Supplementary information for the paper:

Switchable Mechanical DNA "Arms" Operating on Nucleic Acid Scaffolds Associated with Electrodes or Semiconductor Quantum Dots

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Experimental Section

Materials. β-Cyclodextrin, adamantane carboxylic acid, 4-carboxyphenyl boronic acid, ferrocene carboxylic acid, (N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride) (EDC), N-Hydroxysuccinimide (NHS), and adenosine monophosphate (AMP), were purchased from Sigma-Aldrich. Core/shell CdSe/ZnS quantum dots (6 nm diameter) were purchased from Evident Technologies (USA). Ultrapure water from a NANOpure Diamond (Barnstead Int., USA) source was used throughout the experiments. All oligonucleotides were purchased from Integrated DNA Technologies Inc. (USA). The following DNA sequences were used:

(**1**) 5'-NH_2-TATCAG TCATCCAACGAA-3'

(**3**) 5'-NH_2-TTGGGAACCTTCCTGGGGGAGTATTGCGGAGGAAGGTTCCCAC TAAGGCATGA

(**5**) 5'-SH-TTTTTCGTTGGATGATCATGCCTTAGT-3'

(**6**) 5'-GGGAACCTTCCTCCGCAATACACCAT-3'

(**7**) 5'-ATGGTGTATTGCGGAGGAAGGTTCCC-3'

(**8**) 5'-NH_2-TAACCTGGGGGAGTATTGCGGAGGAAGGTACTAAGG CATGA-3'

Chemical modifications and assembly of the systems. The β cyclodextrin-modified nucleic acid (**2**) was prepared by incubating the oligonucleotide (**1**), 100 μM, and 4-carboxyphenyl boronic acid, 1 mM, for 1 hour in a phosphate buffer solution, PB, (10 mM, pH=7.2) that contained 10 mM EDC/NHS, followed by the separation of the resulting boronic acid-modified sequence (**2**) using a 3 kDa Amicon filter. The boronic acid-modified (**2**) was, then, reacted with β-cyclodextrin, 1 mM, for 1 hour in PB (100 mM, pH=8.2), and the resulting product was purified using the Amicon filter.

Ferrocene-modified (**4**), or (**9**), were prepared by incubating nucleic acids (**3**) or (**8**), 100 μM, and ferrocene carboxylic acid, 1 mM, for 1 hour in a PB solution (pH=7.2) that contained 10 mM EDC/NHS, followed by the separation of the resulting product using the Amicon filter. The modified nucleic acids (**2**), (**4**), or (**9**), were hybridized for 20 minutes with the scaffold sequence (**5**), at a 1.2:1.0 ratio (in the presence of adamantane carboxylic acid, 1mM), to form the thiolated nucleic acid functional structures.

Clean Au wires were treated for 30 minutes with an aqueous solution of 3-mercaptoethanol, 2 mM. The resulting mercaptoethanol monolayer-modified Au

wires were, then, reacted with the thiolated nucleic acid functional structures for 6 hours to yield the functionalized systems on the electrodes surfaces. Prior to the experiments, the electrodes were extensively washed with a PB solution (pH=8.2, containing 0.1 M NaCl and 0.1 M KCl), to remove any remains of the adamantane molecules, until a steady and reproducible electrochemical signal appeared.

DNA-modified quantum dots were prepared according to a previously reported procedure.[1]

Instrumentation and measurements. Absorbance measurements were carried out using a Shimadzu UV-2401PC UV/Vis spectrophotometer. Emission experiments were performed using a Cary Eclipse Fluorimeter (Varian Inc.). Differential pulse voltammograms were recorded using a PC-controlled (Autolab GPES software) potentiostat (modulation amplitude: 100 mV, step potential: 10 mV). A Au wire (d=0.5 mm), a graphite rod (d=3 mm), and a saturated calomel (SCE) electrodes were used as the working, counter and reference electrodes, respectively. All measurements were performed in a 10 mM phosphate buffer (pH=8.2, containing 0.1 M NaCl and 0.1 M KCl).

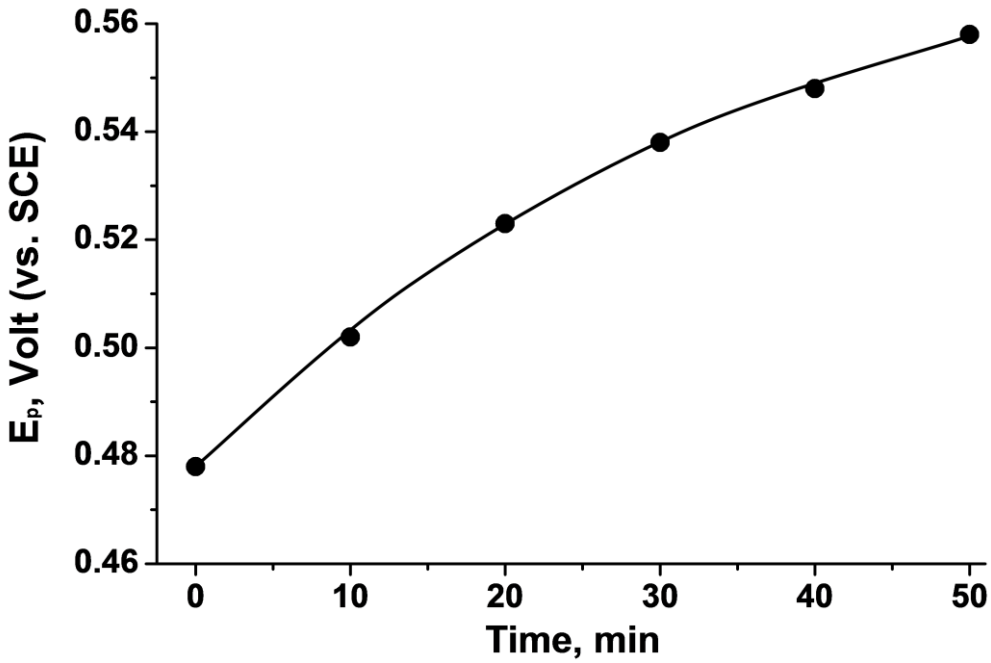

Figure S1. Time-dependent potential values corresponding to the peak amperometric responses of the Fc unit, upon the interaction of the system in State II, with the anti-fuel (**7**).

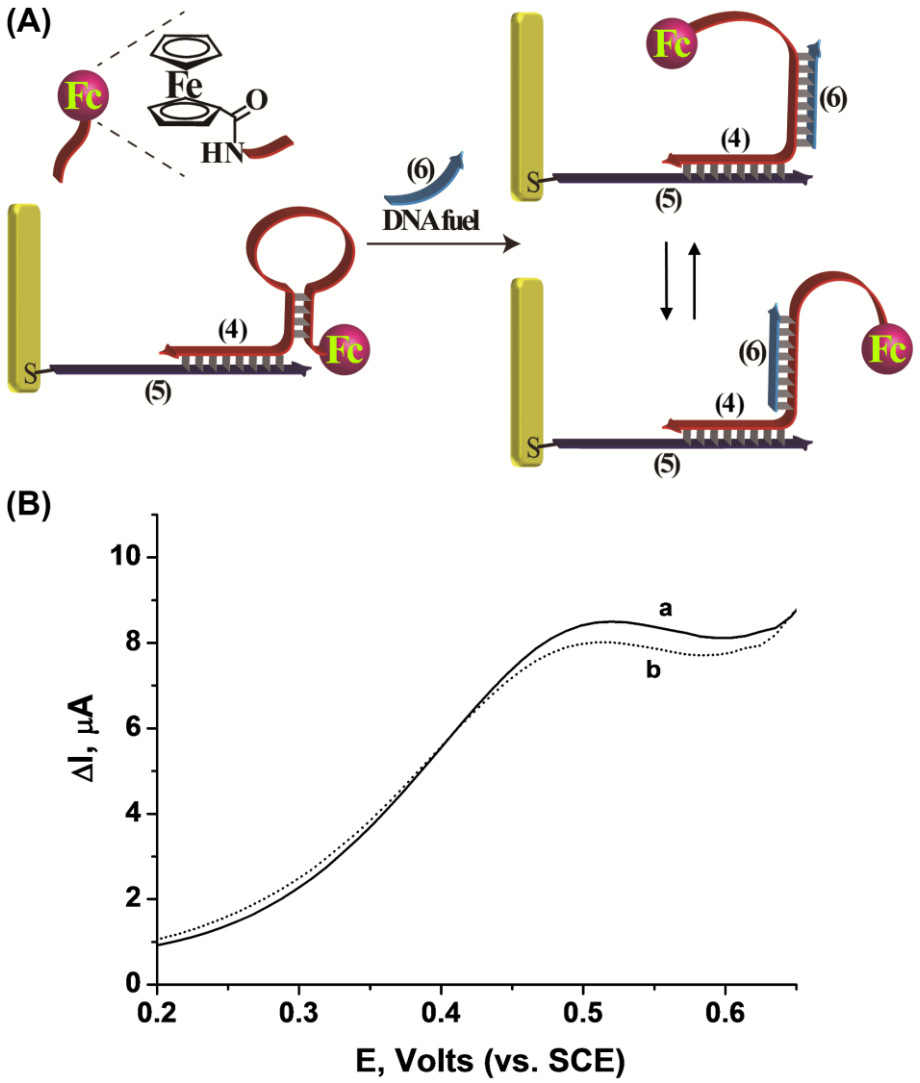

Figure S2. (A) DNA fuel (**6**)-triggered opening of a Fc-functionalized nucleic acid hairpin (**4**) hybridized to a DNA scaffold (**5**), linked to a Au electrode. (B) Differential pulse voltammograms corresponding to the system: (a) Before addition of (**6**), and (b) After incubation for 30 minutes with (**6**), 1 μM.

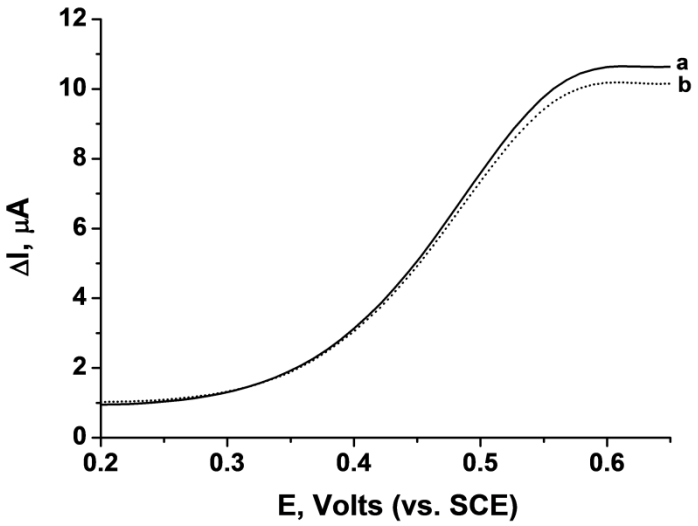

Figure S3. Differential pulse voltammograms corresponding to the AMP-triggered opening of a Fc-functionalized nucleic acid hairpin (**4**) hybridized to a DNA scaffold (**5**), linked to a Au electrode: (a) Before addition of AMP, and (b) After incubation for 30 minutes with AMP, 100 μM.

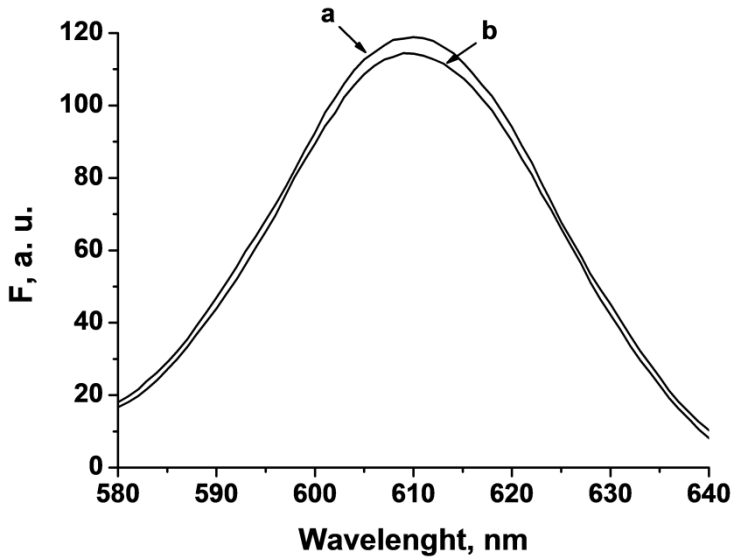

Figure S4. Emission responses corresponding to the DNA fuel (**6**)-triggered opening of a Fc-functionalized nucleic acid hairpin (**4**) hybridized to a DNA scaffold (**5**), linked to a CdSe/ZnS quantum dot: (a) Before addition of (**6**), and (b) After incubation for 20 minutes with (**6**).

References:

1. F. Patolsky, R. Gill, Y. Weizmann, T. Mokari, U. Banin, I. Willner, *J. Am. Chem. Soc.*, 2003, **125**, 13918-13919.