

Electronic Supplementary Information

# Cooperative formation of silver(I)-mediated base pairs

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## Experimental Details

The phosphoramidites of the imidazole nucleoside was prepared according to a published procedure.<sup>1</sup> All other phosphoramidites were purchased from Glen Research. The oligonucleotides were synthesized and purified as described previously.<sup>2</sup>

The desalted oligonucleotides were characterized by MALDI-TOF mass spectrometry (**I**, strand a: calcd for  $[M+H]^+$ : 7944 Da; found: 7937 Da; **I**, strand b: calcd for  $[M+H]^+$ : 7982 Da; found: 7976 Da; **II**, strand a: calcd for  $[M+H]^+$ : 7886 Da; found: 7873 Da; **II**, strand b: calcd for  $[M+H]^+$ : 7915 Da; found: 7902 Da; **III**, strand a: calcd for  $[M+H]^+$ : 7828 Da; found: 7816 Da; **III**, strand b: calcd for  $[M+H]^+$ : 7848 Da; found: 7836 Da).

The UV melting experiments were carried out on a UV spectrometer CARY 100 Bio (Varian). A 1 cm quartz cuvette was used. The UV melting profiles were measured in buffer (150 mM NaClO<sub>4</sub>, 5mM MOPS, pH 6.8) either with or without AgNO<sub>3</sub> (1 μM (**I**; **II**; **III**), 2 μM (**III**)) at a scan rate of 0.2 °C min<sup>-1</sup> with detection at 260 nm. The concentration of the duplex DNA was 1 μM.

CD spectra were measured with a J-815 Spectropolarimeter (JASCO) at 10 °C in buffer (150 mM NaClO<sub>4</sub>, 5mM MOPS, pH 6.8) either with or without AgNO<sub>3</sub> (1 μM (**I**; **II**; **III**), 2 μM (**III**)). A 1 cm quartz cuvette was used. The concentration of the duplex DNA was 1 μM.

Isothermal titration calorimetry experiments were performed with a Nano-ITC III (Calorimetry Sciences Corporation, USA). The reference cell was filled with buffer (150 mM NaClO<sub>4</sub>, 5mM MOPS, pH 6.8). All solutions were degassed for 20 min at room temperature. The AgNO<sub>3</sub> solution (1 mM) in buffer (150 mM NaClO<sub>4</sub>, 5mM MOPS, pH 6.8) was titrated in 20 injections of 5 μL (**I** and **II**) and 45 injections of 5.15 μL (**I** and **III**), respectively, to a DNA solution (0.04 mM) in buffer (150 mM NaClO<sub>4</sub>, 5mM MOPS, pH 6.8) with an interval of 300 s at 25 °C. The stirring rate was 250 rpm. The data were fitted to a 1:1 (**II** and **III** with one binding site) and 2:1 model (**III** with two binding sites), respectively, using a spread sheet method.<sup>3</sup>

1. J. Müller, D. Böhme, P. Lax, M. Morell Cerdà and M. Roitzsch, *Chem. Eur. J.*, 2005, **11**, 6246-6253.
2. D. A. Megger, C. Fonseca Guerra, J. Hoffmann, B. Brutschy, F. M. Bickelhaupt and J. Müller, *Chem. Eur. J.*, 2011, **17**, 6533-6544.
3. J. Huskens, H. Van Bekkum and J. A. Peters, *Computers Chem.*, 1995, **19**, 409-416.

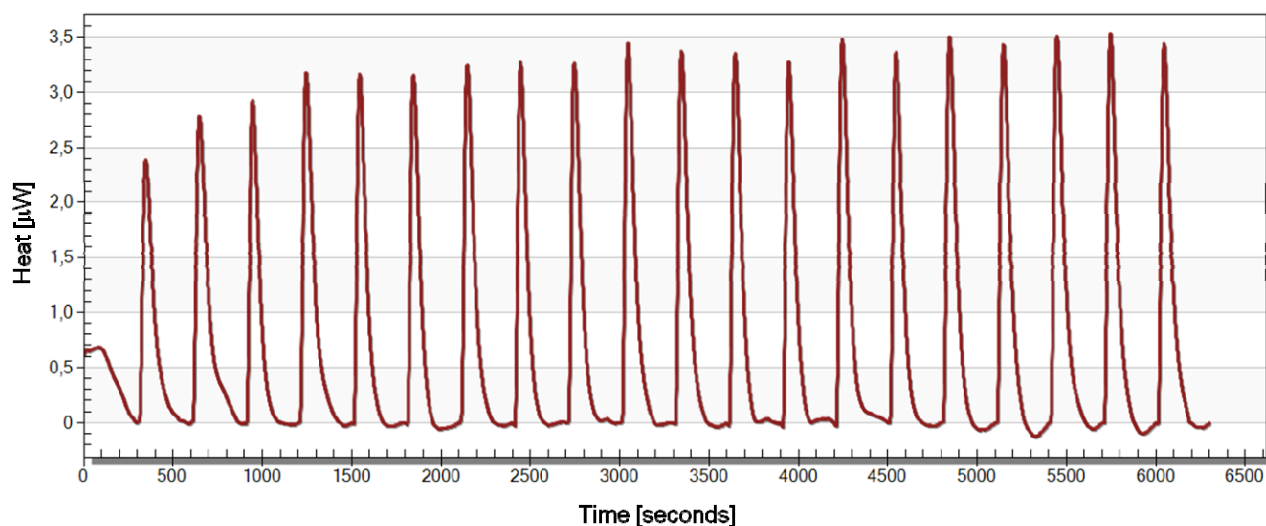


Figure S1: ITC data of titration of duplex I with 20 injections of AgNO<sub>3</sub> solution.

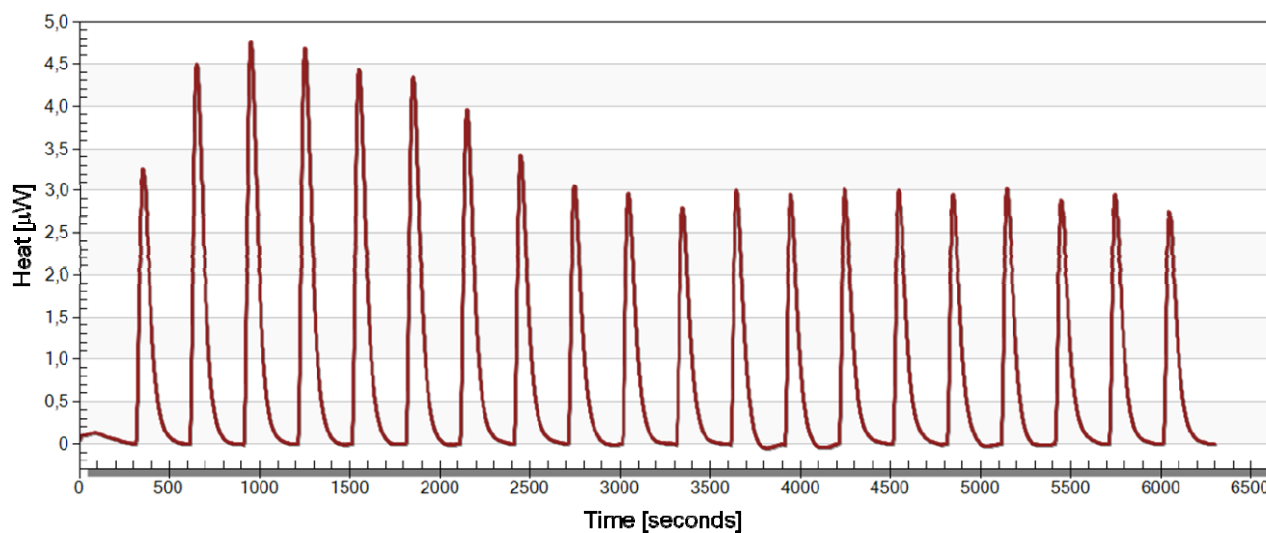


Figure S2: ITC data of titration of duplex II with 20 injections of AgNO<sub>3</sub> solution.

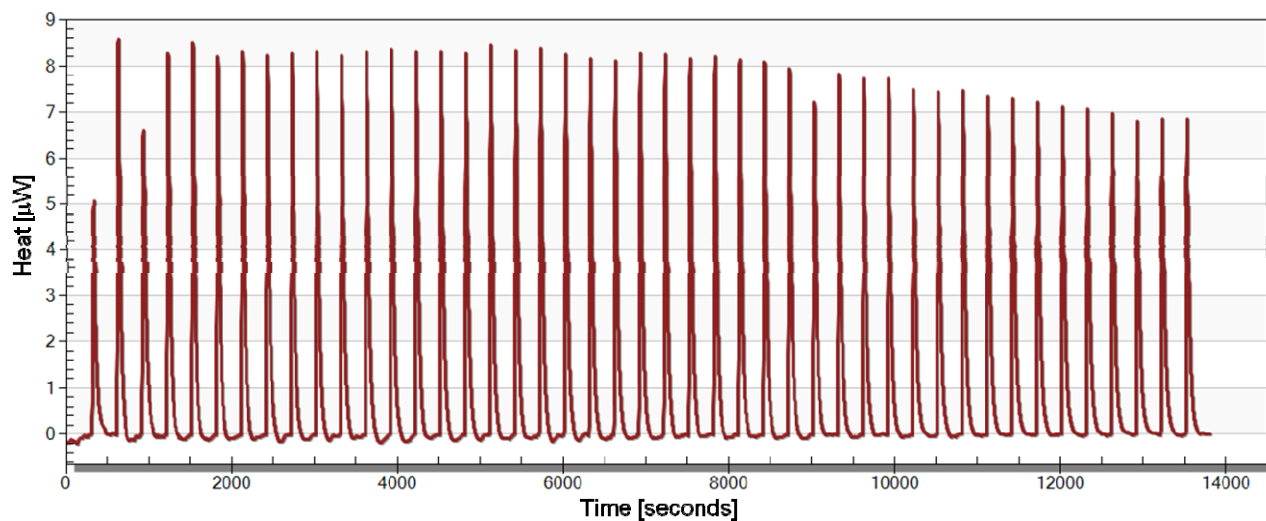


Figure S3: ITC data of titration of duplex I with 45 injections of AgNO<sub>3</sub> solution.

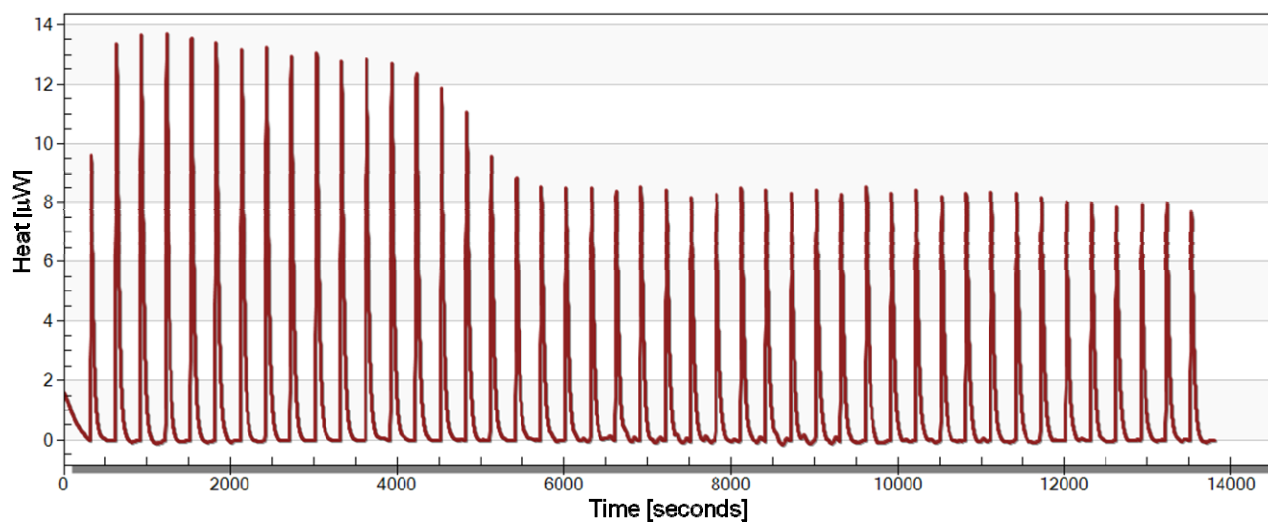


Figure S4: ITC data of titration of duplex **III** with 45 injections of  $\text{AgNO}_3$  solution.

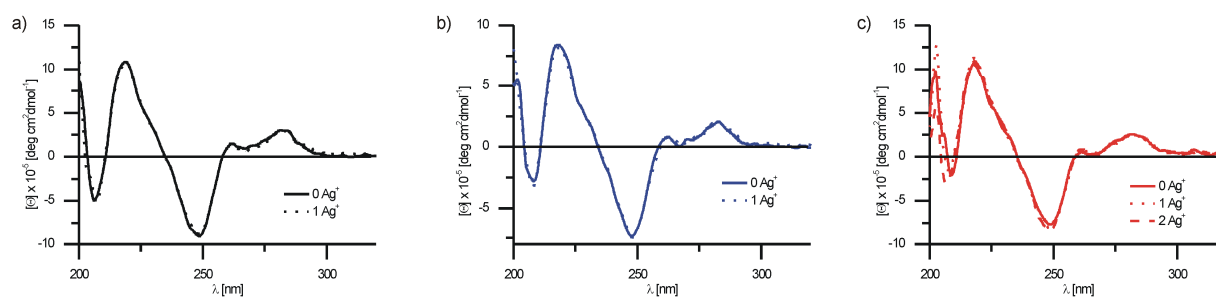


Figure S5: CD spectra of oligonucleotide duplexes **I**, **II**, and **III** in the presence of various amounts of  $\text{Ag(I)}$ .