

## **Selective conversion of nitroarenes using a carbon nanotube-ruthenium nanohybrid**

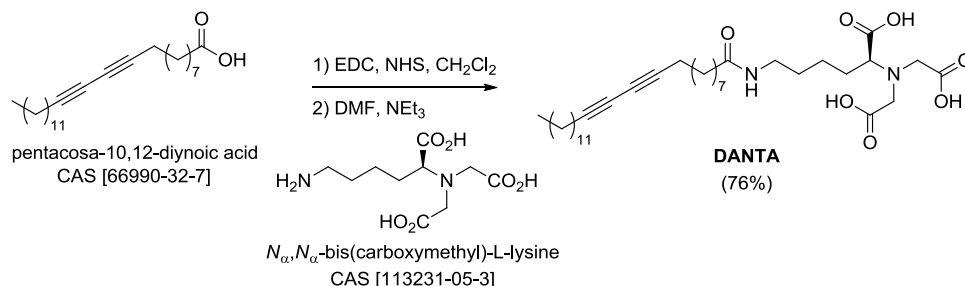
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### **Table of contents**

<b>A.</b>	<b>RuCNT preparation and characterization .....</b>	<b>S1</b>
1.	<b>DANTA synthesis .....</b>	<b>S1</b>
2.	<b>Self-assembly and polymerization of the amphiphile on the CNT .....</b>	<b>S1</b>
3.	<b>Assembly of the second layer on the nanoring-coated nanotubes .....</b>	<b>S2</b>
4.	<b>Synthesis and deposition of RuNPs .....</b>	<b>S2</b>
<b>B.</b>	<b>Catalysis .....</b>	<b>S3</b>
3.	<b>Recycling experiment .....</b>	<b>S3</b>
4.	<b>Spectral data for compounds 2a-j.....</b>	<b>S4</b>
5.	<b>Spectral data for compounds 3a-j.....</b>	<b>S5</b>

## A. RuCNT preparation and characterization

### 1. DANTA synthesis



Pentacos-10,12-diynoic acid (5 g, 13.4 mmol, 1 equiv.), 3-(ethyliminomethyleneamino)-*N,N*-dimethylpropan-1-amine (EDC, 3.1 g, 20.1 mmol, 1.5 equiv.) and *N*-hydroxysuccinimide (NHS, 2.8 g, 24.1 mmol, 1.8 equiv.) were solubilized in 250 mL of anhydrous CH<sub>2</sub>Cl<sub>2</sub>. The solution was stirred at RT for 12 h under N<sub>2</sub> and quenched with H<sub>2</sub>O. The aqueous phase was extracted twice with CH<sub>2</sub>Cl<sub>2</sub> and the organic phases were collected, dried and concentrated under vacuum. The obtained white solid was dissolved in DMF (250 mL) and added to a solution of *N*<sub>α</sub>,*N*<sub>α</sub>-bis(carboxymethyl)-L-lysine (4.2 g, 16.0 mmol, 1.2 equiv.) and NEt<sub>3</sub> (13 mL, 96.5 mmol, 7 equiv.) in DMF (500 mL + sufficient amount of water to induce solubilization). The solution was stirred at RT for 12 h, concentrated under vacuum, taken into H<sub>2</sub>O, and acidified with 37% HCl. The solid was then filtered off, washed with water and dried overnight under vacuum (white solid, 6.3 g, 10.2 mmol, 76%).

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 7.68 (t, *J* = 5.6 Hz, 1H), 3.39–3.50 (AB, *J*<sub>AB</sub> = 17.6 Hz, 4H), 3.35 (t, *J* = 7.3 Hz, 1H), 2.97 (m, 2H), 2.24 (t, *J* = 6.8 Hz, 4H), 2.00 (t, *J* = 7.2 Hz, 2H), 1.1–1.6 (m, 38H), 0.82 ppm (t, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>): δ 174.3, 173.6 (2C), 172.2, 78.0 (2C), 65.7, 64.7 (2C), 53.7 (2C), 38.6, 35.8, 31.7–28.0 (16C), 25.7, 23.5, 22.5, 18.7 (2C), 14.3 ppm; MS (ESI<sup>+</sup>, *m/z*): 619 [*M* + H]<sup>+</sup>, 641 [*M* + Na]<sup>+</sup>, (ESI<sup>-</sup>, *m/z*): 617 [*M* - H]<sup>-</sup>; HRMS (ESI<sup>-</sup>, *m/z*): for C<sub>35</sub>H<sub>57</sub>N<sub>2</sub>O<sub>7</sub> calc 617.4166 [*M* - H]<sup>-</sup>, found 617.4165 [*M* - H]<sup>-</sup>; IR (KBr): ν = 3323, 2925, 2853, 1929, 1732, 1645, 1546, 1464, 1425, 1256, 983, 892, 720 cm<sup>-1</sup>.

### 2. Self-assembly and polymerization of the amphiphile on the CNT

DANTA (20 mg) was dissolved in 25 mM Tris aqueous buffer (2 mL, pH 8) before MWNTs (50 mg) were added. After 10 min of sonication with an ultra-sonic probe (5 min, 300 ms pulses per second, 25 W output power) a stable suspension was obtained and transferred into two 1.5 mL Eppendorf® tubes and centrifuged at 5000 *xg* for 3 min to remove amorphous carbon. The supernatants were collected and centrifuged at 11000 *xg* for 45 min to separate the DANTA-decorated nanotubes from amphiphile in

excess. The supernatant was discarded while the pellets were resuspended in fresh Tris-buffer and centrifuged again at 11000  $\times g$  for 45 min. The final pellets were resuspended in 1.5 mL of buffer and submitted to UV irradiation (254 nm) for 8 h to polymerize the diacetylene groups and yield stabilized nanoring assemblies. Polymerization reinforces the cohesion of the amphiphile on the surface of the nanotube and leads to more robust assemblies.

### **3. Assembly of the second layer on the nanoring-coated nanotubes**

After polymerization, the Tris-buffer volume is adjusted to 1.5 mL and the suspension was stirred in the presence of PDADMAC (700  $\mu\text{L}$  of a 20% water solution) for 1 h to permit the formation of the two layer assembly. Polymer in excess was removed by centrifugation at 11000  $\times g$  for 30 min and the pellets were resuspended in 2 mL of Tris-buffer. This operation was repeated twice with Tris-buffer and two more times with pure water. The final pellets were resuspended in 1 mL of water and split in 10 equal parts in separate Eppendorf<sup>®</sup> tubes.

### **4. Synthesis and deposition of RuNPs**

Ru nanoparticles were synthesized according to the procedure reported by Wang *et al.* (*Chem. Mater.* 2000, **12**, 1622). Briefly, 5 mL of an aqueous solution of  $\text{RuCl}_3 \cdot 6\text{H}_2\text{O}$  (95.0 mg, 0.30 mmol) was added to 100 mL of ethylene glycol, followed by 5 mL of aqueous NaOH (0.5 M) with stirring. The reaction mixture was heated at 160 °C for 3 h to afford a clear homogeneous dispersion of RuNP. To each Eppendorf<sup>®</sup> tube containing the MWCNT/DANTA/PDADMAC hybrid, freshly prepared ruthenium nanoparticles (1 mL of the 3 mM colloid described above) were added and the mixture was left to stand at room temperature with 1 min vortex-stirring every 30 min (4 h). The suspension was then centrifuged at 3000  $\times g$  for 5 min and the nearly colorless supernatant was discarded and replaced with fresh RuNP colloid suspension (1 mL). The same process was repeated two more times to ensure optimal loading of the tubes with RuNPs. The obtained pellets were washed 3 times by centrifugation/redispersion in water. All pellets were combined and redispersed in 12 mL of water to yield the RuCNT suspension that was used for catalysis experiments.

## B. Catalysis

### 1. A typical procedure for the preparation of anilines is given starting from 4-bromo nitrobenzene

A mixture of 4-bromo nitrobenzene (0.13 mmol), hydrazine monohydrate (1.3 mmol) and RuCNT (0.4 mol %) was stirred in H<sub>2</sub>O (2 mL) for 5 h and the progress of reaction monitored by TLC. The reaction mixture extracted with EtOAc (4 x 2 mL) and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under vacuum to afford 4-bromo aniline.

### 2. A typical procedure for the preparation of hydroxylamines is given starting from 4-bromo nitrobenzene

A mixture of 4-bromo nitrobenzene (0.13 mmol), hydrazine monohydrate (1.3 mmol) and RuCNT (0.4 mol %) was stirred in THF (2 mL) for 2.5 h and the progress of reaction monitored by TLC. The reaction mixture was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under vacuum to afford *N*-(4-bromophenyl) hydroxylamine.

### 3. Recycling experiment

The catalyst was recovered by centrifugation. A sample of the supernatant was used for Ru quantification by ICP-MS and the remainder was collected and worked up as described above to measure the yield of the reaction. The precipitated catalyst was reused without further purification in a subsequent reaction.

After 5 cycles, the recovered catalyst was analyzed by TEM (Figure S1).

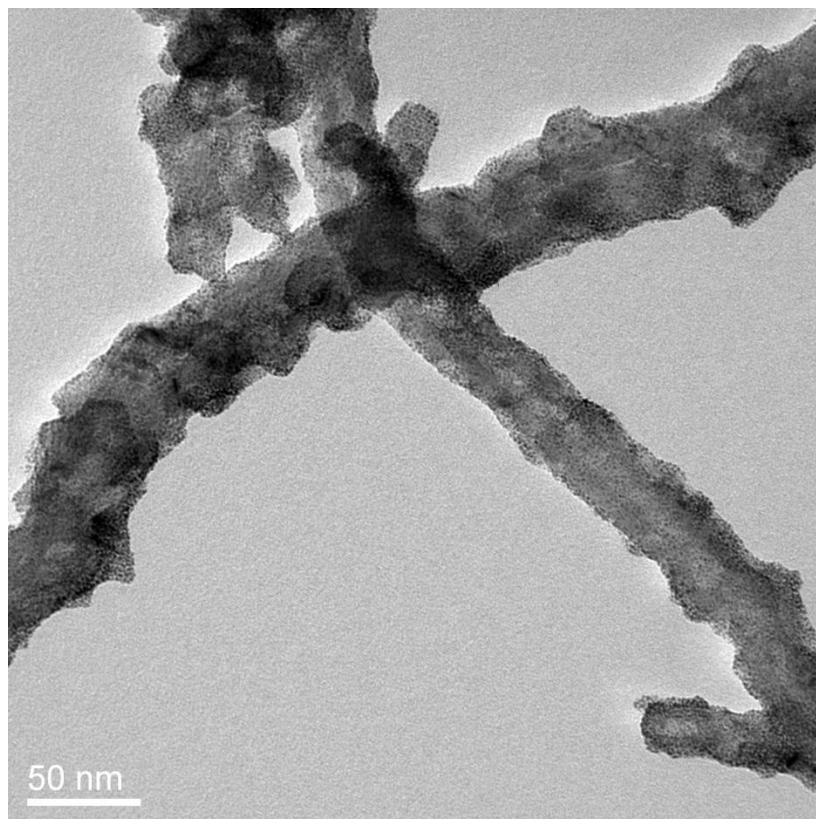
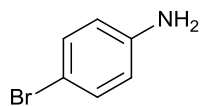


Figure S1. TEM image of the RuCNT catalyst after 5 cycles.

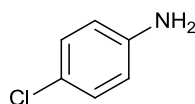
4. Spectral data for compounds 2a-j



2a

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 3.64 (br s, 2H), 6.55 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H) ppm.

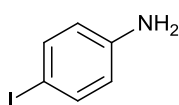
<sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 110.1, 116.6, 131.9, 145.3 ppm.



2b

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 3.62 (br s, 2H), 6.60 (d, *J* = 8.5 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H) ppm.

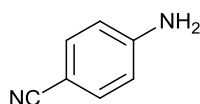
<sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 116.1, 123.1, 129.0, 144.8 ppm.



2c

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 3.63 (br s, 2H), 6.46 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H) ppm.

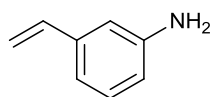
<sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 79.3, 117.2, 137.8, 146.0 ppm.



2d

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 4.17 (br s, 2H), 6.64 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H) ppm.

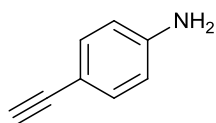
<sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 100.1, 114.3, 120.0, 133.7, 150.3 ppm.



2e

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 3.64 (brs, 2H), 5.21 (d, *J* = 10.8 Hz, 1H), 5.70 (d, *J* = 17.5 Hz, 1H), 6.59-6.67 (m, 2H), 6.75 (s, 1H), 6.83 (d, *J* = 7.5 Hz, 1H), 7.13 (m, 1H) ppm.

<sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 112.7, 113.5, 114.7, 116.9, 129.3, 136.92, 138.6, 146.3 ppm.

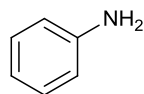


2f

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 2.96 (s, 1H), 3.81 (br s, 2H), 6.59 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H) ppm.

<sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 74.8, 84.3, 111.2, 114.5, 133.4, 146.9 ppm.

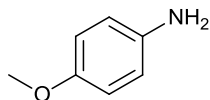
Electronic Supplementary Information



2g

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  3.47 (br s, 2H), 6.70 (d,  $J = 7.5$  Hz, 2H), 6.79 (m, 1H), 7.17 (m, 2H) ppm.

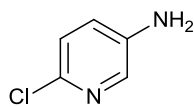
$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  115.0, 118.5, 129.2, 146.2 ppm.



2h

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  3.27 (br s, 2H), 3.74 (s, 3H), 6.66 (d,  $J = 8$  Hz, 2H), 6.75 (d,  $J = 8$  Hz, 2H) ppm.

$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  55.6, 114.8, 116.3, 139.8, 152.8 ppm.

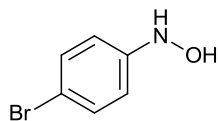


2i

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  3.70 (br s, 2H), 6.96 (d,  $J = 7.5$  Hz, 1H), 7.08 (d,  $J = 7.5$  Hz, 1H), 7.84 (d,  $J = 2.5$  Hz, 1H) ppm.

$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  124.0, 124.7, 136.2, 140.2, 141.5 ppm.

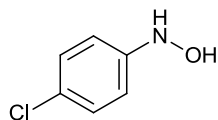
5. Spectral data for compounds 3a-j



3a

$^1\text{H-NMR}$  ( $\text{CD}_3\text{OD}$ ):  $\delta$  6.86 (d,  $J = 8.5$  Hz, 2H), 7.31 (d,  $J = 8.5$  Hz, 2H) ppm.

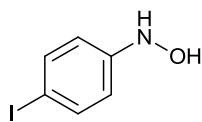
$^{13}\text{C-NMR}$  ( $\text{CD}_3\text{OD}$ ):  $\delta$  113.3, 116.5, 132.4, 152.2 ppm.



3b

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  6.10 (br s, H), 6.92 (d,  $J = 7.5$  Hz, 2H), 7.23 (d,  $J = 7.5$  Hz, 2H) ppm.

$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  115.7, 127.0, 128.8, 148.1 ppm.

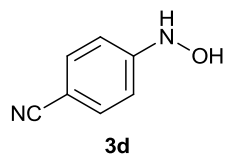


3c

$^1\text{H-NMR}$  ( $\text{CD}_3\text{OD}$ ):  $\delta$  6.75 (d,  $J = 8.5$  Hz, 2H), 7.47 (d,  $J = 8.5$  Hz, 2H) ppm.

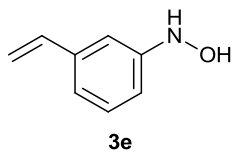
$^{13}\text{C-NMR}$  ( $\text{CD}_3\text{OD}$ ):  $\delta$  82.6, 116.9, 138.4, 152.8 ppm.

Electronic Supplementary Information



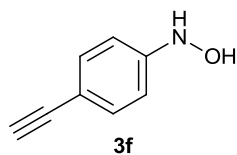
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  5.54 (br s, 1H), 6.99 (d,  $J = 8.5$  Hz, 2H), 7.52 (d,  $J = 8.5$  Hz, 2H) ppm.

$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  103.7, 113.4, 119.5, 133.2, 153.7 ppm.



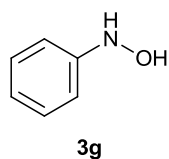
$^1\text{H-NMR}$  ( $\text{CD}_3\text{OD}$ ):  $\delta$  5.19 (dd,  $J = 10.5$  and 0.8 Hz, 1H), 5.72 (dd,  $J = 17.5$  and 0.8 Hz, 1H), 6.67 (dd,  $J = 17.5$  and 10.5 Hz, 1H), 6.86 (d,  $J = 8$  Hz, 1H), 6.93 (d,  $J = 8$  Hz, 1H), 7.04 (s, 1H), 7.16 (t,  $J = 8$  Hz, 1H) ppm.

$^{13}\text{C-NMR}$  ( $\text{CD}_3\text{OD}$ ):  $\delta$  112.4, 113.7, 114.8, 120.2, 129.8, 138.5, 139.5, 153.0 ppm.



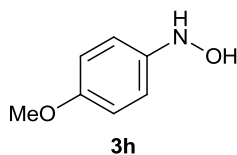
$^1\text{H-NMR}$  ( $\text{CD}_3\text{OD}$ ):  $\delta$  3.25 (s, 1H), 6.89 (d,  $J = 8.5$  Hz, 2H), 7.29 (d,  $J = 8.5$  Hz, 2H) ppm.

$^{13}\text{C-NMR}$  ( $\text{CD}_3\text{OD}$ ):  $\delta$  76.2, 85.1, 114.2, 115.0, 133.6, 153.5 ppm.



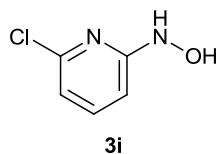
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  5.90 (br s, 1H), 7.01 (d,  $J = 8.5$  Hz, 2H), 7.28 (m, 3H) ppm.

$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  114.6, 122.3, 128.9, 149.5 ppm.



$^1\text{H-NMR}$  ( $\text{CD}_3\text{OD}$ ):  $\delta$  3.73 (s, 3H), 6.81 (d,  $J = 8.5$  Hz, 2H), 6.95 (d,  $J = 8.5$  Hz, 2H) ppm.

$^{13}\text{C-NMR}$  ( $\text{CD}_3\text{OD}$ ):  $\delta$  56.0, 115.1, 117.7, 145.7, 156.5 ppm.



$^1\text{H-NMR}$  ( $\text{CD}_3\text{OD}$ ):  $\delta$  7.25 (d,  $J = 8.5$  Hz, 1H), 7.34 (dd,  $J = 2.5$  Hz and 8.5 Hz, 1H), 7.87 (d,  $J = 2.5$  Hz, 1H) ppm.

$^{13}\text{C-NMR}$  ( $\text{CD}_3\text{OD}$ ):  $\delta$  125.1, 125.6, 135.7, 142.3, 148.9 ppm.