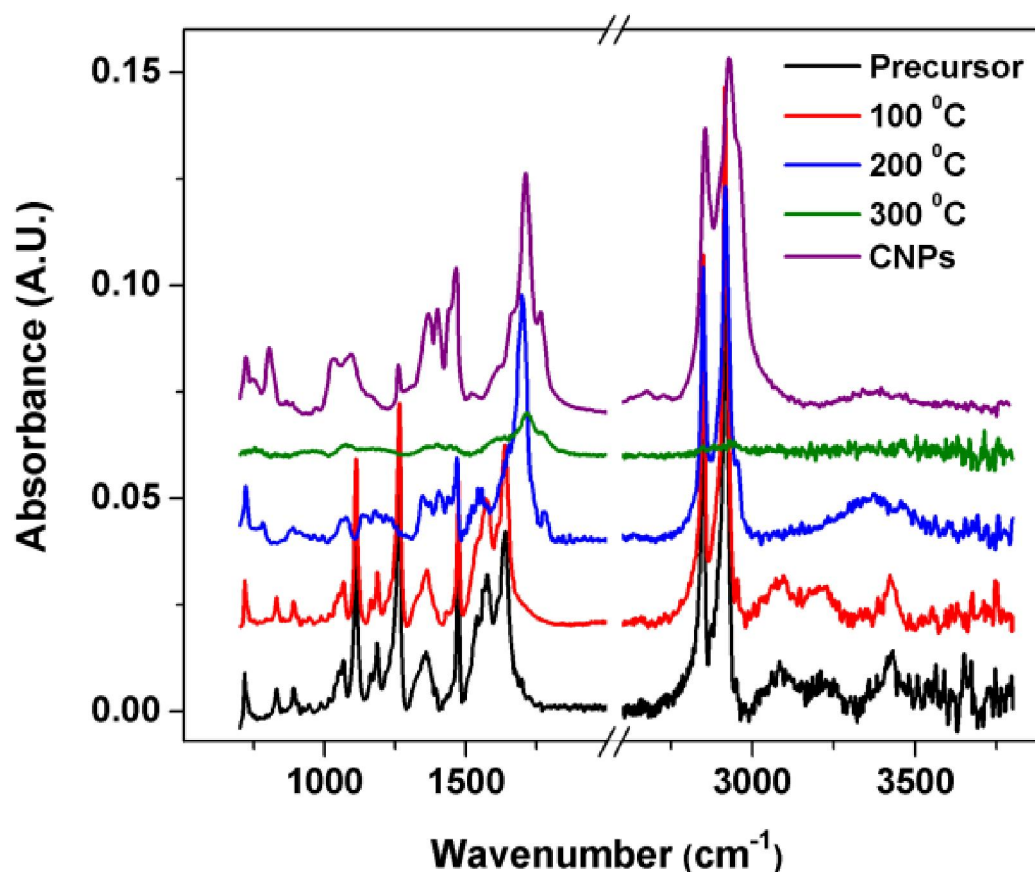


Figure 3S. FT-IR spectra of purified CNPs (magenta) and ammonium salt (black). While, the red, blue, and green lines corresponds to the precursor treated at different temperatures. The spectra are vertically offset for clarity purposes.

The most intense and diagnostic bands of the precursor, octadecyl-1-ammonium citrate, are the $-\text{CH}_2$ rocking vibration at 720 cm^{-1} , the C–C–O asymmetric stretching of the tertiary alcohol at 1110 cm^{-1} , the C–OH asymmetric bending at 1265 cm^{-1} , a broad multiple band between 1300 and 1400 cm^{-1} which can be assigned to C–H bending and wagging plus C–O symmetric stretching vibrations from methylene and tertiary alcohol groups, the

$-\text{CH}_2$ deformation at 1470 cm^{-1} , the $-\text{NH}_3^+$ asymmetric and symmetrical bending vibration between $1500\text{--}1600\text{ cm}^{-1}$, the $-\text{CO}_2^-$ asymmetric stretching vibration at 1640 cm^{-1} , and the $-\text{CH}_2$ asymmetric and symmetric stretching vibrations at 2915 and 2850 cm^{-1} . The spectrum for the salt treated at 100°C does not show significant changes. However, clear differences are observed in the FTIR signal for the sample heated at 200°C . There are losses of the characteristic absorption bands associated to the tertiary alcohol, carboxylates and ammonium groups corresponding to the citrate and octadecylammonium ions respectively. Simultaneously to the loss of absorption from carboxylates and amino groups appear new bands at 1700 and 1775 cm^{-1} with a shoulder at 1750 cm^{-1} which can be assigned to secondary amide groups. This observation is in agreement with the pyrolysis mechanism for the ammonium salts of carboxylic acids where the typical reaction at temperatures around 150°C is the formation of amides.²

The spectrum of the purified nanoparticles shows absorption bands observed in the range of $2800\text{--}3200\text{ cm}^{-1}$ which are assigned to C–H stretching originated from C–H vibrations in carbon atoms in various hybrid states, such as sp^2 , sp^3 , cyclic and aromatic states of carbon. Three obvious absorptions bands at 2960 , 2930 and 2855 are due to the C–H stretch vibrations in sp^3 $-\text{CH}_3$ (asymmetric), both sp^3 $-\text{CH}_2-$ (asymmetric) and sp^3 CH , and sp^3 $-\text{CH}_3$ (symmetric) respectively. The contribution from other expected C–H stretch vibrations, *e.g.* olefinic, aromatic at wavenumber higher than 2975 cm^{-1} were not readily observed. The broad absorption bands at 1710 and 1760 cm^{-1} are assigned to C=O stretching mode from ketone, lactone, lactam and imide groups. Alternate assignments are dismissed due to the lack of aldehyde C–H stretching modes near $2700\text{--}2820\text{ cm}^{-1}$, O–H and N–H stretching absorption, which would indicate carboxylic acids, primary and secondary amide, as well as bands above 1775 cm^{-1} often due to anhydrides (doublet), or strained ring carbonyl. The two broad bands located between 1560 and 1670 cm^{-1} can be originated from stretching mode absorptions of sp^2 C=O in tertiary amides, and C=N in structures like oxazimes, oxazoline, oxazolones, *etc.* The vibrations in the range $1425\text{--}1480\text{ cm}^{-1}$ are attributed to the asymmetric bending modes for sp^3 $-\text{CH}_3$ (1440 cm^{-1} =C– CH_3 mode and 1465 cm^{-1} –C– CH_3 mode) and sp^3 $-\text{CH}_2-$. The band at around 1400 cm^{-1} is assigned to sp^2 $-\text{CH}$ in olefinic configuration and sp^2 $-\text{CH}_2$. The broad band centered at

1370 cm^{-1} can be attributed to symmetric sp^3 $-\text{CH}_3$ bending mode including, $=\text{C}-\text{CH}_3$, $-\text{C}-\text{CH}_3$, and $=\text{N}-\text{CH}_3$, $\text{N}-\text{CH}_3$ units. The band clusters between 1000 and 1280 cm^{-1} are assigned to the stretching modes of $-\text{C}-\text{O}-$ and $-\text{C}-\text{N}-$ moieties as found in ethers, epoxides, esters, aliphatic amines, amides, *etc.* Finally, absorptions in the range from 700 to 900 cm^{-1} are assigned to out-of-plane bending mode from $\text{C}-\text{H}$ bonds. Aromatic features such as $=\text{C}-\text{H}$ stretching vibrational bands at 3060 cm^{-1} , and $-\text{C}=\text{C}-$ groups between 1610 and 1600 cm^{-1} can also be identified in the spectrum. Only out-of-plane bending vibrations of aromatic $=\text{C}-\text{H}$ groups are observed between 700 and 900 cm^{-1} , probably because their intensity is higher than the intensity of the stretching bands. The bands at 1040, 1362, and 1718 cm^{-1} have also been observed in fullerene-like multishell nanoparticle.³

EELS

Energy-loss spectra were measured in diffraction mode with a collection angle of about 6 mrad. A JEOL JEM-ARM 200F operated at 200 kV and equipped with a Tridiem Gatan spectrometer was used.

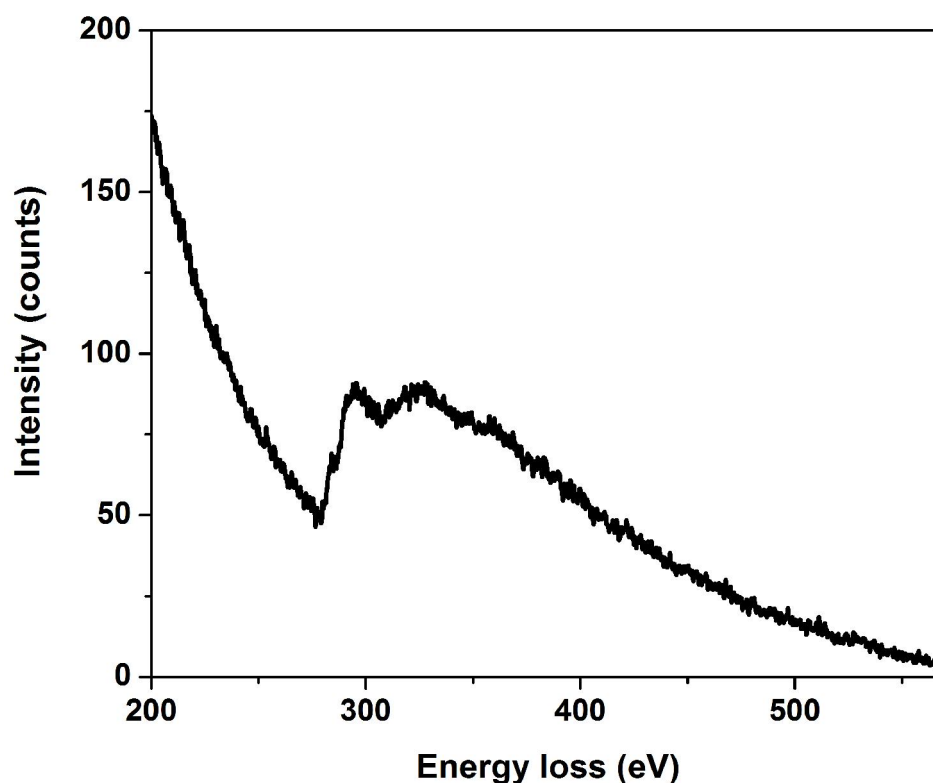


Figure 4S. Characteristic EELS spectrum of a single carbon nanoparticle.

¹³C NMR

NMR data were collected with a Bruker 400 MHz Advance II spectrometer by dissolving 50 mg of CNPs in 1 mL of d-chloroform. ¹H NMR: δ (ppm) = 0.88 (m); 1.25 (s); 1.66 (s); 2.17 (s); 3.72 (m). ¹³C NMR: δ (ppm) = 14.25 (s); 22.83 (s); 29.50 (m); 29.84 (m); 31.05 (s); 32.06 (s).

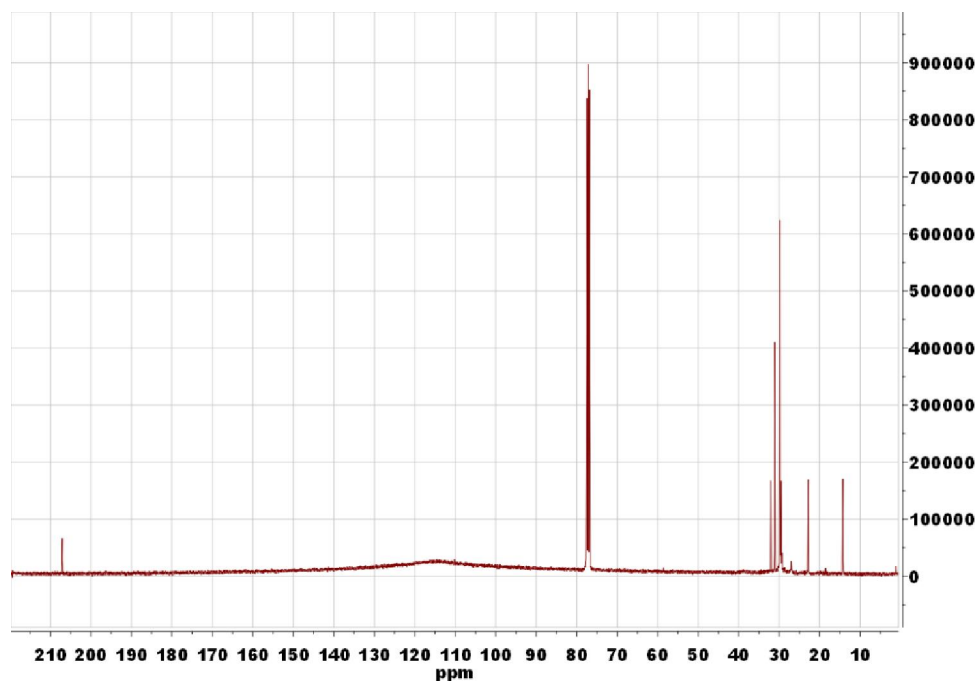


Figure 5S. ¹³C-NMR spectrum of CNPs in CDCl₃. t 77 (chloroform); s 206 (acetone), signals below 40 ppm (carbon sp³).

Electrochemical Characterization

Electrochemical measurements were performed with an Autolab PGSTAT12, potentiostat/galvanostat. The Pyrex electrochemical cell was a closed standard three-electrode cell operated at room temperature, featured an inlaid Pt disk as the working electrode, a platinum coil as the counter electrode, and a silver wire as a quasireference electrode (QRE). The working electrode prior to each experiment was polished on a felt with 0.3 μm alumina, sonicated, rinsed with deionized water and absolute alcohol and dried with a hot air gun.

The CNP are relatively soluble in DCE and THF. However, THF was chosen as solvent because of its larger electrochemical window for negative potentials, and higher solubility

which produces a better quality, reproducibility and more reliability of electrochemical experiments. Experiments were carried out in dried THF, containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte. All measurements were made under a dry argon atmosphere. When the electrochemical experiments were complete, ferrocene was added to the cell as an internal standard; and the QRE calibrated with ferrocene/ferrocenium couple; $Fc/Fc^+ = 0.40$ V vs SCE.⁴

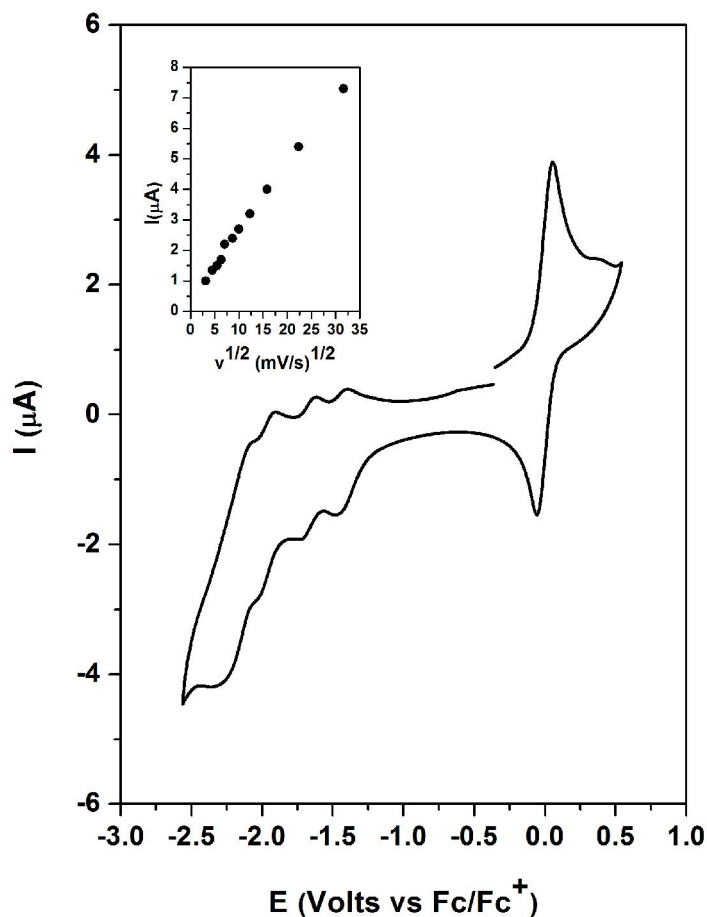


Figure 6S. Cyclic voltammograms of the CNPs on a Pt electrode in THF solution with 0.1 M of TBAPF₆, $v = 40 \text{ mVs}^{-1}$. The reversible wave observed at 0.0 V corresponds to the ferrocene/ferrocenium couple used as an internal standard. Inset shows the correlation between the first peak current as a function of the square root of the scan rate.

Electrogenerated chemiluminescence (ECL)

The ECL experiments were carried out using a three-electrode system consisting 3 mm-diameter platinum disk as working electrode, a platinum wire as the counter electrode and a silver wire as QRE. The platinum wire counter electrode was covered in order to avoid the detection of spurious ECL. The ECL measurements were carried out in 0.1 M TBAPF₆ in

THF as supporting electrolyte, employing benzoyl peroxide (BPO) as cathodic coreactant. The ECL spectra were obtained by positioning the Pyrex electrochemical cell in a homemade holder adapted to a SPEX spectrofluorometer Fluoromax Instrument. Subsequently, the electrochemical cell was electrically connected to a potentiostat/galvanostat. Most of the experimental measurements were made using an integration time of 0.2 and 0.4 s spectrophotometer with 4 mm aperture emission slit.

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