

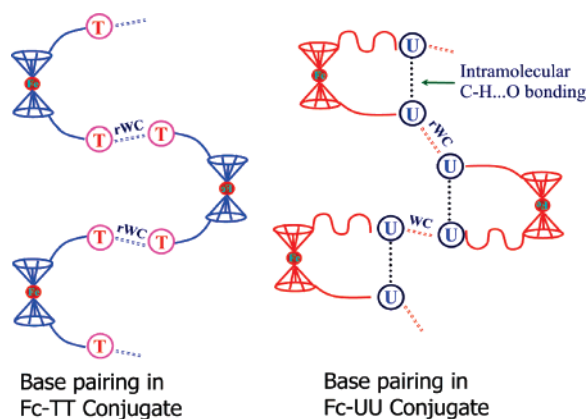
Ferrocene-Linked Thymine/Uracil Conjugates: Base Pairing Directed Self-Assembly and Supramolecular Packing

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Ferrocene-linked bis(nucleobase) (**1a–c**) and chimeric nucleobase (**1d**) conjugates have been synthesized from mono- and bis(hydroxybutyl)ferrocene **6** via Mitsunobu reaction as the key step. X-ray crystallographic studies of ferrocene bis(nucleobase) conjugates reveal two-dimensional supramolecular organizations of backbones through self-assembled Watson–Crick and reverse Watson–Crick type pairs. Ferrocene–bis(thymine) conjugate self-assembles by reverse Watson–Crick pairing, while the corresponding bis(uracil) conjugate self-assembles by alternating WC and reverse WC type pairing. Such continuous assemblies are not seen in monosubstituted ferrocene nucleobase conjugates which form only planar sheets. The results are interesting from the point of understanding and engineering supramolecular assemblies through rational design of base pairing patterns.

Development of supramolecular assemblies into well-defined architecture has been a subject of great interest in recent years in view of both its importance in the synthesis of artificial models for natural processes and its significance to obtain insight into the conformational features of biomolecules such as proteins, lipids, and nucleic acids.¹ A system of evolutionary perfection for molecular self-assembly is DNA/RNA.² The two antiparallel strands of DNA are held together by A:T and C:G base pairs to form the double helix where hydrogen bonding

between complementary bases and π -stacking interactions between the adjacent and stacked base pairs stabilize the double helical architecture.² Given the four natural nucleobases A, G, C, and T/U, at least 28 types of base pair modes are possible involving all combinations of self-base pairing and complementary base pairing through the diverse hydrogen bond donor–acceptor sites.² However, nature prefers only two types in the form of the canonical Watson–Crick (WC) and Hoogsteen (HG) complementary base pairing in most DNA/RNA structures. Hydrogen bond mediated supramolecular interactions have

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