

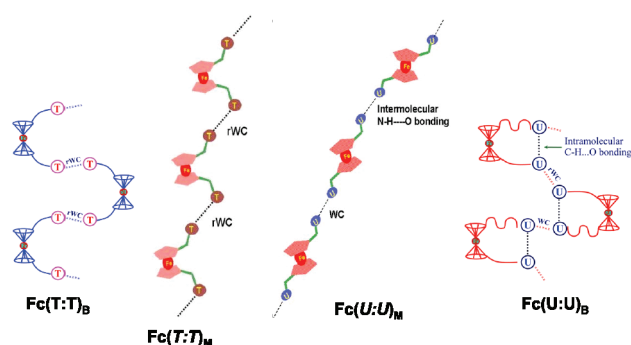
Ferrocene–Bis(thymine/uracil) Conjugates: Base Pairing Directed, Spacer Dependent Self-Assembly and Supramolecular Packing

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Base pairing Fc-(Thymine/Uracyl) conjugates with different spacer chain

X-ray crystallographic studies of methylene linked Ferrocene-bis(thymine/uracil) conjugates $Fc(T:T)_M$ and $Fc(U:U)_M$ reveal base dependent 2-D supramolecular assemblies generated via wobble self-pairing for bis-thymine and reverse wobble self-pairing for bis-uracil conjugates, differing in architecture from the corresponding butylene spacer linked conjugates

Development of supramolecular assemblies¹ into well-defined architectures has been a subject of great interest in recent years in view of its importance in understanding principles of molecular recognition and the associated structural features of biomolecules such as proteins, lipids, and nucleic acids that are important for self-organization. A system of evolutionary perfection for molecular self-assembly is DNA/RNA.² The hydrogen bond mediated supramolecular interactions found in nucleic acids have provided inspiration to design a number of

novel self-assembling systems.^{3,4} In recent years, bio-organometallic chemistry has grown rapidly, networking the classical organometallic chemistry to biology and molecular biotechnology.^{3,5} The redox active ferrocene unit linked to self-base pairing nucleobases⁶ or DNA/RNA could be a useful building block in supramolecular chemistry. When coupled to molecular recognition and electrochemistry, this may lead to electrochemical recognition of DNA/RNA binding substrates.⁵ Recently we have reported⁷ a study on ferrocenyl mono- and bis(thymine/uracil) conjugates with an *n*-butyl spacer [$Fc(T:T)_B$, $Fc(U:U)_B$] whose crystal structures exhibited base pair induced self-assembly leading to novel supramolecular packing. The structure of $Fc(U:U)_B$ is perhaps the first example wherein both wobble and reverse wobble self-pairings are simultaneously present within the same crystal lattice. The 5-substituent (H, Me, Br) on the pyrimidine base seems to sterically influence the supramolecular packing by inhibiting specific intermolecular C–H···O contacts as seen in the structure of $Fe(5-BrU:5-BrU)_B$ and the chimeric $Fe(T:U)_B$. The base pairing directed contiguous self-assemblies are seen only in bis substituted ferrocene conjugates and as expected are absent in mono T/U substituted ferrocene conjugates. Ferrocene type scaffolds have also utility in inducing chain reversal⁸ in peptides.

The same butyl (C4) spacer chain induced different packing in the two conjugates, and in $Fc(U:U)_B$ even the two spacers in the same molecule have different conformations. In order to examine the role of spacer chain in directing the base pairing and molecular packing, herein we present synthesis and studies on self-assembling properties of ferrocenyl bis-thymine and bis-uracil conjugates (**5a–b**) having a C1 methylene spacer [$Fe(T:T)_M$ and $Fe(U:U)_M$] (Figure 1), which was chosen because of ease of synthesis. It is seen that the replacement of C4 butyl chain spacer with C1 methylene spacer still results in self-pairing but has different consequences in T and U conjugates in directing the self-assembly and molecular packing in crystals.

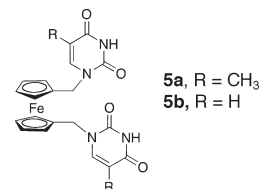


FIGURE 1. Ferrocene linked thymine/uracil conjugates with methylene spacer **5a** $Fe(T:T)_M$ and **5b** $Fe(U:U)_M$.

1,1'-Ferrocene dicarbaldehyde **2** (Scheme 1) was synthesized from ferrocene **1** in good yield by treating the dilithioferrocene–TMEDA complex with dimethylformamide (DMF).⁹

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