Electronic Supporting Information

Supramolecular assembly of cobaloxime on nanoring-coated carbon nanotubes: addressing the stability of pyridine-cobalt linkage under hydrogen evolution turnover.

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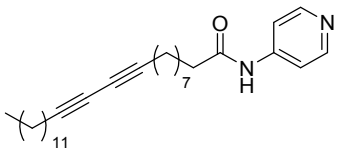
1) Chemicals and materials

Chemicals were obtained from Sigma-Aldrich and used without further purification. THF was distilled over sodium/benzophenone and dichloromethane over CaH_2 prior to use. Multi-walled carbon nanotubes (CNTs) were purchased from n-Tec (Norway). $[Co(dmgH)(dmgH_2)Cl_2]$ was prepared as previously reported.[1]

2) Synthesis of *N*-(pyridin-4-yl)pentacosa-10,12-diynamide (DAPy)



To a solution of EDCI (650 mg, 3.40 mmol) and DMAP (453 mg, 3.74 mmol) in dry dichloromethane (10 mL) was added pentacosa-10,12-diynoic acid (1.00 g, 2.67 mmol) and pyridin-4-amine (302 mg, 3.20 mmol) at 0 °C. The mixture was stirred overnight at room temperature under nitrogen atmosphere. 1 M NaOH (10 mL) of was then added and the mixture was extracted with dichloromethane (3 × 15 mL). The combined organic layer was washed with water, dried over anhydrous $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (dichloromethane/MeOH 98:2 to 95:5) to afford the desired compound as a white solid (1.01 g, 84%).

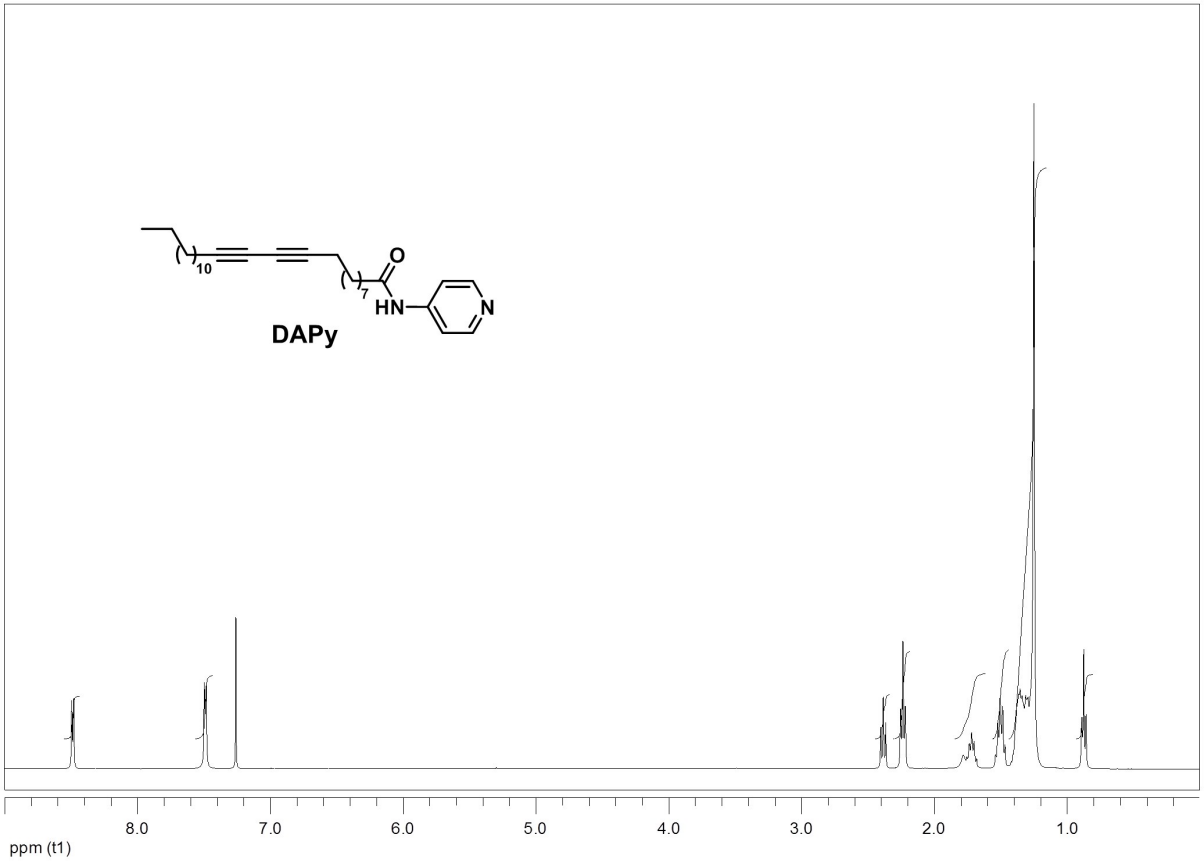
^{1}H NMR ($CDCl_3$) δ (ppm) 8.49 (d, *J* = 6.0 Hz, 2H), 7.48 (d, *J* = 6.0 Hz, 2H), 2.39 (t, *J* = 7.4 Hz, 2H), 2.23 (t, *J* = 6.8 Hz, 4H), 1.78 (br s, 1H), 1.72 (q, *J* = 7.3 Hz, 2H), 1.54–1.47 (m, 4H), 1.36–1.25 (m, 26H), 0.88 (t, *J* = 6.6 Hz, 3H).

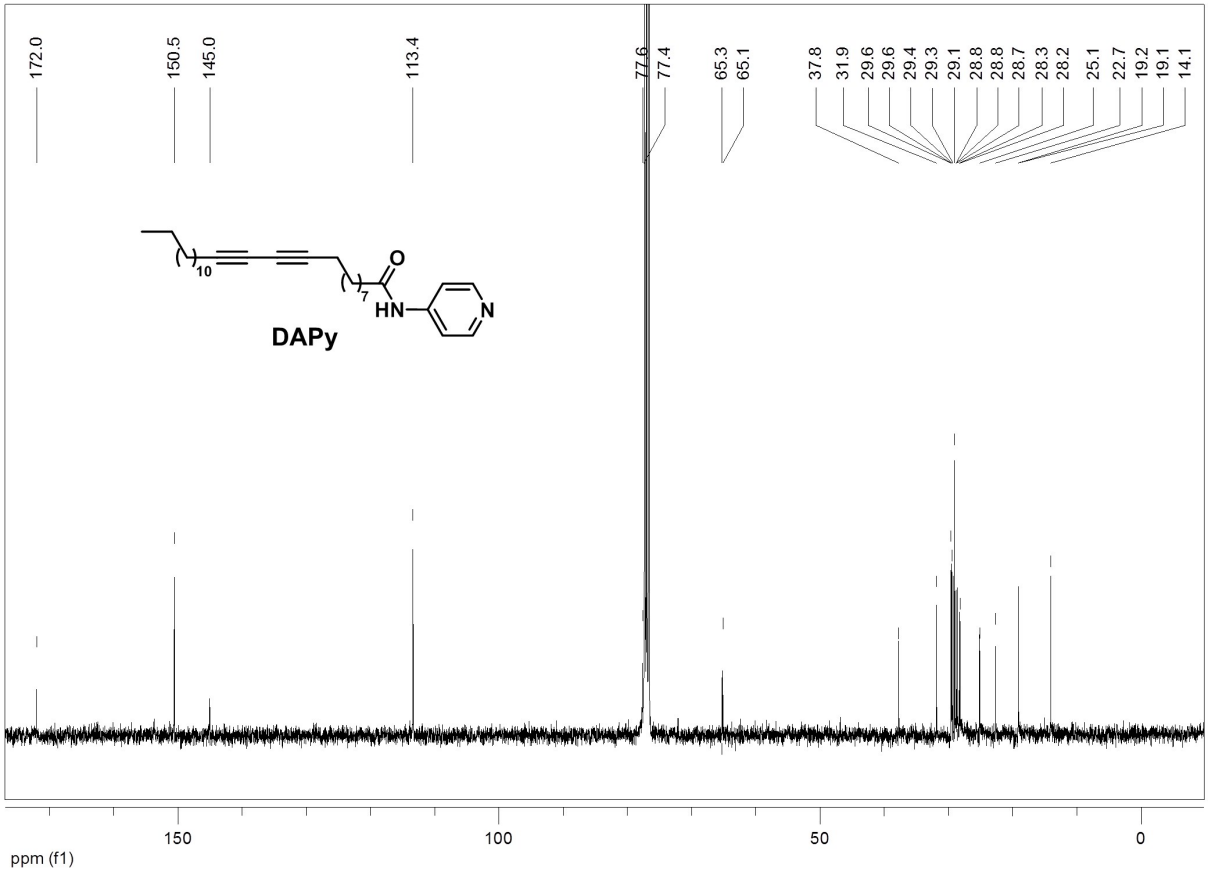
^{13}C NMR ($CDCl_3$) δ (ppm) 172.4, 150.4 (2C), 145.5, 113.5 (2C), 77.7, 77.4, 65.3, 65.2, 37.6, 31.9, 29.6–28.2 (13C), 25.2, 22.6, 19.1 (2C), 14.1.

FTIR *v* (cm^{-1}) 2919, 2849, 1703, 1686, 1592, 1514, 1466, 1328, 1160, 824, 720.

MS (ESI): 451 $[M+H]^+$.

3) ^{1}H and ^{13}C NMR of DAPy





4) Self-assembly and polymerization of the pyridine-amphiphile on the CNT: preparation of CNT-pDAPyH$^+$

N-(pyridin-4-yl)pentacosa-10,12-diynamide **DAPy** (75 mg) was dissolved in 0.1 M HCl (10 mL) before MWCNTs (200 mg, n-Tec) were added. After 20 min of sonication with an ultra-sonic probe (10 min, 300 ms pulses per second, 25 W output power) a stable suspension was obtained and centrifuged at 5000 × *g* for 3 min to remove amorphous carbon. The supernatant was collected and centrifuged at 15000 × *g* for 45 min to separate the amphiphile-decorated nanotubes from amphiphile in excess. The supernatant was discarded while the pellets were resuspended in fresh 0.1 M HCl solution and centrifuged again at 15000 × *g* for 45 min. The final pellets were resuspended in 0.1 M HCl (10 mL) and submitted to UV irradiation (254 nm) for 6 h, to polymerize the diacetylene groups and yield stabilized nanoring assemblies around the nanotube.

5) Assembly of cobalt on the coated nanotubes: preparation of CNT-pDAPy-Co

After polymerization, the solution was centrifuged at 15000 × *g* for 45 min. The supernatant was discarded while the pellets were resuspended in 0.1 M NaOH solution (10 mL) in order to neutralize the pyridine head groups. The mixture was then centrifuged again at 15000 × *g* for 15 min. The supernatant was discarded while the pellets were resuspended in acetonitrile (5 mL). Oxygen was removed from the mixture by bubbling nitrogen gas through the solution for 10 min before the [Co(dmgH)(dmgH$_2$)Cl$_2$] complex (60 mg) was added. The resulting mixture was stirred overnight under nitrogen atmosphere. The solution was centrifuged at 15000 × *g* for 10 min and the pellets were washed with fresh acetonitrile (2 × 5 mL).

6) Fabrication of glassy carbon electrodes modified with CNT-pDAPy-Co

The CNT-pDAPy-Co assembly (2 mg) was suspended in methanol and drop casted onto a glassy carbon electrode (1.27 cm^2). The electrode was then dried under a flow of nitrogen gas.

7) Reference

1. W. C. Trogler, R. C. Stewart, L. A. Epps and L. G. Marzilli, *Inorg. Chem.*, 1974, **13**, 1564-1570.

8) Thermogravimetric analysis of CNT-pDAPyH$^+$

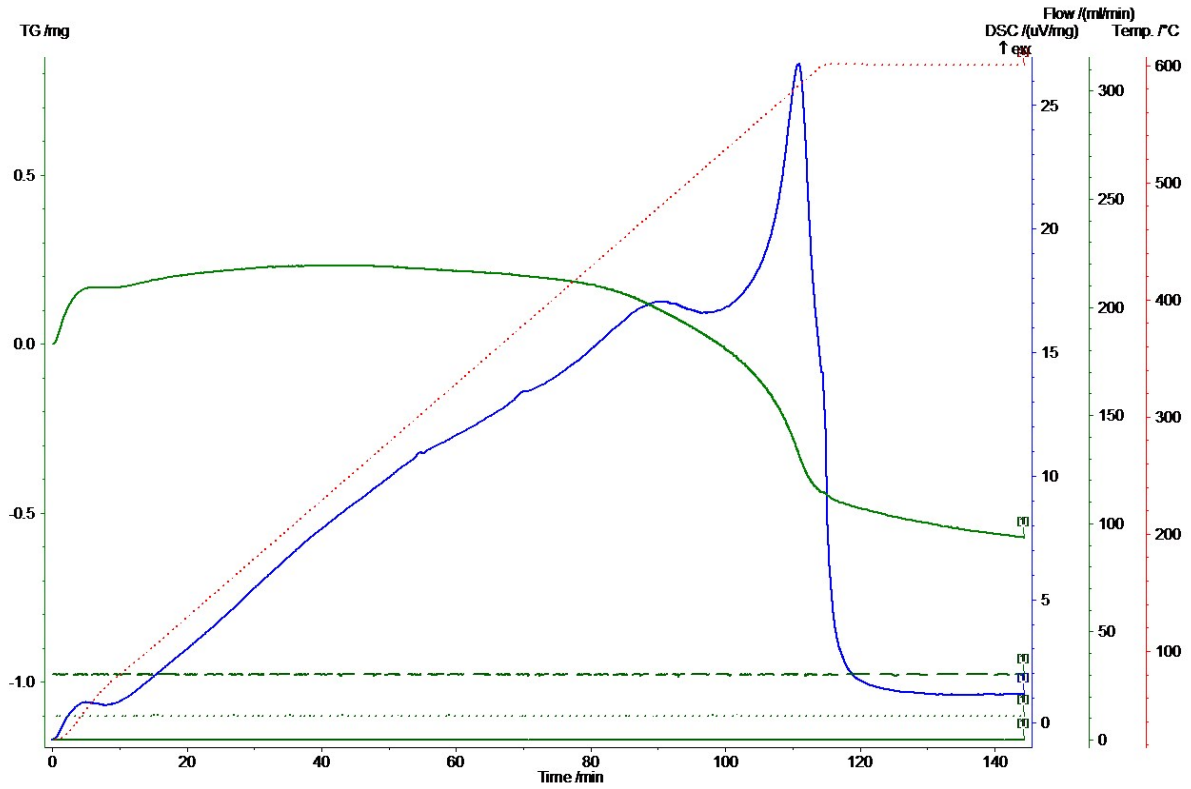


Figure S1: Thermogravimetric analysis of carbon nanotubes coated with photopolymerized DaPy (CNT-pDaPyH$^+$).

9) XPS Spectra

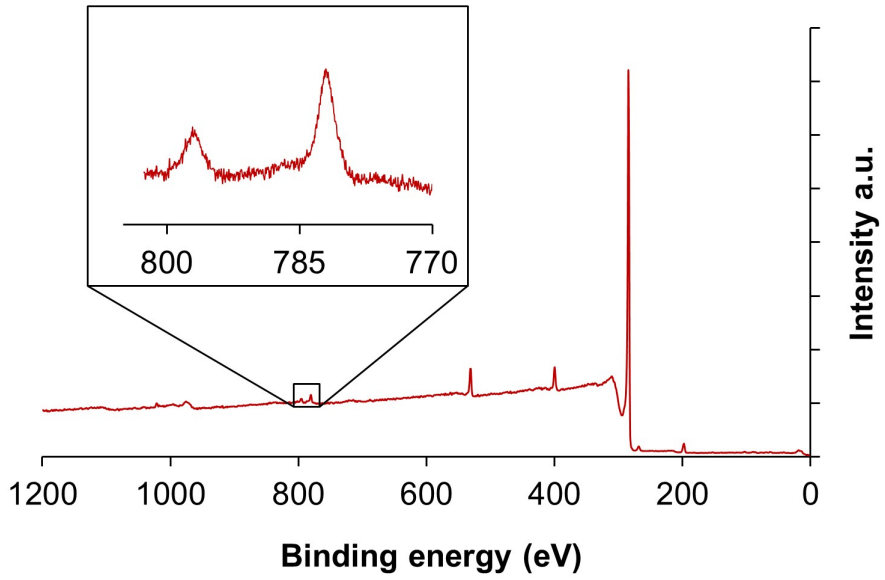


Figure S2: XPS survey and Co 2p region of CNT-pDAPy-Co as prepared

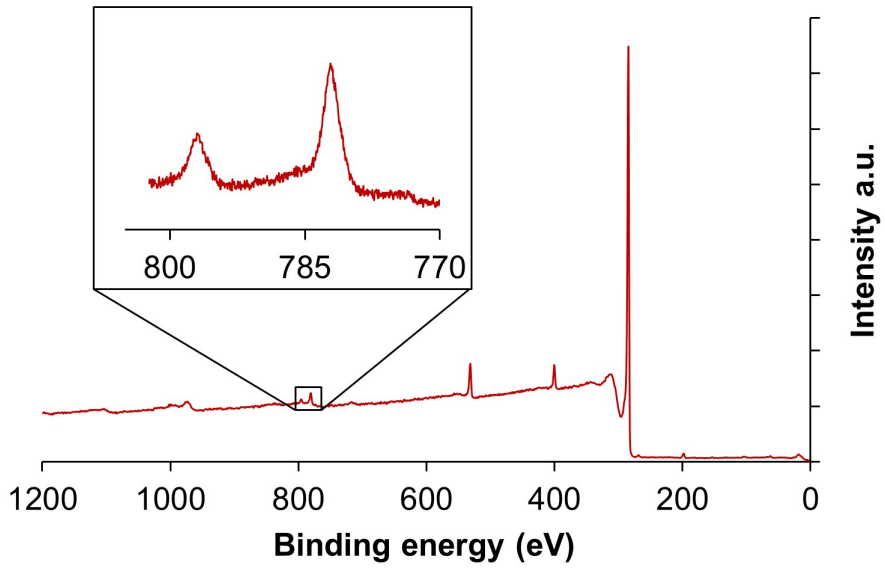


Figure S3: XPS survey and Co 2p region of CNT-pDAPy-Co after electrolysis