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Crystal structure of metallo-DNA duplex containing T-Hg(II)-T base pairs

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The DNA duplex containing mercury-mediated base pairs (T-Hg(II)-T) is an attractive biomacromolecular nanomaterials. In a recent study, it was confirmed that the Hg(II) ion significantly stabilizes a DNA duplex by binding selectively to a T-T mispair [1]. Based on the phenomenon observed, a DNA-based sensing system that selectively and sensitively detects Hg(II) ions in aqueous solution was developed [2]. In the present study, we have solved the first crystal structure of a B-form DNA duplex containing two consecutive T-Hg(II)-T base pairs [3]. The Hg(II) ion occupies the center between two T residues. The geometry of the T-Hg(II)-T base pair is very similar to that of the canonical Watson-Crick base pairs. The distance of N3-Hg(II) bond is 2.0 Å, suggesting that the N3 nitrogen releases an imino-proton even at neutral pH (pKa of N3 position of T is 9.8) and directly bonds to Hg(II). In the B-form DNA, the helical axis runs through the center of base pairs, and the Hg(II) ions are therefore aligned along the helical axis. The distance between the two neighboring Hg(II) ions is 3.3 Å. The relatively short Hg(II)-Hg(II) distance indicates that the metallophilic attraction could exit between them and may stabilize the B-form duplex. To support this, the DNA duplex is largely distorted and adopts an unusual non-helical conformation in the absence of Hg(II). In conclusion, the Hg(II) ion is essential for maintaining the B-form conformation of the DNA duplex containing T-T mispairs. The structure of the Hg(II)-DNA hybrid duplex itself and the Hg(II)-induced structural switching from the non-helical form to the B-form provide the basis for the structure-based design of metal-conjugated nucleic acid nanomaterials.

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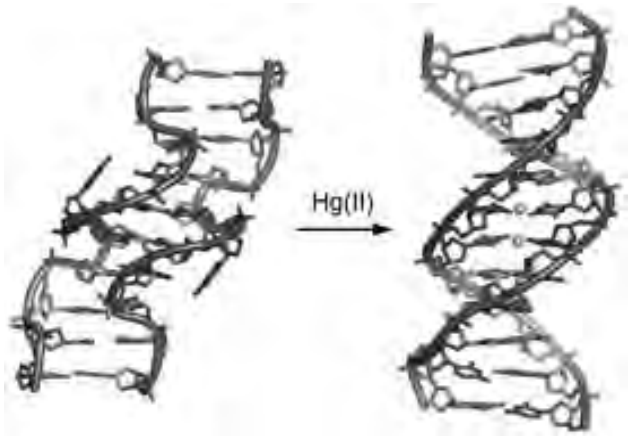

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