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Electronic Supplementary Information

Room temperature Suzuki coupling of aryl iodides, bromides, and chlorides using a heterogeneous carbon nanotube-palladium nanohybrid catalyst

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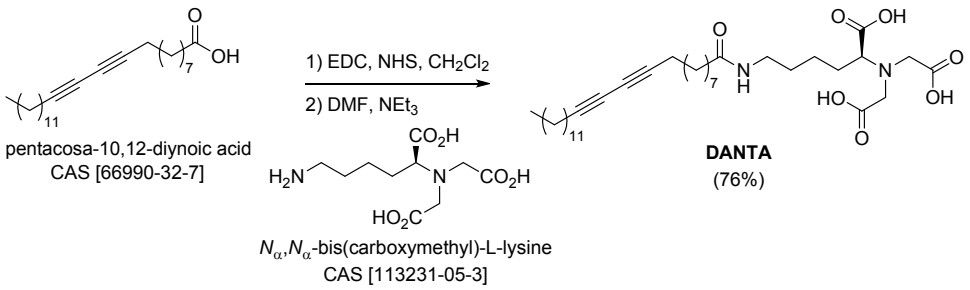
A. PdCNT preparation and characterization

1. DANTA synthesis



Pentacosa-10,12-diynoic acid (5 g, 13.4 mmol, 1 equiv.), 3-(ethyliminomethyleneamino)-*N*,*N*-dimethyl-propan-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_2Cl_2. The solution was stirred at RT for 12 h under N_2 and quenched with H_2O. The aqueous phase was extracted twice with CH_2Cl_2 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_α,N_α-bis(carboxymethyl)-L-lysine (4.2 g, 16.0 mmol, 1.2 equiv.) and NEt_3 (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 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%).

^{1}H NMR (DMSO-d_6): δ 7.68 (t, J = 5.6 Hz, 1H), 3.39−3.50 (AB, J_{AB} = 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); ^{13}C NMR (DMSO-d_6): 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$^+$, m/z): 619 [M + H]$^+$, 641 [M + Na]$^+$, (ESI$^-$, m/z): 617 [M − H]$^-$; HRMS (ESI$^-$, *m*/*z*): for $C_{35}H_{57}N_2O_7$ calc 617.4166 [M − H]$^-$, found 617.4165 [M − H]$^-$; IR (KBr): ν = 3323, 2925, 2853, 1929, 1732, 1645, 1546, 1464, 1425, 1256, 983, 892, 720 cm^{-1}.

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 $\times g$ for 3 min to remove amorphous carbon. The supernatants were collected and centrifuged at 11000 $\times g$ 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 $\times g$ 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 µL 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® tubes.

4. Synthesis and deposition of PdNPs

Pd nanoparticles were synthesized according to a procedure that was inspired by the work of Quiros *et al.* (*Langmuir,* 2002, **18***,* 1413). Briefly, [$PdCl_2(CH_3CN_2)$] (98 mg – 0.38 mmol) and dimethyldidodecylammonium bromide (693 mg – 1.5 mmol) were dissolved in ahydrous THF (60 mL), under N_2 atmosphere. The mixture was stirred at room temperature until apparition of a light orange color. A 1 M solution of lithium triethylborohydride in THF (1.2 mL) was then added, leading to the formation of a dark brown PdNP colloid. To each Eppendorf® tube containing the MWCNT/DANTA/PDADMAC hybrid, freshly prepared palladium nanoparticles (1 mL of the 6 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 PdNP colloid suspension (1 mL). The same process was repeated two more times to ensure optimal loading of the tubes with PdNPs. 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 PdCNT suspension that was used for catalysis experiments. It should be noted that when the PdNP colloid is exposed to air, rapid sintering is observed, but once the particles are deposited on the multi-layer assembly, manipulation under ambient atmosphere is no longer an issue.

5. X-ray photoelectron spectroscopy (XPS)

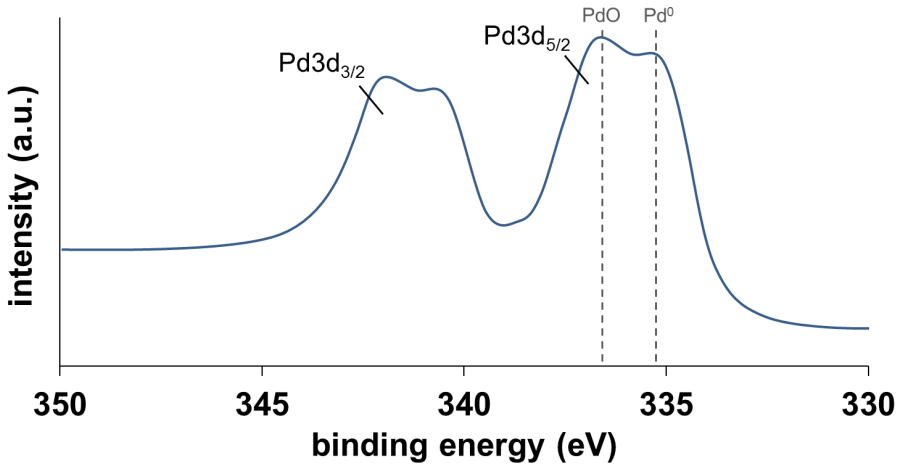


Figure S1. Narrow scan XPS analysis of PdCNT nanohybrid.

B. Catalysis

1. General procedure for Suzuki coupling

The preparation of **3a** is given as a representative example: 4-iodonitrobenzene (0.05 mmol), 4-methoxyphenylboronic acid (0.06 mmol), K_2CO_3 (0.1 mmol) and PdCNT (100 µL of a 6 mM suspension, 1.2 mol%) was added to a 1:1 mixture of EtOH/H_2O (3 mL). The reaction mixture was stirred at room temperature and progress of the reaction was monitored by TLC. After completion of the reaction, EtOH (1.5 mL) added to dissolve the solid precipitate of the product and the catalyst was removed by filtration. EtOH was removed under vacuum and the aqueous layer was extracted using EtOAc (3 × 3 mL). The organic layer was washed with 0.5 M NaOH (2 × 3 mL), dried over Na_2SO_4, filtered, and concentrated under vacuum to afford compound **3a** as a colorless solid in 98% yield.

2. Recycling experiment

4-iodonitrobenzene (0.05 mmol), 4-methoxyphenylboronic acid (0.06 mmol), K_2CO_3 (0.1 mmol) and PdCNT (100 µL of a 6 mM suspension, 1.2 mol%) was added to a 1:1 mixture of EtOH/H_2O (3 mL). The mixture was stirred at room temperature and after 6 h of reaction, EtOH (1.5 mL) was added to dissolve the solid precipitate corresponding to the product. The catalyst was recovered by centrifugation and

reused without further purification in a subsequent reaction. The supernatant was concentrated under vacuum to remove EtOH and the aqueous layer was extracted using EtOAc (3 × 3 mL). The organic layer was washed with 0.5 M NaOH (2 × 3 mL), dried over Na_2SO_4, filtered, and concentrated under vacuum to afford compound **3a** as a colorless solid.

After five runs, the catalyst was analyzed by XPS and TEM (see Figure S2).

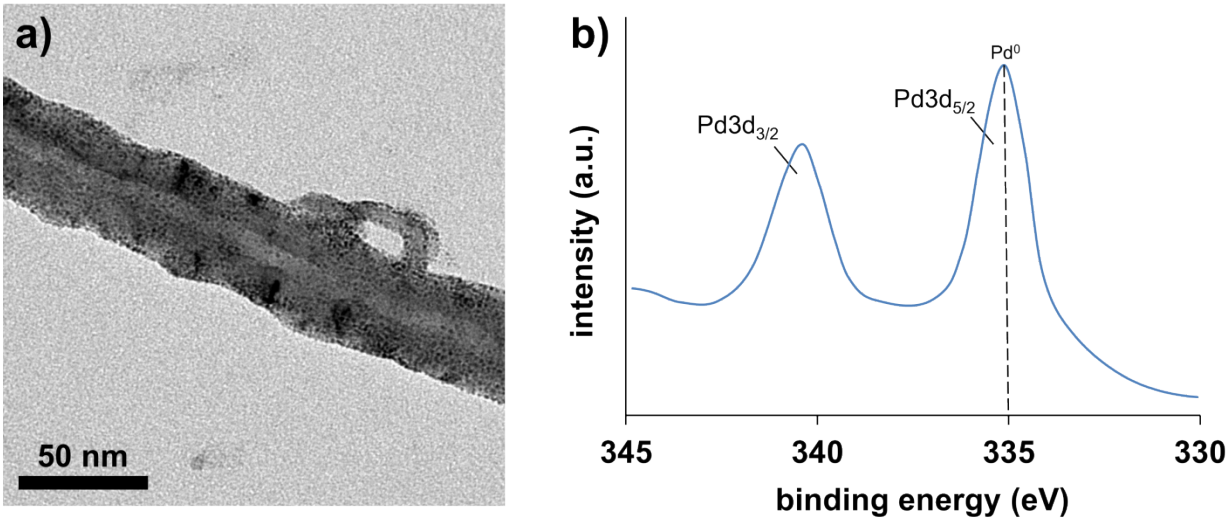
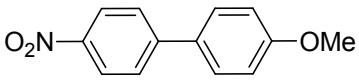


Figure S2. a) TEM image and b) XPS analysis of the PdCNT catalyst after 5 uses.

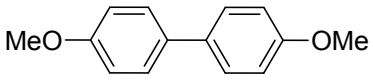
3. Spectral data for compounds 3a-o



3a

^{1}H-NMR ($CDCl_3$): δ 3.88 (s, 3H), 7.02 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H) , 7.69 (d, *J* = 8.4 Hz, 2H), 8.26 (d, *J* = 8.4 Hz, 2H) ppm.

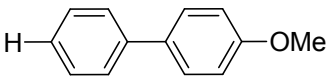
^{13}C-NMR ($CDCl_3$): δ 55.4, 114.6, 124.1, 127.0, 128.5, 131.0, 146.5, 147.2, 160.4 ppm.



3b

^{1}H-NMR ($CDCl_3$): *δ* 3.85 (s, 6H), 6.96 (d, *J* = 8.8 Hz, 4H), 7.48 (d, *J* = 8.8 Hz, 4H) ppm.

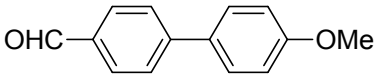
^{13}C-NMR ($CDCl_3$): *δ* 55.3, 114.1, 127.7, 133.4, 158.6 ppm.



3c

^{1}H-NMR ($CDCl_3$): *δ* 3.86 (s, 3H), 6.99 (d, *J* = 8.8 Hz, 2H), 7.31 (m, 1H), 7.42 (m, 2H), 7.54 (m, 4H) ppm.

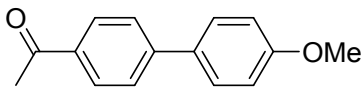
^{13}C-NMR ($CDCl_3$): *δ* 55.3, 114.1, 126.6, 126.7, 128.1, 128.7, 133.7, 140.8, 159.1 ppm.



3d

^{1}H-NMR ($CDCl_3$): δ 3.87 (s, 3H), 7.01 (d, J = 8.8 Hz, 2H), 7.59 (d, J = 8.8 Hz, 2H), 7.72 (d, J = 8 Hz, 2H), 7.93 (d, J = 8 Hz, 2H), 10.04 (s, 1H) ppm.

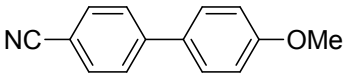
^{13}C-NMR ($CDCl_3$): δ 55.4, 114.4, 127.0, 128.5, 130.3, 132.0, 134.6, 146.7, 160.0, 191.9 ppm.



3e

^{1}H-NMR ($CDCl_3$): δ 2.63 (s, 3H), 3.87 (s, 3H), 7.01 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 8.6 Hz, 2H), 7.65 (d, J = 8.3 Hz, 2H), 8.01 (d, J = 8.6 Hz, 2H).

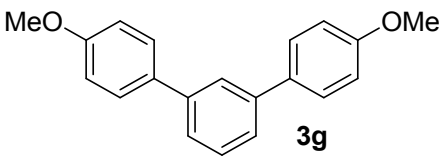
^{13}C-NMR ($CDCl_3$): δ 26.6, 55.3, 114.4, 126.6, 128.3, 128.9, 132.2, 135.2, 145.3, 159.9, 197.7 ppm.



3f

^{1}H-NMR ($CDCl_3$): δ 3.87 (s, 3H), 7.01 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H) ppm.

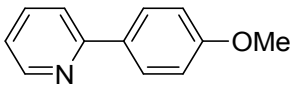
^{13}C-NMR ($CDCl_3$): δ 55.3, 110.1, 114.5, 119.0, 127.0, 128.3, 131.5, 132.5, 145.2, 160.2 ppm.



3g

^{1}H-NMR ($CDCl_3$): δ 3.87 (s, 6H), 7.00 (d, J = 8.8 Hz, 4H), 7.48 (m, 3H), 7.58 (d, J = 8.8 Hz, 4H), 7.72 (s, 1H) ppm.

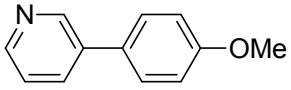
^{13}C-NMR ($CDCl_3$): δ 55.3, 114.2, 125.1, 125.3, 128.2, 129.1, 133.7, 141.3, 159.1 ppm.



3h

^{1}H-NMR ($CDCl_3$): δ 3.87(s, 3H), 7.00 (m, J = 8.4 Hz, 2H), 7.17 (m, 1H), 7.66–7.73 (m, 2H), 7.95 (d, J = 8.4 Hz, 2H), 8.66 (d, J = 4.4 Hz, 1H) ppm.

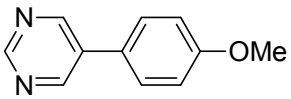
^{13}C-NMR ($CDCl_3$): δ 55.3, 114.1, 119.8, 121.3, 128.1, 132.0, 136.6, 149.5, 157.1, 160.4 ppm.



3i

^{1}H-NMR ($CDCl_3$): δ 3.87 (s, 3H), 7.02 (d, J = 8 Hz, 2H), 7.35 (m, 1H), 7.52 (d, J = 8 Hz, 2H), 7.85 (d, J = 8 Hz, 1H), 8.56 (br s, 1H), 8.33 (br s, 1H) ppm.

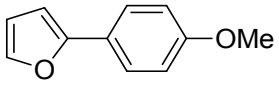
^{13}C-NMR ($CDCl_3$): δ 55.3, 114.5, 123.5, 128.2, 128.6, 130.2, 133.8, 147.8, 147.9, 159.7 ppm.



3j

^{1}H-NMR ($CDCl_3$): δ 3.88 (s, 3H), 7.05 (d, J = 8.8 Hz, 2H), 7.53 (m, J = 8.8 Hz, 2H), 8.93 (s, 2H), 9.16 (s, 1H) ppm.

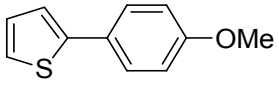
^{13}C-NMR ($CDCl_3$): δ 55.3, 114.9, 126.4, 128.1, 132.2, 154.3, 156.7, 160.4 ppm.



3k

^{1}H-NMR ($CDCl_3$): δ 7.63 (m, 2H), 7.45 (d, J = 2.0 Hz, 1H), 6.94 (m, 2H), 6.54 (d, J = 3.3 Hz, 1H), 6.47 (d, J = 3.3 Hz, 1H), 3.86 (s, 3H).

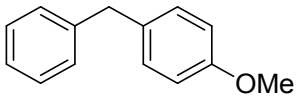
^{13}C-NMR ($CDCl_3$): δ 159.2, 154.2, 141.5, 125.4, 124.3, 114.3, 111.8, 103.5, 55.4 ppm.



3l

^{1}H-NMR ($CDCl_3$): δ 3.84 (s, 3H), 6.92 (d, J = 8.7 Hz, 2H), 7.05 (dd, J = 5 Hz, 4.5 Hz, 1H), 7.21 (m, 2H), 7.54 (d, J = 8.7 Hz, 2H).

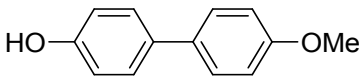
^{13}C-NMR ($CDCl_3$): δ 55.3, 114.2, 122.0, 123.8, 127.2, 127.3, 127.9, 144.3, 159.1 ppm.



3n

^{1}H-NMR ($CDCl_3$): δ 3.78 (s, 3H), 3.93 (s, 2H), 6.83 (d, J = 8.6 Hz, 2H), 7.11 (d, J = 8.3 Hz, 2H), 7.19 (m, 3H), 7.29 (m, 2H).

^{13}C-NMR ($CDCl_3$): δ 41.0, 55.2, 113.8, 125.9, 128.4, 128.7, 129.8, 133.2, 141.5, 157.9 ppm.



3o

^{1}H-NMR ($CDCl_3$): δ 3.85 (s, 3H), 4.87 (br s, 1H), 6.88 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 7.41–7.47 (m, 4H) ppm

^{13}C-NMR ($CDCl_3$): δ 55.3, 114.1, 115.5, 127.6, 127.9, 132.8, 133.4, 154.6, 158.6 ppm.