

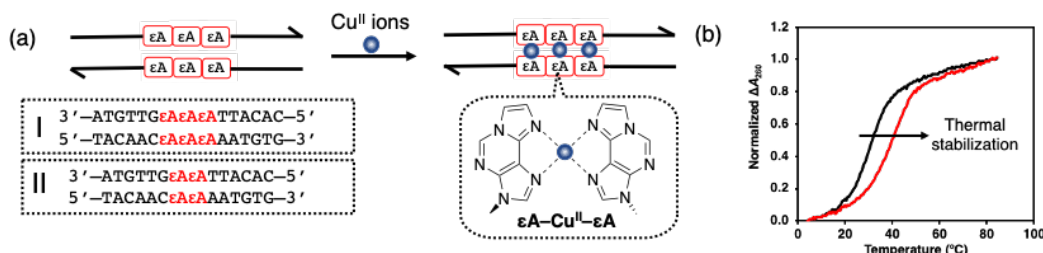
## DNA-templated assembly of Cu(II) ions using 1,*N*<sup>6</sup>-ethenoadenosine nucleobases as metal binding sites

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Functionalized molecular materials with metal centers have received a great deal of attention due to their outstanding chemical and physical properties. DNA scaffolds are utilized as template ligands for building metal arrays by precisely controlling the number and type of metal ions assembled. We have previously developed such DNA-templated metal assemblies using artificial ligand-type nucleobases such as hydroxypyridone.<sup>[1]</sup> Since fully artificial nucleobases require cumbersome synthesis, we have been exploring the potential of modified pyrimidine<sup>[2]</sup> and purine bases as metal ligands that can be easily derived from their natural analogues.

In this study, a modified purine nucleobase, 1,*N*<sup>6</sup>-ethenoadenosine ( $\epsilon$ A), was used as a metal ligand (Fig. 1a). Although  $\epsilon$ A has previously been shown to form a four-coordinate 2:1 complex with Cu<sup>II</sup> (i.e., Cu<sup>II</sup>-mediated  $\epsilon$ A–Cu<sup>II</sup>– $\epsilon$ A base pair) within the DNA duplexes,<sup>[3]</sup> metal assembly within duplexes containing the  $\epsilon$ A bases has not been achieved yet. To this end, we synthesized DNA duplexes I and II with three and two  $\epsilon$ A– $\epsilon$ A mismatch pairs, respectively (Fig. 1a). Duplex melting experiments have shown that the thermal stability of duplex I was significantly enhanced by the addition of 3 equiv of Cu<sup>II</sup> ions ( $\Delta T_m = +11.5$  °C) (Fig. 1b). ESI mass spectrometry revealed three Cu<sup>II</sup> ions were successfully bound to duplex I (found: 1898.87 ( $z = 5$ ); calcd for  $[I + 3\text{Cu}^{II} - 11\text{H}^+]^{5-}$ : 1898.35). These results suggest that three consecutive  $\epsilon$ A–Cu<sup>II</sup>– $\epsilon$ A base pairs are formed within the duplex. Similarly, it was observed that two Cu<sup>II</sup> ions were successfully assembled in the duplex II as seen in the results of ESI-MS spectrometry (found :1751.47 ( $z = 5$ ); calcd for  $[II + 2\text{Cu}^{II} - 9\text{H}^+]^{5-}$ : 1751.15). These findings raise the possibility that the number of Cu<sup>II</sup> ions assembled can be controlled by varying the number of  $\epsilon$ A– $\epsilon$ A mismatch base pairs. Therefore, DNA duplexes containing  $\epsilon$ A nucleobases would serve as versatile template ligands for constructing Cu<sup>II</sup> arrays in a highly programmable manner.



**Figure 1.** (a) DNA-templated Cu<sup>II</sup> self-assembly using 1,*N*<sup>6</sup>-ethenoadenosine as metal ligands. (b) Melting profiles in the absence (black) and presence of 3 equiv of Cu<sup>II</sup> ions (red). [duplex] = 2.0  $\mu$ M, [Cu<sup>II</sup>] = 0, 6.0  $\mu$ M in 10 mM HEPES buffer (pH 7.0), 100 mM NaCl, 0.2 °C/ min.

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