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Electronic Supplementary Information

# Mild and Selective Catalytic Oxidation of Organic Substrates by a Carbon Nanotube-Rhodium Nanohybrid

Simon Donck, Edmond Gravel, Alex Li, Praveen Prakash, Nimesh Shah, Jocelyne Leroy, Haiyan Li, Irishi N. N. Namboothiri,\* and Eric Doris\*

## **Table of contents**

RhCNT preparation and characterization	S1
DANTA synthesis	S1
Self-assembly and polymerization of the amphiphile on the CNT	S1
Assembly of the second layer on the nanoring-coated nanotubes	S2
Synthesis and deposition of RhNPs	S2
General procedures for oxidation reactions	S3
General procedure for the formation of quinones	S3
General procedure for the formation of silanols	S3
General procedure for the formation of azoxy and nitroso derivatives	S3
General procedure for the formation of azo derivatives	S3
General procedure for the formation of disulfides	S4
Recycling experiments	S4
Spectral data	S4
Quinones (cf. Table 1)	S4
Silanes (cf. Table 2)	S4
Nitroso and azoxy derivatives (cf. Table 3)	S5
Azo derivatives and disulfides (cf. Table 4)	S6
	RhCNT preparation and characterization DANTA synthesis Self-assembly and polymerization of the amphiphile on the CNT Assembly of the second layer on the nanoring-coated nanotubes Synthesis and deposition of RhNPs General procedures for oxidation reactions General procedure for the formation of quinones General procedure for the formation of silanols General procedure for the formation of azoxy and nitroso derivatives. General procedure for the formation of azo derivatives General procedure for the formation of disulfides Recycling experiments Spectral data Quinones (cf. Table 1) Silanes (cf. Table 2) Nitroso and azoxy derivatives (cf. Table 3) Azo derivatives and disulfides (cf. Table 4)

## A. RhCNT preparation and characterization



Pentacosa-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 anhydrous  $CH_2Cl_2$  (250 mL). The solution was stirred at RT for 12 h under  $N_2$  and quenched with  $H_2O$  (250 mL). The aqueous phase was extracted twice with  $CH_2Cl_2$  (150 mL) 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  $N_{\alpha}$ , $N_{\alpha}$ -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  $H_2O$ , and acidified (pH 2) with 37% HCI. The solid was then filtered off, washed with water (500 mL) and dried overnight under vacuum (white solid, 6.3 g, 10.2 mmol, 76%).

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  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 (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  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):  $\nu$  = 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 ×g for 3 min to remove amorphous carbon. The supernatants were collected and centrifuged at 11000 ×g 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 ×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  $\mu$ 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 ×*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 RhNPs

The synthesis of Rh particles was carried out following a protocol described by Wang *et al.* (*Chem. Mater.* 2000, **12**, 1622). Briefly, a solution of RhCl<sub>3</sub>·3H<sub>2</sub>O (79.0 mg, 0.30 mmol) in water (5 mL) was added to ethylene glycol (100 mL). An aqueous solution of NaOH 0.5 M (5 mL) was added to the stirred mixture and the reaction was heated at 160 °C. After 3 h, a stable transparent brown homogeneous solution of RhNPs was formed. To each Eppendorf® tube containing the MWCNT/DANTA/PDADMAC hybrid, freshly prepared rhodium nanoparticles (1 mL of the *ca.* 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 ×*g* for 5 min and the nearly colorless supernatant was discarded and replaced with fresh RhNP colloid suspension (1 mL). The same process was repeated four more times to ensure optimal loading of the tubes with RhNPs. 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 RhCNT suspension that was used for catalysis experiments.

## B. General procedures for oxidation reactions

#### 1. General procedure for the formation of quinones

The preparation of 1,4-benzoquinone **2a** is given as a representative example. To a solution of hydroquinone (22.0 mg, 0.2 mmol) in a 3:1 CHCl<sub>3</sub>/H<sub>2</sub>O mixture (1 mL,) was added the RhCNT catalyst (5 mM aqueous suspension, 100  $\mu$ L, 0.25 mol%). The resulting mixture was stirred at room temperature under air for 5 h. The mixture was then diluted with water (2 mL) and extracted with dichloromethane (3 × 5 mL). The combined organic extract was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under vacuum to afford **2a** as a yellow powder (20.7 mg, 96%).

### 2. General procedure for the formation of silanols

The preparation of dimethyl(phenyl)silanol **4a** is given as a representative example. To a solution of dimethyl(phenyl)silane (27.2 mg, 0.2 mmol) in THF (1 mL) was added the RhCNT catalyst (5 mM aqueous suspension, 100  $\mu$ L, 0.25 mol%). The resulting mixture was stirred at room temperature under air for 2 h. The mixture was then diluted with water (2 mL) and extracted with dichloromethane (3 × 5 mL). The combined organic extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under vacuum to afford dimethyl(phenyl)silanol **4a** as a colorless oil (29.2 mg, 96%).

#### 3. General procedure for the formation of azoxy and nitroso derivatives

The preparation of 1,2-diphenyldiazene oxide **6c** is given as a representative example. To a solution of *N*-phenylhydroxylamine (21.8 mg, 0.2 mmol) in a 3:1 CHCl<sub>3</sub>/H<sub>2</sub>O mixture (1 mL) was added the RhCNT catalyst (5 mM aqueous suspension, 100  $\mu$ L, 0.25 mol%). The resulting mixture was stirred at room temperature under air for 12 h. The mixture was then diluted with water (2 mL) and extracted with dichloromethane (3 × 5 mL). The combined organic extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under vacuum to afford 1,2-diphenyldiazene oxide **6c** as a white powder (18.4 mg, 93%).

#### 4. General procedure for the formation of azo derivatives

The preparation of azobenzene **8a** is given as a representative example. To a solution of 1,2diphenylhydrazine (36.8 mg, 0.2 mmol) in a 3:1 CHCl<sub>3</sub>/H<sub>2</sub>O mixture (1 mL) was added the RhCNT catalyst (5 mM aqueous suspension, 100  $\mu$ L, 0.25 mol%). The resulting mixture was stirred at room temperature under air for 12 h. The mixture was then diluted with water (2 mL) and extracted with dichloromethane (3 × 5 mL). The combined organic extracts were dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated under vacuum to afford azobenzene **8a** as a red solid (33.5 mg, 92%).

#### 5. General procedure for the formation of disulfides

The preparation of diphenyl disulfide **8d** is given as a representative example. To a solution of benzenethiol (22.0 mg, 0.2 mmol) in a 3:1 CHCl<sub>3</sub>/H<sub>2</sub>O mixture (1 mL) was added the RhCNT catalyst (5 mM aqueous suspension, 100  $\mu$ L, 0.25 mol%). The resulting mixture was stirred at room temperature under air for 12 h. Then the mixture was diluted with water (2 mL) and extracted with dichloromethane (3 × 5 mL). The combined organic extracts were dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated uner vacuum to afford diphenyl disulfide **8d** as a colorless solid (20.9 mg, 96%).

## C. Recycling experiments

Oxidation reactions were carried out following the general procedures described above. After completion of the conversion, the catalyst was recovered by centrifugation, and the supernatant was worked up as described in the corresponding procedure. The recovered catalyst was washed with water and reused in subsequent oxidation reactions. This process was repeated over 5 consecutive cycles for each substrate.

Table S1. Recycling of RhCNT for the oxidation of 1ainto 2a.

1a OH OH	RhCNT (0.25 mol%)	0 2a 0
Entry	RhCNT	Yield of 2a
1	fresh	96 %
2	1 <sup>st</sup> reuse	95 %
3	2 <sup>nd</sup> reuse	94 %
4	3 <sup>rd</sup> reuse	95 %
5	4 <sup>th</sup> reuse	93 %

Table S3. Recycling of RhCNT for the oxidation of 5cinto 6c.

5c	Ph <sub>N</sub> OH	RhCNT (0.25 mol%)	O ∳ Ph <sub>\N</sub> ∽N <sub>\</sub> Ph	6c	
	Н	CHCl <sub>3</sub> /H <sub>2</sub> O 3:1, 12 h			

Entry	RhCNT	Yield of 6c
1	fresh	92 %
2	1 <sup>st</sup> reuse	90 %
3	2 <sup>nd</sup> reuse	91 %
4	3 <sup>rd</sup> reuse	90 %
5	4 <sup>th</sup> reuse	89 %





Table S4. Recycling of RhCNT for the oxidation of 7ainto 8a.

7a Ph<sub>N</sub>, N<sub>Ph</sub> H Ph<sub>N</sub>, N<sub>Ph</sub> H CHCl<sub>3</sub>/H<sub>2</sub>O 3:1, 5 h Ph<sub>N</sub><sup>∞</sup>N<sub>Ph</sub> 8a

Entry	RhCNT	Yield of 8a
1	fresh	91 %
2	1 <sup>st</sup> reuse	90 %
3	2 <sup>nd</sup> reuse	92 %
4	3 <sup>rd</sup> reuse	89 %
5	4 <sup>th</sup> reuse	90 %

## D. Spectral data

1. Quinones (cf. Table 1)



(**2a**): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 6.78 (s, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 187.2 (2C), 136.5 (4C).



(**2b**): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 6.55 (s, 1 H), 2.04–2.00 (m, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 187.8, 187.5, 145.2, 140.8, 140.7, 133.0, 15.9, 12.3, 12.0.



(**2c**): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.08 (dd, J = 5.6 Hz, J = 3.6 Hz, 2H), 7.76 (dd, J = 5.6 Hz, J = 3.6 Hz, 2H), 7.0 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ (ppm) 185.0 (2C), 138.6 (2C), 133.9 (2C), 131.8 (2C), 126.4 (2C).



(**2d**): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.02 (d, J = 2.4 Hz, 1H), 6.94–6.91 (m, 1H), 6.83–6.80 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 184.9, 179.0, 144.1, 136.8, 136.0, 133.7.



(**2f**): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.20 (dd, J = 2,0 Hz, J = 10.4 Hz, 1H), 6.38 ppm (d, J = 10.4 Hz, 1H), 6.26 (d, J = 2.0 Hz, 1H), 1.22 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 180.2 (2C), 162.1, 140.1, 129.3, 123.7, 35.6, 27.7 (3C).

### 2. Silanes (cf. Table 2)



(4a): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.61–7.59 (m, 2H), 7.40–7.39 (m, 3H),
2.18 (br s, 1H), 0.41 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 139.1, 133.0 (2C), 129.6, 127.9 (2C), -0.1 (2C).



(4b): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.69–7.63 (m, 6H), 7.46–7.34 (m, 9H);
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 135.2 (3C), 134.9 (6C), 130.2 (3C), 127.9 (6C).



(**4c**): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 1.51 (brs, 1H), 1.04 (s, 21H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 17.7 (6C), 12.2 (3C).



(**4d**): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.72–7.55 (m, 4H), 7.47–7.38 (m, 6H), 2.89 (br s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 134.3 (6C), 130.6 (2C), 128.0 (4C).



(4e): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.24–7.22 (m, 2H), 7.12–7.06 (m, 3H),
2.19 (s, 2H), 0.14 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 138.9, 128.4 (2C),
128.1 (2C), 124.3, 28.0, -0.7 (2C).

#### 3. Nitroso and azoxy derivatives (cf. Table 3)

(**6a**): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 1.27 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 96.2, 23.1 (3C).



(**6b**): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 5.07 (tt, J = 3.8 Hz, J = 11.6 Hz, 1H), 1.97–1.94 (m, 2H), 1.89–1.86 (m, 2H), 1.69–1.65 (m, 2H), 1.43–1.31 (m, 2H), 1.28–1.20 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 65.6, 28.2 (2C), 25.0, 24.5 (2C).



(**6c**): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.33–8.31 (m, 2H), 8.19–8.17 (m, 2H), 7.58–7.48 (m, 5H), 7.42–7.39 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 148.3, 143.9, 131.6 (2C), 129.6, 128.8 (2C), 128.7, 125.5 (2C), 122.3 (2C).



(6d): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.46 (d, *J* = 7.2 Hz, 2H), 8.23 (d, *J* = 7.2 Hz, 2H), 7.87 (d, *J* = 7.2 Hz, 2H), 7.79 (d, *J* = 7.2 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 150,2, 146.2, 133.1 (2C), 132.8 (2C), 126.0 (2C), 123.3 (2C), 118.2, 117.3, 116.1, 113.1.



(**6e**): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.28 (d, J = 6.8 Hz, 2H), 8.25 (d, J = 6.8 Hz, 2H), 6.98 (d, J = 6.8 Hz, 2H), 6.96 (d, J = 6.8 Hz, 2H), 3.89 (s, 3H), 3.88 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 161.8, 160.1, 141.6, 137.9, 127.8 (2C), 123.7 (2C), 113.7 (2C), 113.5 (2C), 55.6, 55.4.

#### 4. Azo derivatives and disulfides (cf. Table 4)



(**8a**): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.96–7.94 (m, 4H), 7.56–7.47 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 152.6 (2C), 130.9 (2C), 129.0 (4C), 122.8 (4C).



(**8b**): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.75 (dd, J = 2.0 Hz, J = 7.6 Hz, 2H), 7.47–7.16 (m, 18H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 152.1, 143.9 (3C), 130.5 (6C), 128.9 (3C), 127.9 (2C), 127.6 (6C), 127.0, 122.6 (2C), 87.2.



(**8c**): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.51–7.49 (m, 4H), 7.32–7.29 (m, 4H), 7.25–7.21 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 139.9 (2C), 129.0 (4C), 127.4 (4C), 127.1 (2C).



(8d): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.19 (d, *J* = 9.0 Hz, 4H), 7.62 (d, *J* = 9.0 Hz, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 146.9 (2C), 144.0 (2C), 126.3 (4C), 124.4 (4C).



(**8e**): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.45 (d, *J* = 8.4 Hz, 4H), 7.34 (d, J = 8.4 Hz, 4H), 1.31 (s, 18H);  $^{13}\mathrm{C}$  NMR (100 MHz, CDCl\_3)  $\delta$  (ppm) 150.4 (2C), 134.0 (2C), 127.7 (4C), 126.1 (4C), 34.5 (2C), 31.2 (6C).

*t*Bu