Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Co-catalytic oxidative coupling of primary amines to imines using an organic nanotube-gold nanohybrid

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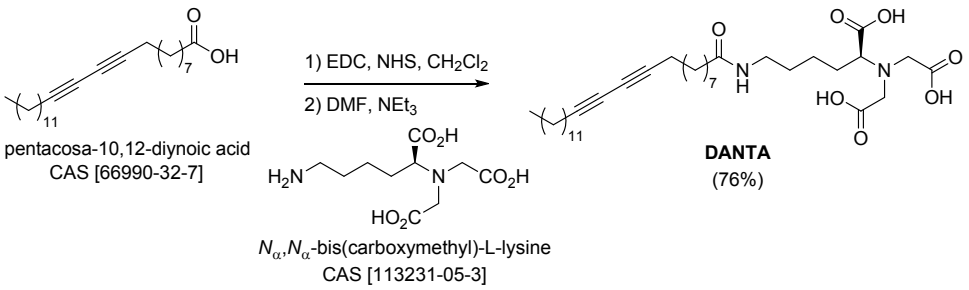
A. AuONT preparation and characterization

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. ONT synthesis and PDADMAC adsorption

a) DANTA (10 mg – 0.016 mmol) was added to a 1:1 EtOH/MeOH mixture (200 µL) and bath-sonicated until complete dissolution. The solution was then added to pure water (2 mL) and the mixture was stirred at room temperature for 1 h, giving rise to a turbid suspension resulting from the formation of bilayer assemblies. Several cycles of centrifugation (2 000 ×g, 15 min) and dispersion (in water) were performed to remove free-standing amphiphiles. TEM observation of the precipitate confirmed that

organic nanotubes were the predominant objects in the mixture, even though some ribbons and helices could be observed (especially at the tip of nanotubes, see Figure S1)

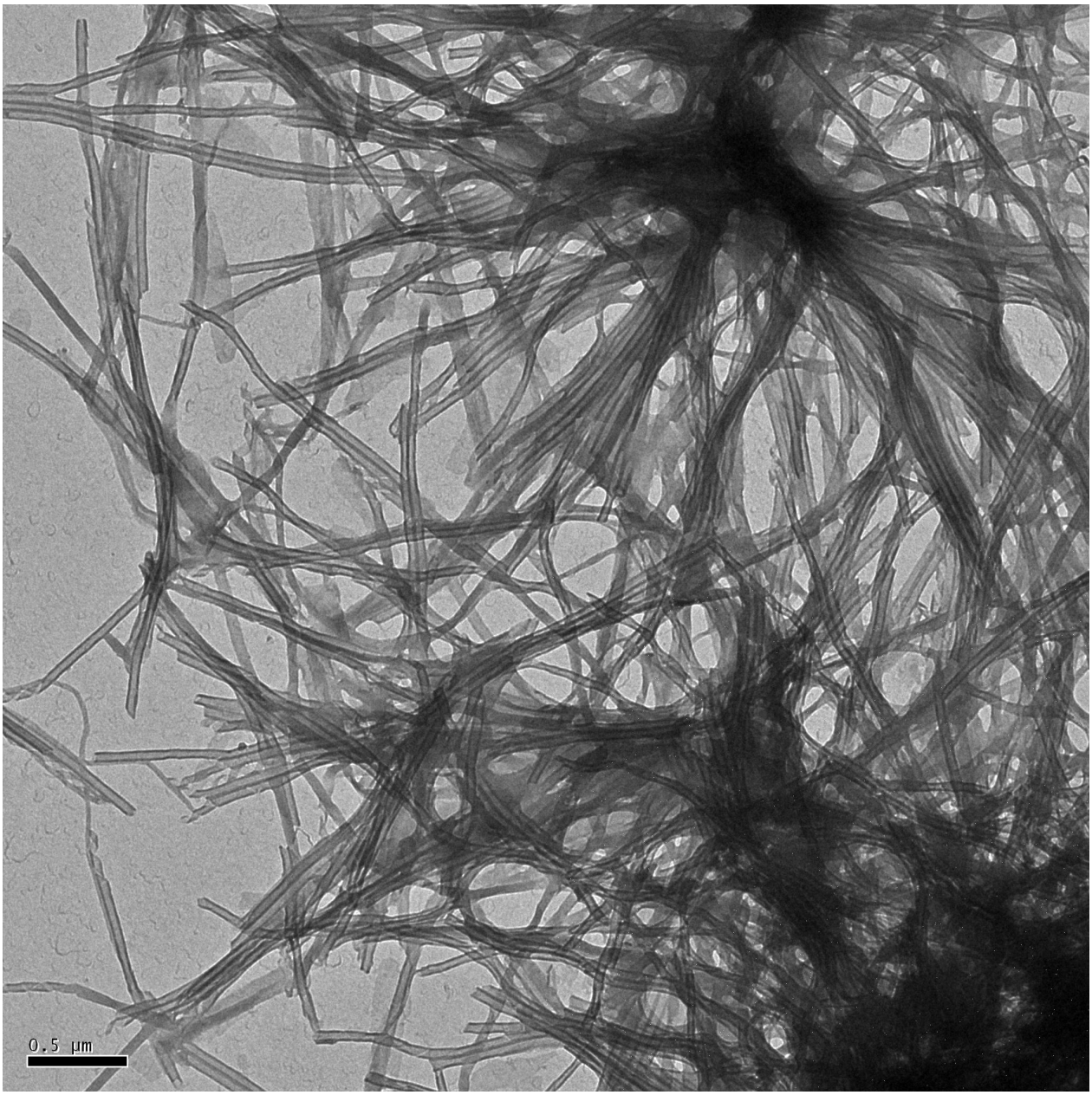


Figure S1. Bilayer assemblies formed after precipitation of DANTA in neutral water.

b) The turbid suspension was then subjected to UV irradiation (254 nm, low pressure mercury UV lamp, Heraeus) for 5 min, resulting in the development of an intense blue color.

c) PDADMAC (1 mL of a 20% water solution) was added to the suspension which shifted from blue to purple, and finally red, after 1 h of stirring at room temperature. Polymer in excess was removed by centrifugation of the ONT at 11000 ×*g* for 30 min and the pellets were resuspended in 2 mL of water.

This operation was repeated three more times. The final pellets were resuspended in 1 mL of water and split in 20 equal parts in separate Eppendorf® tubes.

3. AuNPs synthesis and deposition on ONT

To ultrapure water (42.5 mL) was added NaOH (1.5 mL of a 0.2 M solution) followed by tetrahydroxymethylphosphonium chloride (THPC, 1 mL of a 0.8 % aqueous solution). After 2 min of agitation, $HAuCl_4$ (5 mL of a 0.01 M aqueous solution) was added and the mixture turned brown-orange within a few seconds. The freshly prepared gold nanoparticles (1 mL of the 1 mM colloid suspension described above) were added to each tube containing the DANTA/PDADMAC hybrid 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 1 mL of fresh gold colloid suspension. The same process was repeated two more times to ensure optimal loading of the tubes with AuNPs. The obtained pellets were washed 3 times by centrifugation/redispersion in water. All pellets were combined and redispersed in 4 mL of water to yield the AuONT suspension that was used for catalysis experiments.

4. X-ray photoelectron spectroscopy (XPS) characterization

An aliquot of the AuONT suspension was filtered through a polypropylene membrane which was then dried under vacuum overnight. XPS analysis showed only the presence metallic gold in the nanohybrid sample (Figure S2).

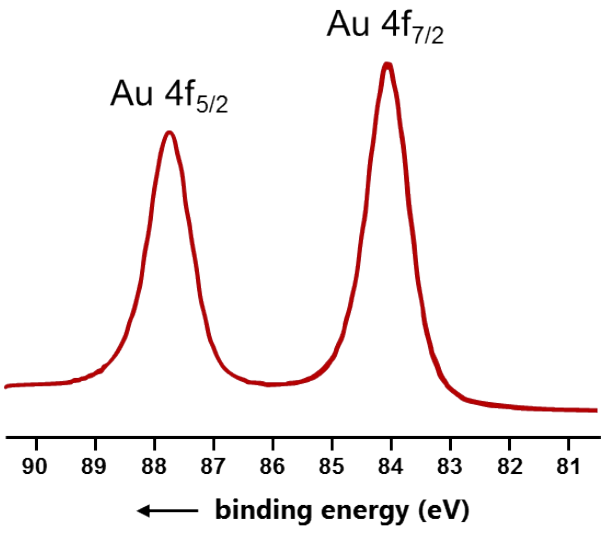


Figure S2. Narrow scan XPS analysis of AuONT nanohybrids.

5. Inductively coupled plasma mass spectrometry (ICP-MS) assessment of gold content

A sample of AuONT was mineralized by stirring in aqua regia overnight at room temperature. The solution was then diluted 1000 times in ultrapure water, then 100 times in 2% HCl and injected via a peristaltic pump equipped with Tygon tubing at 100 µL min^{-1} flow rate. Nebulization of samples was performed by means of a microconcentric nebulizer. A 7700x ICP-MS (Agilent) was used as elemental detector. ICP conditions were the following: nebulization gas flow rate: 1 L min^{-1}, dilution gas flow rate: 0.1 L min^{-1}, plasma gas flow rate: 15 L min^{-1}, auxiliary gas flow rate: 1 L min^{-1}. Plasma power was set to 1550 W. Other parameters were adjusted to both maximize the analyte signal and minimize oxide and doubly charged ions formation. Quantification of gold was performed at m/z = 197 using external standards. Between analyses, the system was rinsed for 3 min with 2% HCl and a blank was injected to control the absence of any memory effect.

Analysis of the AuONT nanohybrid suspension gave a gold concentration of 0.5 mM.

B. Catalysis

1. General procedure for the oxidative dimerization of amines

Benzylamine 1a (0.1 mmol), AuONT (200 µL of a 0.5 mM suspension in water, 0.1 mol%), and THAP (0.003 mmol, 3 mol%) were mixed in water (1 mL) and stirred at room temperature, under air, for 24 h. After removal of the catalyst by filtration, the mixture was extracted with EtOAc (5 × 3 mL) and the combined organic layers were dried over MgSO4, filtered, and concentrated under vacuum. Pure imine 2a was obtained as a waxy solid (95%).

2. Recycling experiments

A typical oxidative dimerization of 1a was set up. After 24 h of stirring, the mixture was centrifuged (2 000 ×g, 20 min) and the supernatant was collected and worked-up as above. The next reaction cycle was then started by resuspending the pellet in water (1 mL) to which THAP (0.003 mmol, 3 mol%) and benzylamine (0.1 mmol) were added. This sequence was repeated five consecutive times, and isolated yields were calculated for each run.

3. TON and TOF experiments

Benzylamine **1a** (0.1 mmol), AuONT (20 µL of a 0.5 mM suspension in water, 0.01 mol%), and THAP (0.003 mmol, 3 mol%) were mixed in water (1 mL) and stirred at room temperature, under air. After 24 h of reaction, 29% conversion was achieved. Turn-over parameters were calculated as follows:

Considering the global amount of gold:

TON_{Tot} = product (mmol) / catalyst (mmol)
= 0.029 / 0.00001 = 2 900

TOF_{Tot} = TON_{Tot} / time
= 2900 / 24 = 121 h^{-1}

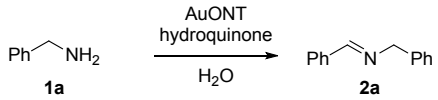
Considering only gold surface atoms:

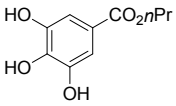
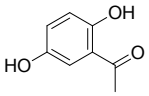
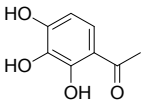
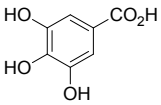
TON_{Surf} = product (mmol) / surface catalyst (mmol)
= 0.029 / 0.000003 = 9 667

TOF_{Surf} = TON_{Surf} / time
= 9 667 / 24 = 403 h^{-1}

4. Supplementary tables

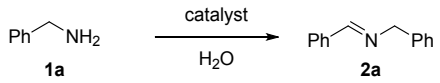
Table S1. Selection of the hydroquinone co-catalyst based on the oxidative dimerization of benzylamine.[a]



Entry	Hydroquinone co-catalyst	Conv. (%)[b]	Entry	Hydroquinone co-catalyst	Conv. (%)[b]
1		15	4		40
2		17	5		95
3		38			

[a] *Conditions:* Benzylamine (0.1 mmol), AuONT (200 µL of a 0.5 mM suspension in H_2O, 0.1 mol%), co-catalyst (0.003 mmol, 3 mol%), H_2O (1 mL), room temp., under air, 24 h. [b] Conversion determined by ^{1}H-NMR.

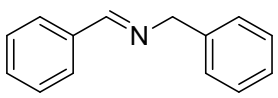
Table S2. Control experiments using different combinations.[a]



Entry	Catalytic system	Conv. (%)[b]
1	THAP	NR[c]
2	$HAuCl_4$ + THAP	NR[c]
3	AuNPs + THAP	15
4	AuONT + THAP	95
5	ONT/PDADMAC + THAP	NR[c]

[a] *Conditions:* Benzylamine (0.1 mmol), gold source (0.1 mol% when applicable), THAP (0.003 mmol, 3 mol%), H_2O (1 mL), room temp., under air, 24 h. [b] Conversion determined by ^{1}H-NMR. [c] No reaction.

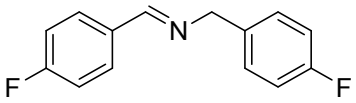
5. Spectral data



2a: ^{1}H NMR ($CDCl_3$): δ 4.85 (s, 2H), 7.27–7.43 (m, 8H), 7.79–7.81 (m, 2H), 8.41 (s, 1H) ppm;

^{13}C NMR ($CDCl_3$): δ 65.0, 126.9, 127.1, 127.9, 128.2, 128.4, 128.6, 130.7, 136.0, 139.2, 162.0 ppm;

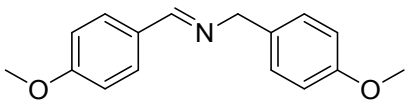
MS (ESI$^+$, *m*/*z*): 196 $[M + H]^+$.



2b: ^{1}H NMR ($CDCl_3$): δ 4.77 (s, 2H), 7.01–7.12 (m, 4H), 7.28–7.31 (m, 2H), 7.75–7.79 (m, 2H), 8. 35 (s, 1H) ppm;

^{13}C NMR ($CDCl_3$): δ 64.1, 115.1, 115.3, 115.6, 115.8, 129.4, 129.5, 130.1, 130.2, 132.2, 134.8, 160.5, 163.1, 165.6 ppm;

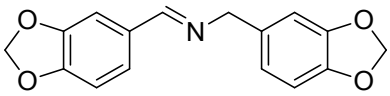
MS (ESI$^+$, *m*/*z*): 232 $[M + H]^+$.



2c: ^{1}H NMR ($CDCl_3$): δ 3.80 (s, 3H), 3.84 (s, 3H), 4.73 (s, 2H), 6.87–6.93 (m, 4H), 7.25 (d, *J* = 8 Hz, 2H), 7.71 (d, *J* = 8 Hz, 2H), 8. 30 (s, 1H) ppm;

^{13}C NMR ($CDCl_3$): δ 55.2, 55.3, 64.3, 113.8, 113.9, 129.1, 129.8, 131.6, 158.6, 160.9, 161.6 ppm;

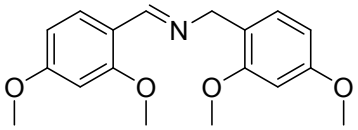
MS (ESI$^+$, *m*/*z*): 256 $[M + H]^+$.



2d: ^{1}H NMR ($CDCl_3$): δ 4.67 (s, 2H), 5.93 (s, 2H), 5.99 (s, 2H), 6.77–6.83 (m, 4H), 7.13 (d, J = 8 Hz, 1H), 7.39 (s, 1H), 8.23 (s, 1H) ppm;

^{13}C NMR ($CDCl_3$): δ 64.2, 100.8, 101.4, 106.7, 108.0, 108.2, 108.6, 121.0, 124.5, 130.9, 133.2, 146.5, 147.7, 148.2, 149.9, 160.9 ppm;

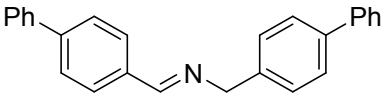
MS (ESI$^+$, m/z): 284 $[M + H]^+$.



2e: ^{1}H NMR ($CDCl_3$): δ 3.79 (s, 3H), 3.81 (s, 3H), 3.81 (s, 3H), 3.84 (s, 3H), 4.72 (s, 2H), 6.43–6.52 (m, 4H), 7.18 (d, J = 8 Hz, 1H), 7.95 (d, J = 8 Hz, 1H), 8.71 (s, 1H) ppm;

^{13}C NMR ($CDCl_3$): δ 55.3, 55.4, 55.5, 59.1, 98.0, 98.4, 103.9, 105.2, 118.1, 120.7, 128.7, 129.8, 157.5, 158.1, 159.8, 160.0, 162.9 ppm;

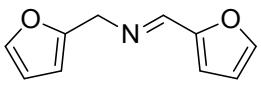
MS (ESI$^+$, m/z): 316 $[M + H]^+$.



2f: ^{1}H NMR ($CDCl_3$): δ 4.91 (s, 2H), 7.34–7.50 (m, 8H), 7.60–7.69 (m, 8H), 7.90 (d, J = 8 Hz, 2H), 8.49 (s, 1H) ppm;

^{13}C NMR ($CDCl_3$): δ 64.8, 127.0, 127.1, 127.3, 127.7, 128.4, 128.7, 128.8, 135.0, 138.3, 140.0, 140.3, 141.0, 143.5, 161.8 ppm;

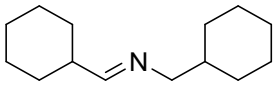
MS (ESI$^+$, m/z): 348 $[M + H]^+$.



2g: ^{1}H NMR ($CDCl_3$): δ 4.75 (s, 2H), 6.27 (m, 1H), 6.34 (m, 1H), 6.47–6.48 (m, 1H), 6.79 (d, J = 3 Hz, 1H), 7.38 (s, 1H), 7.51 (s, 1H), 8.11 (s, 1H) ppm;

^{13}C NMR ($CDCl_3$): δ 56.8, 107.9, 110.3, 111.6, 114.5, 142.3, 144.9, 151.2, 151.4, 151.8 ppm;

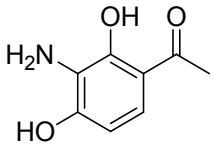
MS (ESI$^+$, m/z): 176 $[M + H]^+$.



2j: ^{1}H NMR ($CDCl_3$): δ 0.83–0.87 (m, 2H), 1.18–1.27 (m, 8H), 1.60–1.76 (m, 11H), 2.15–2.16 (m, 1H), 3.17 (d, J = 6 Hz, 2H), 7.41 (d, J = 5 Hz, 1H) ppm;

^{13}C NMR ($CDCl_3$): δ 25.4, 26.0, 26.0, 26.6, 29.8, 31.2, 38.4, 43.4, 68.3, 168.9 ppm;

MS (ESI$^+$, m/z): 208 $[M + H]^+$.



a': ^{1}H NMR (DMSO-*d6*): δ 2.48 (s, 3H), 6.38 (d, J = 8 Hz, 1H), 7.13 (d, J = 8 Hz, 1H) ppm;

^{13}C NMR (DMSO-*d6*): δ 26.5, 107.4, 113.1, 120.8, 123.7, 150.7, 203.9 ppm;

MS (ES^+): *m/z* 168 $[M + H]^+$.