Cryptand-Functionalised Highly Oriented Pyrolytic Graphite Electrodes

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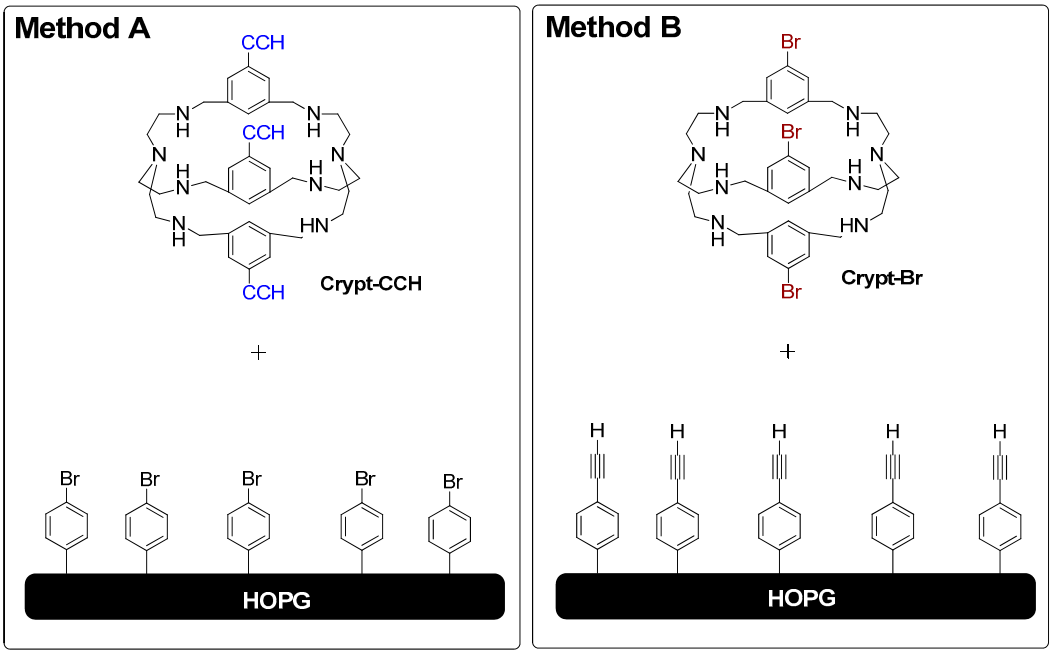

Figure S1. Two different methods used for cryptand grafting onto electrodes using C-C Sonogashira coupling. HOPG-Br produced by electroreduction of 4-Br-N_2^+. HOPG-H is prepared first by electrografting of a diazonium salt formed *in situ* from 4-TMS-NH_2, followed by silyl deprotection to yield a terminal alkyne function.

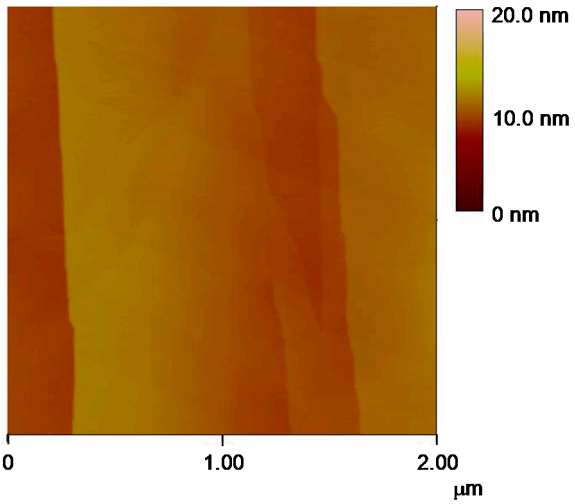

Figure S2. 2D AFM image (2 µm x 2 µm) of an HOPG surface.

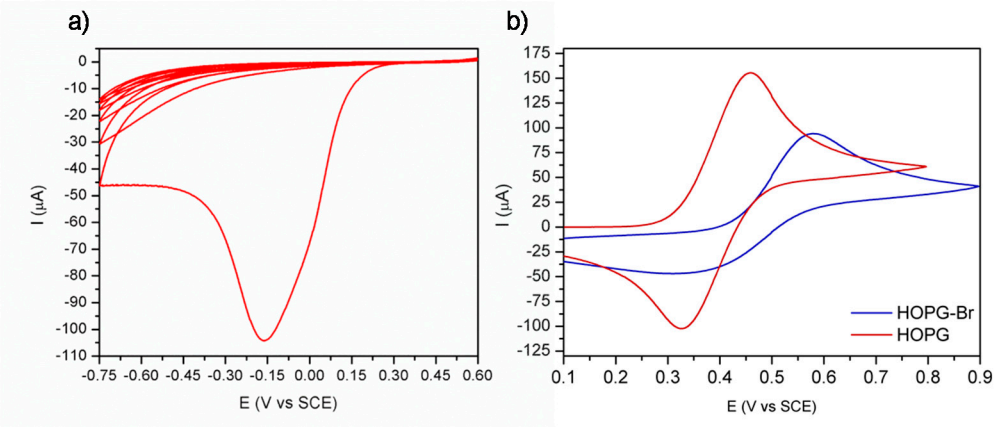

Figure S3. a) CV of 10 mM 4-bromobenzediazonium tetrafluoroborate (4-Br-N_2^+), 6 cycles at 50 mV s^{-1}. b) CV of 1 mM ferrocene using the modified HOPG-Br and unmodified HOPG electrodes, 100 mV s^{-1}, 0.1 M $TBAPF_6$, CH_3CN. Pt wire and SCE are used as counter and reference electrodes, respectively.

Scheme S1. Electroreduction of the silyl capped benzene diazonium salt 4-(trimethylsilyl)ethynylbenzenediazonium tetrafluoroborate reported by Happiot and co-workers.[1]

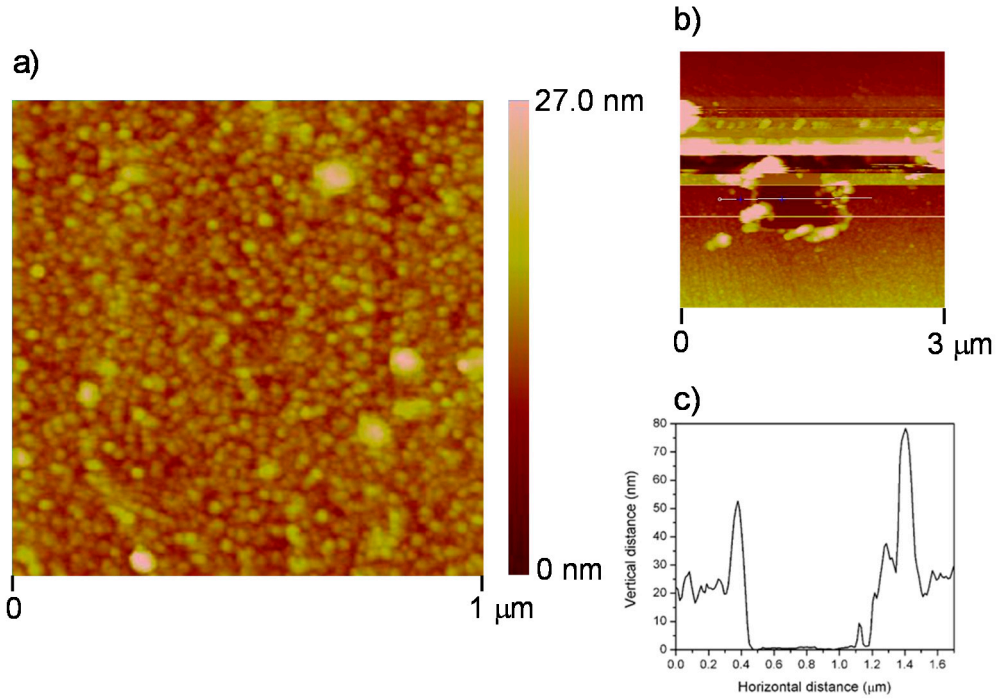

Figure S4. **a**) 2D AFM image (1 µm x 1 µm) of the modified electrode with 4-Br-N_2^+. **b**) 500 x 500 nm trench in the film with AFM contact mode. **c**) Profile section of the AFM scratch for film thickness.

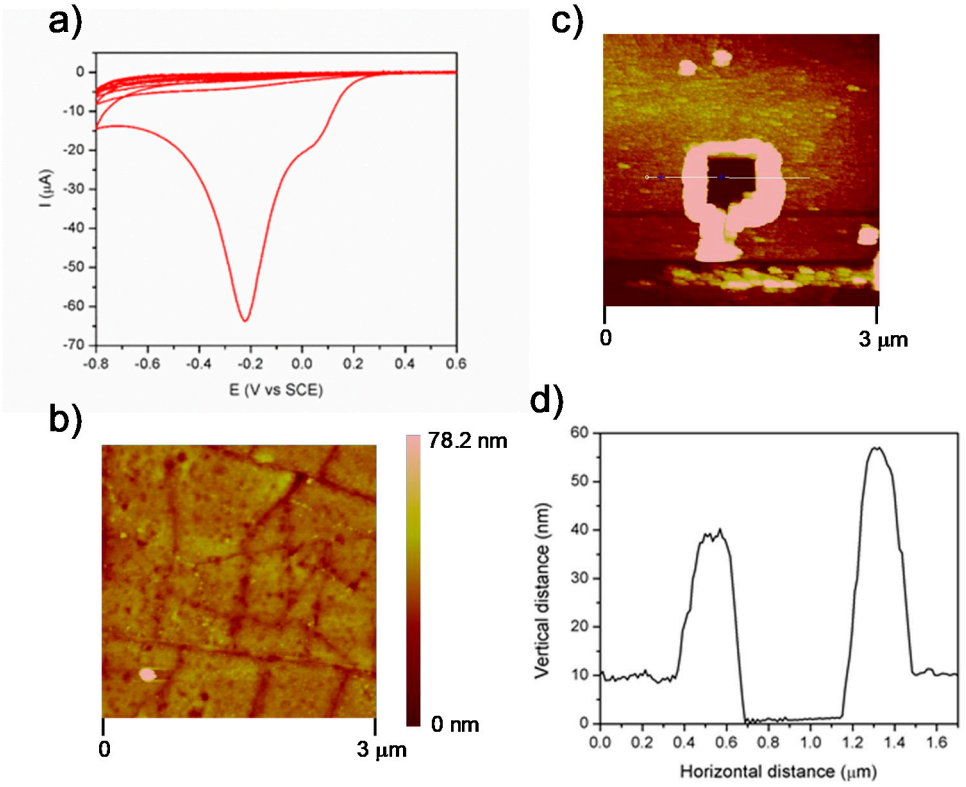

Figure S5. **a**) CV of 10 mM 4-TMS-N_2^+, 6 cycles at 50 mV s^{-1}, 0.1 M $TBAPF_6$, CH_3CN. Pt wire and SCE are used as counter and reference electrodes, respectively. **b**) 2D AFM image (3 m x 3 m) of the modified electrode. **c**) 500

x 500 nm trench in the film formed with AFM contact mode. d) Profile section of the AFM scratch to measure the film thickness.

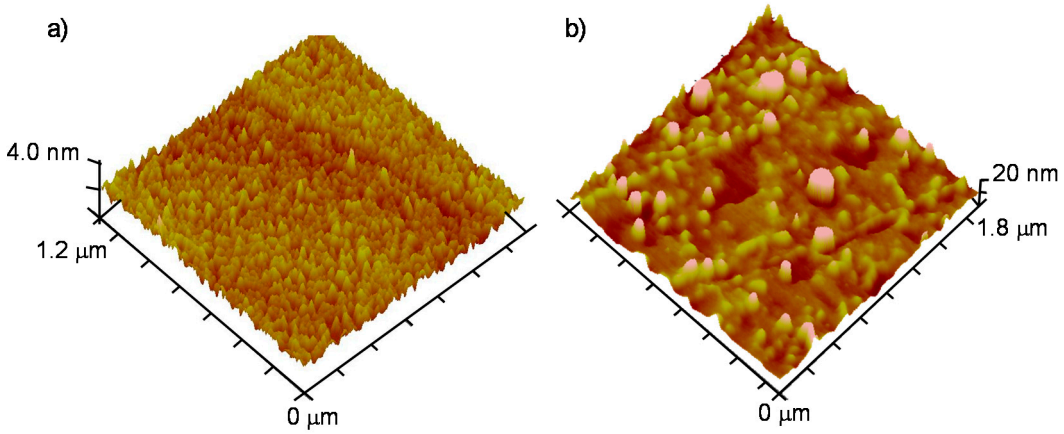

Figure S6. 3D AFM image of **a**) HOPG-TMS and **b**) HOPG-crypt.

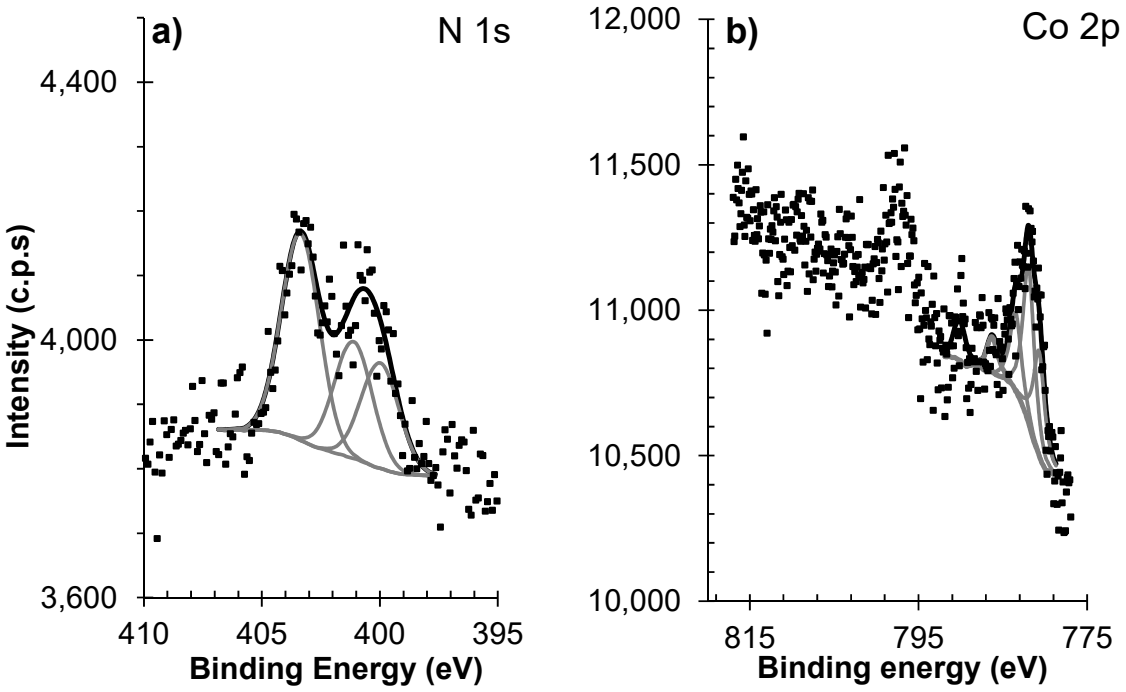

Figure S7. XPS regions **a**) N 1s and **b**) Co 2p of HOPG-crypt-Co after CV.

1. Müri, M.; Gotsmann, B.; Leroux, Y.; Trouwborst, M.; Lörtscher, E.; Riel, H.; Mayor, M. Modular functionalization of electrodes by cross-coupling reactions at their surfaces. Adv. Funct. Mater. **2011**, *21*, 3706–3714.