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

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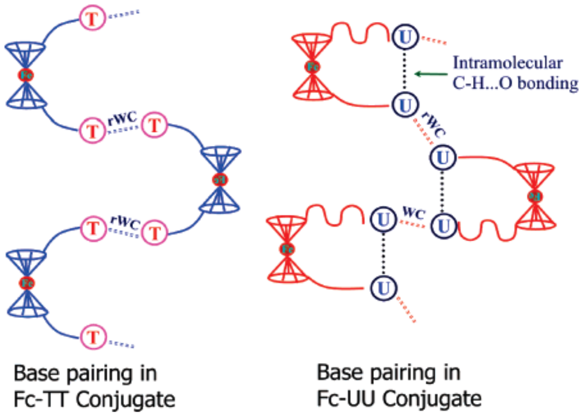

Ferrocene-linked bis(nucleobase) (**1a**−**c**) and chimeric nucleobase (**1d**) conjugates have been synthesized from mono- and bis(hydroxybutyl)ferrocene **6** via Mitsunobu reaction as the key step. X-ray crystallographic studies of ferrocene bis(nucleobase) conjugates reveal two-dimensional supramolecular 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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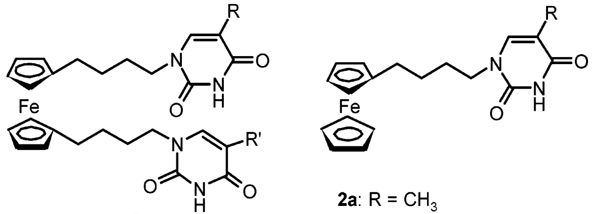
provided inspiration to design a number of novel self-assembling systems.[3] Incorporation of the common nucleobases A, G, C, and T (or U) in the supramolecular environment enables exploration of different pairing characteristics of these nucleobases.[4] Guanine derivative self-assembles through Hoogsteen interaction into either linear tapes or macrocycles.[5] Self-pairing of adenine[6] as well as the 1-dimensional i-motif from C:C$^+$ base pairing via non-Watson−Crick base pairing in DNA[7] and PNA[8] have been reported. In view of these findings, there has been a great interest in developing novel approaches to self-assembled superstructures directed by nucleobase pairing in systems where the sugar−phosphate backbone is modified or replaced by synthetic linkers.[9] Studies of such designed systems are unraveling the importance of non-canonical, unusual modes of base pairing of the nucleobases, which have been recently detected in abundance in continuous 3-dimesional DNA lattice[10] and in DNA complexes having interstrand crosses.[11] Thus the study of unusual base pairings in nucleic acids and their model systems assumes new significance.

Currently bioorganometallic chemistry is growing rapidly, networking classical organometallic chemistry to biology, medicine, and molecular biotechnology.[12−15] Ferrocene and its derivatives have received a lot of importance in molecular recognition research, due to their redox characteristics.[3,15,16] Synthesis and self-association motifs of ferrocene-linked mono-(nucleobase) conjugates with a single carbon methylene spacer have been reported by Houlton's group.[17] An attractive feature of ferrocene is that the two cyclopentadienyl (Cp) rings can rotate around the Fe atom, which can act as a ball bearing,[17] and the vertical distance between the two Cp rings in fererocene is 0.35 nm, which is similar to the distance between the stacked base pairs in DNA.[2,18] The redox active ferrocene units linked to self-base pairing nucleobases or DNA/RNA with a designed spacer could therefore be useful building blocks in supramolecular chemistry coupling molecular recognition with electrochemistry, leading to novel applications for the electrochemical recognition of a large variety of DNA/RNA binding substrates.



1a: R = R' = CH_3
1b: R = R' = H
1c: R = R' = Br
1d: R = H, R' = CH_3

2a: R = CH_3
2b: R = H

FIGURE 1. Structures of **1a**−**d** and **2a**,**b**.

In this paper, we report the construction of a series of new ferrocene-linked bisconjugates 1,1′-bis(*N*1-butylthymine) **1a**, 1,1′-bis(*N*1-butyluracil) **1b**, 1,1′-bis(*N*1-butyl-5-bromouracil) **1c**, and the chimeric 1-(*N*1-butyluracil)-1′-(*N*1-butylthymine) **1d** derivatives, in addition to the monoconjugates 1-(4-(thyminyl)-butyl)ferrocene **2a** and 1-(4-(uracilyl)butyl)ferrocene **2b** (Figure 1). X-ray crystallographic analyses of these ferrocene−nucleobase conjugates reveal highly ordered and self-assembled structures arising from self-pairing of nucleobases in contiguous helical backbones via Watson−Crick (WC) and reverse Watson−Crick (rWC) type base pairings, leading to nucleobase-dependent differential supramolecular packing.

We chose a simple *n*-alkyl spacer to connect ferrocene with the nucleobases T and U and the *n*-butyl chain provided the appropriate hydrophobicity to enhance the solubility of the ferrocene-linked bis(nucleobase) conjugates in common organic solvents. The synthetic route for the bis(nucleobase) ferrocene target compounds involved the key intermediate 1,1′-bis(4-hydroxybutyl)ferrocene **6**[19] while the mono(nucleobase) ferrocene was synthesized from 1-(4-hydroxybutyl)ferrocene **11**. Compounds **6** and **11** were obtained from ferrocene, by reacting with either 1 or 2 equiv of succinic anhydride under Friedel Craft reaction conditions followed by Zn/Hg reduction of carbonyl group and LAH reduction of the carboxylic acid to the corresponding alcohol, which was reacted with N3-protected T/U/5-BrU, under Mitsunobu reaction conditions, to yield **7a**−**c** and **12a**,**b**. This was followed by N3-debenzoylation with aq K_2CO_3 in methanol−toluene or LiOH in THF−methanol to afford the target compounds **1a**−**c** and **2a**,**b** (Scheme 1). Compound **16** was synthesized from **6** in four steps involving protection of one hydroxyl with the TBDMS group to desymmetrize the molecule, Mitsunobu reaction of the second hydroxyl with *N*3-benzoylthymine, desilylation with TBAF, and reaction of the resulting hydroxyl with *N*3-benzoyluracil under Mitsunobu condition, followed by debenzoylation to obtain the chimeric mixed base ferrocene derivative **1d** (Scheme 2).

The crystal structures of **1a**−**d** were determined by single-crystal X-ray diffraction analysis (Supporting Information). The bis(thyminyl) ferrocene compound **1a** occupies crystallographic 2-fold symmetry axis passing through the central Fe atom of the ferrocene moiety with the *n*-butyl chains in the extended

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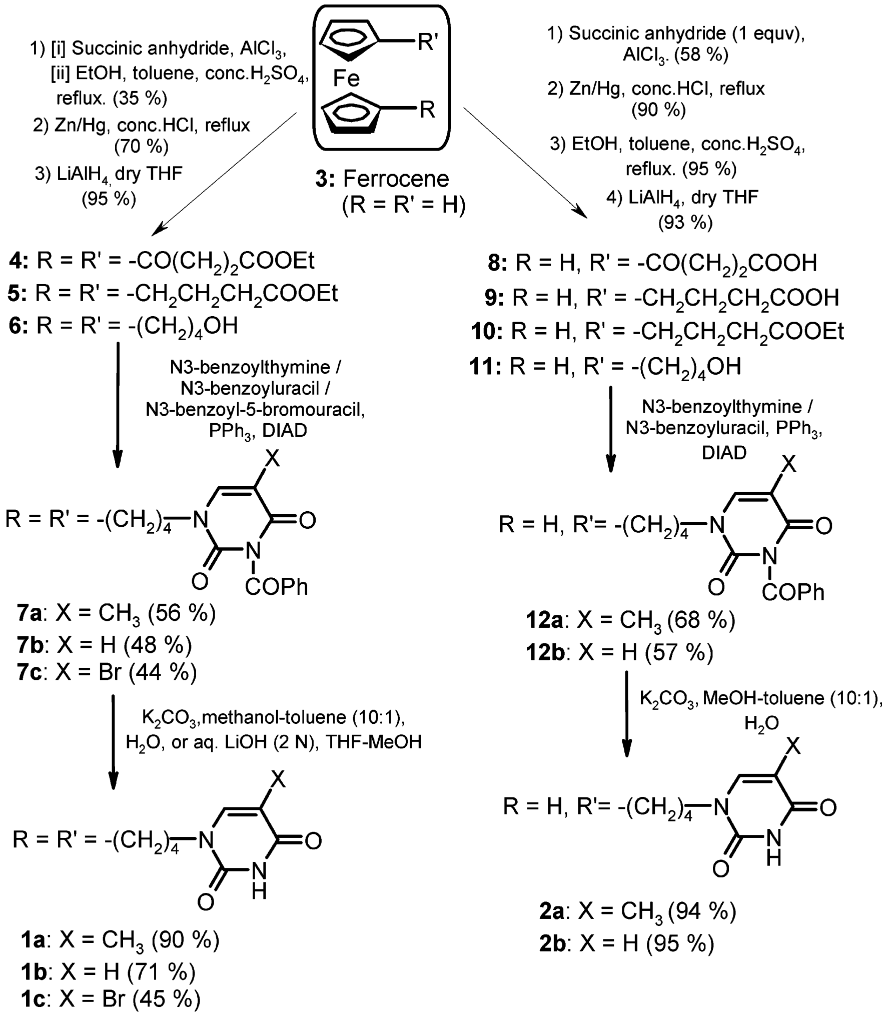
SCHEME 1. Synthesis of Compounds 1a−c and 2a,b[a]



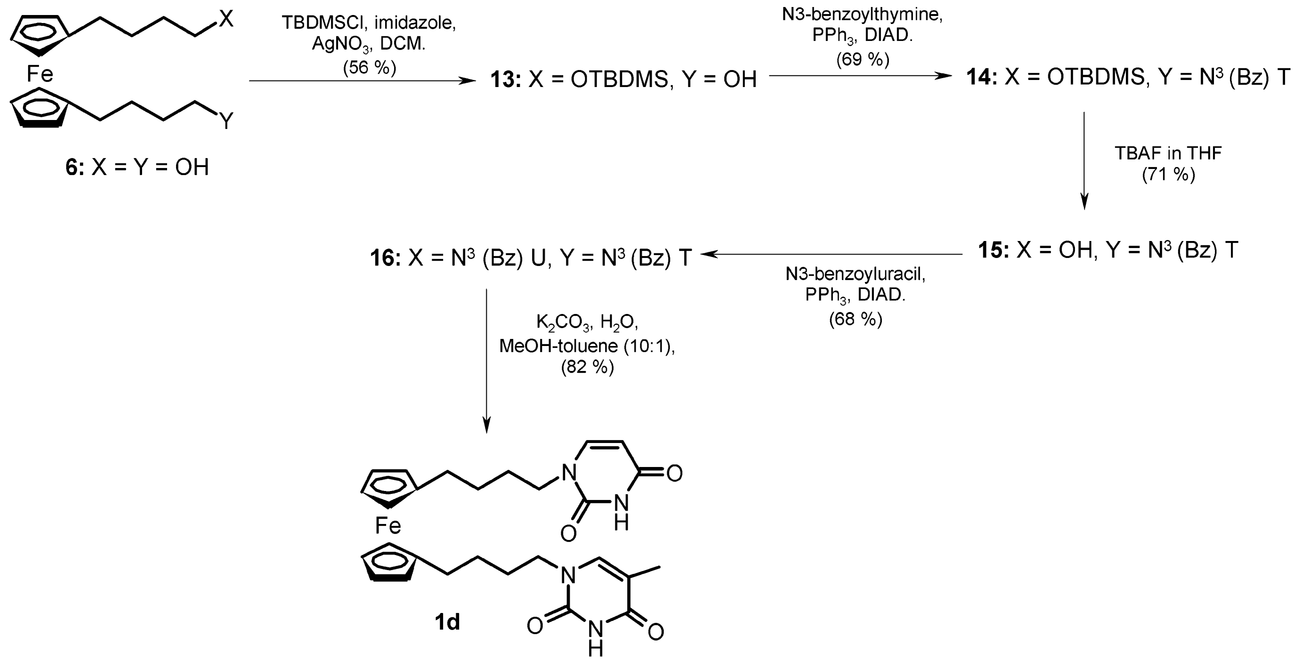
[a] Values in parentheses in each step indicate yields. For details see the experimental procedures.

conformation. A contiguous centrosymmetric, self-base pairing was seen via two N3−H3···O2 hydrogen bonds (H3···O2 = 2.14(3) Å, N3···O2 = 2.913(3) Å, and N3−H3···O2 = 169-(3)°), constituting "reverse Watson−Crick" (rWC defined as pairing involving O2 of T/U) type pairing (Figure 2A).[2,15,17] This self-pairing motif seems to be a dominant synthon in the self-assembly process during crystallization that leads to a regular helical backbone (Figure 2B). The bis-substituents linked to the Cp rings of ferrocene are staggered by ~67 ° around the ferrocene ring, with the methyl groups attached to the C5 atom of thymine bases pointing away from each other (Figure 3A).

Self-Assembly in Bis(ferrocene) Conjugates. The structure of bis(uracil) conjugate **1b** (Figure 2C) was devoid of 2-fold symmetry, with one of the *n*-butyl chains adopting an extended conformation and the other chain in the folded state. The U of the folded chain exhibited WC type self-pairing through O4 rather than O2 and making N3′−H3′···O4′ interaction with U on the folded chain of the next molecule. Interestigly, the U on the extended chain formed a rWC type pairing with the U of the extended chian of the neighboring molecule via N3−H3···O2 hydrogen bond, in comparison to the WC type base pairing of U in the folded chains. This contiguous, alternating WC and rWC pairing motif formed the synthon of the bis(uracil) ferrocene helical backbone. The folded spacer chain conformation leads to additional intramolecular C6−H6···O2′ interaction, which is absent in **1a** and results in relatively eclipsed orientation (~19°) of the two spacer chains in **1b** (Figure 3B).

The presence of the 5-methyl group in **1a** seems to sterically preclude the intermolecular (C5−H5•O4′) and intramolecular (C6−H6•O2′) interactions seen in **1b**, which perhaps leads to two different base pairings in the helical assembly of **1b**. To examine this, the 5-methyl in **1a** was replaced by 5-bromo in **1c**, whose crystal structure was found to be almost identical with that of **1a** (Supporting Information), reiterating the steric role of the 5-substituent in preventing the additional interactions seen in U:U pairings. Additionlly, we also examined the crystal structure of the chimeric conjugate **1d**, in which one of the chains carried a thyminyl residue and the other a uracil moiety. Remarkably, the structure of **1d** was isomorphous to that of **1a**. The chimeric **1d**, which chemically lacks a 2-fold symmetry, acquired it in crystal structure by statistically distributing itself over two equally occupied orientations with the methyl group C7 having only half the occupancy (Supporting Information). Unlike **1b** that had alternate WC and rWC type pairings, compound **1d** exhibited only rWC type hydrogen bonding, inspite of having U:U base pairs as in analogous **1b**. There can be four possibilities of base pairings in **1d**, namely T:T, U:U, T:U, and U:T, but the observed structure corresponded to an average base pairing of $^1/_2$(T+U)···$^1/_2$(T+U).

SCHEME 2. Synthesis Of compound 1d[a]



[a] Values in parentheses in each step indicate yields.

The accurate geometries of the T:T, U:U, and T:U base pairings are of considerable structural interest because of their presence in nucleic acids.[2,20] Very interestingly, the bis(uracil) derivative **1b** shows two different types of U:U base pairings in the same crystal form: a centrosymmetric rWC type with two N3−H3⋯O2 intermolecular contacts (H3⋯N2 = 2.13(3) Å, N3⋯O2 = 2.915(4) Å, and N3−H3⋯O2 = 176(3)°) as in **1a**/**1c**/**1d** and the other being centrosymmetric WC type pairing through two N3′−H3′⋯O4′ H-bonds (H3′⋯O4′ = 2.05(3) Å, N3′⋯O4′ = 2.845(4) Å, and N3′−H3′⋯O4′ = 169(3)° (Figure 2C). O4′ participating in WC motif is involved in bifurcated hydrogen bonding via C5−H5⋯O4′ interactions (H5⋯O4′ = 2.41 Å, C5⋯O4′ = 3.265(4) Å, and C5−H5⋯O4′ = 152°). A weak C−H⋯O interaction of C5−H5 in uracil, possibly due to the absence of the methyl group, seems to cause a bending of one of the side chains in bis(uracil) **1b** causing additional helical twist.

Sheets of infinite one-dimensional chains, self-assembled via base pairings, are shown (Figure 4). In **1a**, a regular helix with a pitch of ∼20.33 Å has its bases almost perpendicular to the helical axis with no significant interhelical interactions in the sheet (Figure 4A). However, there are various C−H⋯O interactions made by a perpendicular interpenetrated sheet (Supporting Information). The planar sheet in **1b** with each helix having two types of U:U pairings almost in the plane of the sheet makes one C15−H15⋯O4 interhelical adhesion in this planar arrangement (Figure 4B) with a lower helical pitch of ∼17.9 Å. **1a**/**1c**/**1d** show a single string of a regular helix (Figure 2B) while in **1b**, the helix is of "zigzag" type (Figure 2D); the absence of C5-methyl in **1b** provides possibilities for additional

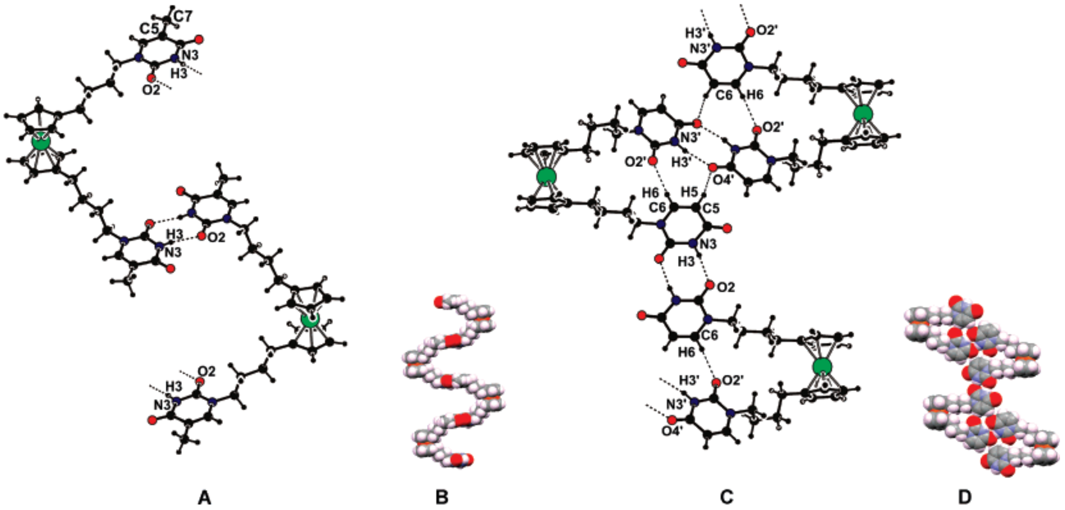


FIGURE 2. T.T and U.U self-base pairing in **1a** (A) and **1b** (C). Molecule **1b** makes an intramolecular C6−H6⋯O2′ contact. The inlay shows the CPK model of a single helical strand for **1a** (B) and **1b** (D).

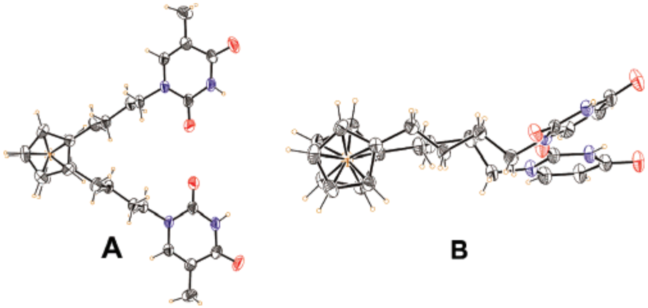


FIGURE 3. ORTEP of **1a** (A) and **1b** (B) viewed perpendicular to Cp rings.

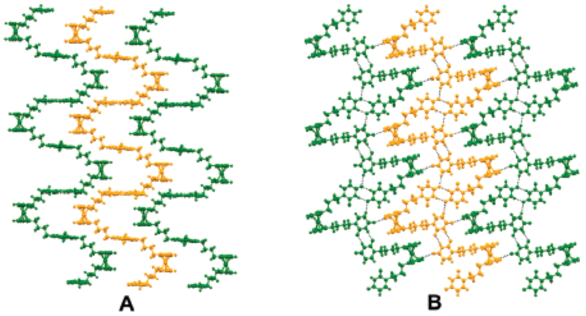


FIGURE 4. A sheet of chain assemblies showing differences in architecture in **1a** (A) and **1b** (B).

interactions. Although coordination-induced self-assembly of helical chains is well-known, this is a novel example where self-base pairing present within the backbone leads to helical assemblies. The slightly different geometries of T:T and U:U base pairs lead to variations in interchain contacts causing different supramolecular structures.

Self-Assembly in Monosubstituted Ferrocene Conjugates. Crystal structures of mono(thyminyl) ferrocene **2a** and mono(uracilyl) ferrocene **2b** were also determined by single-crystal X-ray diffraction method. Both the compounds are almost isostructural. Notably, molecules in both **2a** and **2b** form dimeric centrosymmetric self-base pairing of WC type via N3−H3···O4 (H3···O2 = 2.14(3) Å, N3···O2 = 2.847(3) Å, and N3−H3···O2 = 173(3)°) for **2a** and (H3···O2 = 2.02 Å, N3···O2 = 2.878(4) Å, and N3−H3···O2 = 173°) for **2b** hydrogen bond (Figure 5). These dimeric base pairs in **2a** and **2b** are held together with various C−H···O and C−H···π interactions forming planer sheet unlike **1a** and **1b** where molecules form helical assembly (Figure 6). The methyl group at C5 in **2a** did not make much effect in molecular packing. In **2b**, the side chain is in the extended form involved in WC type base pairing while in the corresponding bisconjugate **1b**, the WC type base pairing is observed with the side chain in folded form. The T:T and U:U base pairing seen in monosubstituted *n*-butyl spacer ferrocene conjugates is similar to that seen earlier in the mono(cytosinyl) ferrocene conjugates with methylene spacer chain.

In conclusion, the newly designed ferrocene-linked mono- and bis(nucleobase) conjugates show different supramolecular assemblies mediated via centrosymmetric base pairings (T:T, BrU:BrU, T:U) of rWC type and U:U pairings of both WC and rWC types. The structure of ferrocene−bis(uracil) **1b** is perhaps the first example of WC and rWC like pairings being simultaneously present within the same crystal lattice. The comparison of structures clearly delineates the steric role of the 5-substituent in influencing the supramolecular packing by inhibiting specific inter- and intramolecular C−H···O contacts. The base pairing-directed self-assemblies are seen only in bis-substituted ferrocene conjugates and this topology is influenced by the C5 substituents. The self-assembly occurs through the use of all available hydrogen-bonding donors in the solid state. Such self-assembling organometallic units have utility in inducing chain reversal[21] and in building supramolecular scaffolds. Studies on different possible analogous base:base interactions in the ferrocene-linked complementary nucleobase (A:T/C:G) conjugates with different spacer chains including introduction of conjugation and their electrochemical studies are underway.

Experimental Section

1,1′-Bis(3-carbethoxypropionyl)ferrocene (4).[19] (A) A mixture of anhydrous aluminum chloride (96 g, 0.72 mol) in 200 mL of methylene chloride was treated with succinic anhydride (36 g, 0.36 mol). The mixture was stirred and shaken a few minutes and a solution of ferrocene **3** (33.3 g, 0.18 mol) in 200 mL of methylene chloride was added in small portions over a 10-min period. Hydrogen chloride gas was evolved and the heat of reaction brought the mixture to 35 °C. The dark violet viscous solution was allowed to stand 7 h at room temperature, poured onto ice, and filtered. The air-dried solid (yield 46 g) was extracted once with 800 mL of boiling water and twice with 150 mL of boiling water. The combined extract was cooled in an ice bath and filtered to obtain 19.7 g (38% yield) of crystalline 1,1′-bis(3-carboxypropionyl)-ferrocene, mp 164−166 °C dec. (B) The above diacid was converted to the corresponding diethyl ester by slowly distilling a solution of the acid (21.3 g, 0.055 mol), sulfutic acid (1.5 g, 0.015 mol), ethyl alcohol (200 mL), and toluene (250 mL) through a small still. After slow distillation for 4 h, the remaining solution was cooled to room temperature and washed with 10% aqueous sodium carbonate solution (75 mL). The toluene solution was dried over magnesium sulfate, filtered, and evaporated at room temperature to obtained 23 g (94%) of red brown crystals of **4**, which were recrystalize from ethyl alcohol as shiny orange-brown platelets, mp 134−136 °C (ethyl alcohol). Yield 35% (combine two steps). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.27 (t, 6H, $J = 7.1$ Hz), 2.67 (t, 4H, $J = 6.2$ Hz), 3.01 (t, 4H, $J = 6.0$ Hz), 4.18 (q, 4H, $J = 7.1$ Hz), 4.57 (2, 4H), 4.87 (s, 4H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 14.0, 27.5, 34.2, 60.3, 70.4, 73.5, 79.7, 172.7, 201.1. MS (LC-MS) (*m*/*z*) calcd for $C_{22}H_{26}O_6Fe$ 442.28 [M^+], found 443.36 [$M^+ + 1$], 465.42 [$M^+ +$ Na]. Anal. Calcd for $C_{22}H_{26}O_6Fe$: C, 59.73; H, 5.92. Found: C, 60.1; H, 5.81.

1,1′-Bis(3-carbethoxypropyl)ferrocene (5). To zinc amalgam (5.0 g) in water (3.0 mL), conc HCl (7.0 mL), benzene (5.0 mL), and ethanol (4.0 mL) is added **4** (2.5 g, 5.65 mmol). The mixture was refluxed briskly for 24−30 h, during which time conc HCl (2.5 mL) was added every 6 h. The solution was cooled to room temperature; the aqueous layer was separated, diluted with water (5.0 mL), and extracted with ether (3 × 3.0 mL). The combined ether and benzene solutions are washed with water and dried over calcium chloride. The solvents are removed by distillation under diminished pressure, and the residue is purified by column chromatography on silica gel, and eluted with petroleum ether/ethyl acetate (8:2) to give **5** as reddish yellow oil. Yield 70%. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.24 (t, 6H, $J = 7.0$ Hz), 1.71−1.85 (m, 4H), 2.26−2.33 (m, 8H), 4.02 (s, 8H), 4.13 (q, 4H, $J = 7.0$ Hz). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 14.2, 26.3, 28.8, 33.9, 60.1, 68.1, 68.8, 88.2, 173.4. MS (LC-MS) (*m*/*z*) calcd for $C_{22}H_{30}O_4Fe$ 414.32 [M^+],

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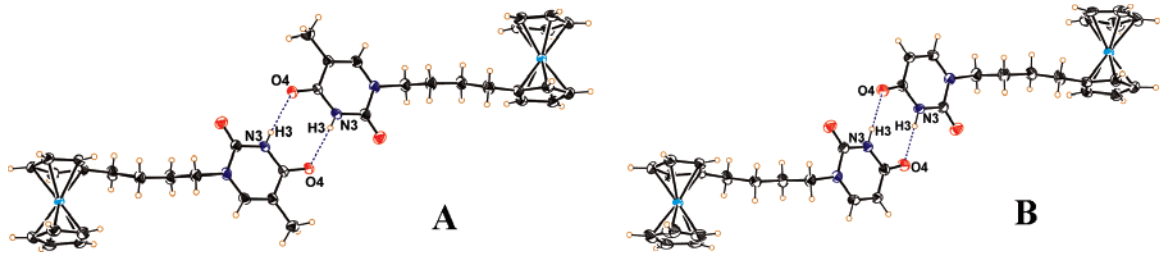

FIGURE 5. Self-base pairing in monosubstituted ferrocene conjugates **2a** (A) and **2b** (B).

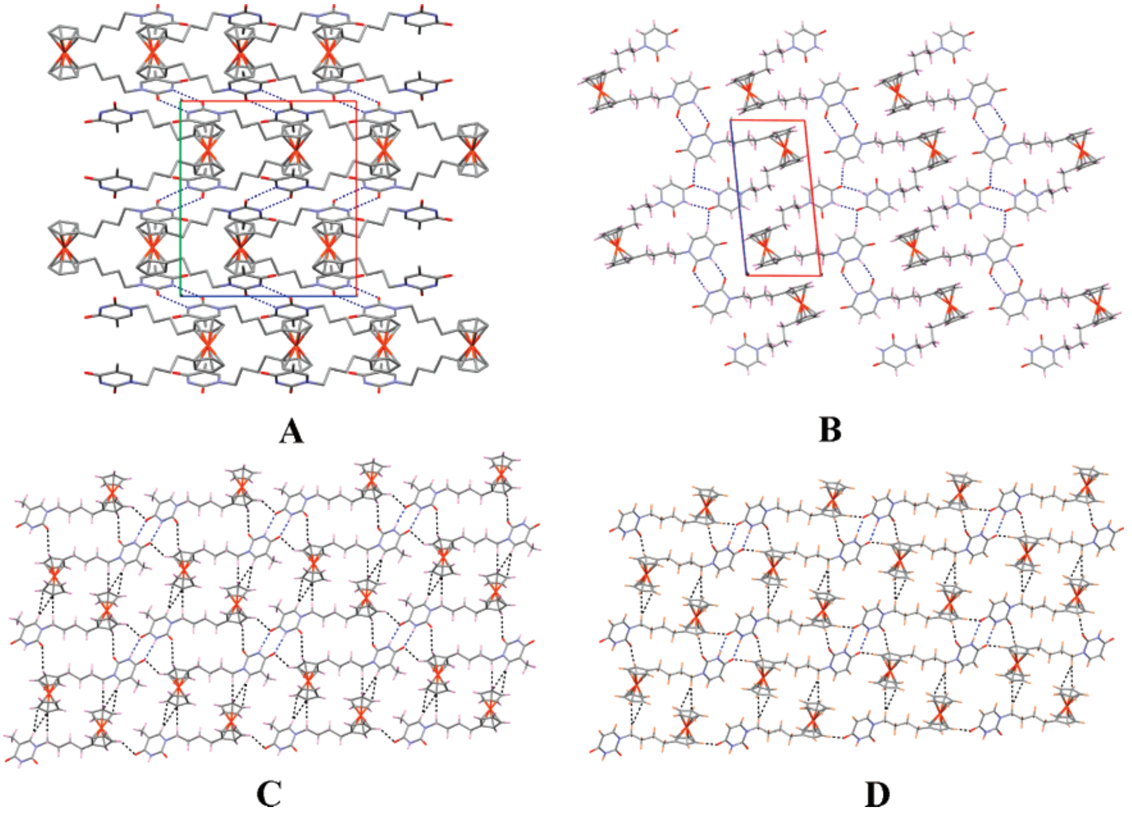

FIGURE 6. Molecular packing diagram of **1a** (A), **1b** (B), **2a** (C), and **2b** (D).

found 414.13 [M$^+$]. Anal. Calcd for $C_{22}H_{30}O_4Fe$: C, 63.76; H, 7.24. Found: C, 63.61; H, 7.62.

1,1′-Bis(4-hydroxybutyl)ferrocene (6). $LiAlH_4$ (1.22 g, 32.1 mmol) in dry THF (40 mL) was stirred for 10 min and a solution of **5** (2.2 g, 5.3 mmol) in dry THF (15 mL) was added drop by drop at such a rate to maintain gentle THF reflux. The reaction mixture was stirred for 3 to 4 h at room temperature followed by cooling in an ice-bath, quenching with slow addition of ice, and stirring for 1 h. The reaction mixture was filtered and washed with ether. The solvents are removed by distillation under diminished pressure, and the residue is purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (3:2) to give **6** as reddish-yellow oil: Yield 95%. ^{1}H NMR (CDCl$_3$, 200 MHz) δ 1.53 (m, 8H), 2.26 (m, 4H), 3.58 (m, 4H), 4.08 (s, 8H). ^{13}C NMR (CDCl$_3$, 50 MHz) δ 27.1, 28.6, 32.3, 62.3, 69.1, 70.1, 91.4. MS (LC-MS) (*m*/*z*) calcd for $C_{18}H_{26}O_2Fe$ 330.24 [M$^+$], found 330.11 [M$^+$]. Anal. calcd for $C_{18}H_{26}O_2Fe$: C, 65.45; H, 7.87. Found: C, 65.11; H, 8.22.

General Procedure for the Preparation of 7a−c via Mitsunobu Reaction. *N*3-Benzoylthymine/*N*3-benzoyluracil (1.89 mmol) and triphenylphosphine (0.60 g, 2.27 mmol) were dissolved in dry THF (10 mL) and the solution was cooled to 0 °C. At this temperature alcohol **6** (0.25 g, 0.75 mmol), dissolved in dry THF (4 mL), was added to the stirred solution followed by dropwise addition of DIAD (0.45 mL, 2.27 mmol). The solution was allowed to gradually reach room temperature and stirring was continued overnight. The solvent was removed under reduced pressure and the resulting solid was purified by flash chromatography on silica gel, packing with petroleum ether/triethylamine (98:2) and eluting with petroleum ether/ethyl acetate (7:3) to give ferrocene-linked *N*3-benzoylprotected nucleobase **7a−c**.

1,1′-Bis(4-(*N*3-benzoylthyminyl)butyl)ferrocene (7a): Yellow foam. Yield 56%. IR (thin film) 1745, 1695, 1650 cm^{-1}. ^{1}H NMR (CDCl$_3$, 200 MHz) δ 1.51−1.36 (m, 4H), 1.80−1.60 (m, 4H), 1.93 (s, 6H), 2.42−2.18 (m, 4H), 3.69 (t, 4H, J = 6.9 Hz), 4.02 (br s, 8H), 7.04 (s, 2H), 7.51−7.43 (m, 4H), 7.67−7.60 (m, 2H), 7.90 (d, 4H, J = 7.8 Hz). ^{13}C NMR (CDCl$_3$, 50 MHz) δ 12.3, 28.0, 28.6, 28.8, 48.4, 67.9, 68.7, 88.1, 110.4, 129.1, 130.3, 131.6, 134.9, 140.2, 149.7, 163.1, 169.2. MS (LC-MS) (*m*/*z*) calcd for $C_{42}H_{42}N_4O_6$-Fe 754.66 [M$^+$], found 754.32 [M$^+$], 777.21 (M$^+$ + Na).

1,1′-Bis(4-(*N*3-benzoyluracyl)butyl)ferrocene (7b): Orange foam. Yield 48%. IR (thin film) 1745, 1703, 1660 cm^{-1}. ^{1}H NMR (CDCl$_3$, 200 MHz) δ 1.58−1.41 (m, 4H), 1.78−1.65 (m, 4H), 2.40−2.26 (m, 4H), 3.79−3.66 (m, 4H), 3.99 (s, 8H), 5.76 (d, 2H, J = 8.1 Hz), 7.21 (d, 2H, J = 8 Hz), 7.51−7.46 (m, 4H), 7.67−7.62 (m, 2H), 7.91 (d, 4H, J = 7.4 Hz). ^{13}C NMR (CDCl$_3$, 50 MHz) δ 28.0, 28.6, 28.9, 48.9, 68.0, 68.8, 88.1, 101.9, 129.2, 130.4, 131.4, 135.1, 144.3, 149.8, 162.5, 169.0. MS (LC-MS) (*m*/*z*) calcd for $C_{40}H_{38}N_4O_6Fe$ 726.61 [M^+], found 727.27 [M^+], 750.27 [$M^+ + Na$]. Anal. Calcd for $C_{40}H_{38}N_4O_6Fe$: C, 66.12; H, 5.27; N; 7.71. Found: C, 65.93; H, 5.38; N, 7.69.

1,1′-Bis[(4-(*N*3-benzoyl)-5-bromouracyl)butyl]ferrocene (7c): Yellow powder, mp 175−177 °C (DCM/petroleum ether). Yield 44%. IR (thin film) 1741, 1695, 1660 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ 1.55−1.35 (m, 4H), 1.78−1.65 (m, 4H), 2.4−2.2 (m, 4H), 3.79−3.65 (m, 4H), 4.08 (br s, 8H), 7.53−7.45 (m, 4H), 7.55 (s, 2H), 7.70−7.62 (m, 2H), 7.89 (d, 4H, $J = 7$ Hz). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 27.2, 27.9, 28.1, 48.4, 67.3, 68.1, 87.5, 94.7, 128.6, 129.7, 130.3, 134.7, 143.9, 148.4, 157.7, 167.2. MS (LC-MS) (*m*/*z*) calcd for $C_{40}H_{36}N_4Br_2O_6Fe$ 884.40 [M^+], found 883.98 [M^+], 906.98 [$M^+ + Na$]. Anal. Calcd for $C_{40}H_{36}N_4Br_2O_6Fe$: C, 54.32, H, 4.10, N, 6.33. Found: C, 54.27; H, 3.77; N, 6.42.

General Procedure for Debenzoylation 1a,b. To a stirred solution of dibenzoyl derivative **7a**,**b** (0.14 mmol) in a methanol/toluene mixture (10:1, 80 mL) was added a saturated solution of K_2CO_3 in water. The resultant mixture was then stirred at room temperature overnight. The solvent was removed under reduced pressure and the residual material was extracted with DCM/methanol (30:1, 3 × 35 mL). The combined organic phases were washed with brine solution, dried over Na_2SO_4, and concentrated. The crude product was chromatographed on a silica gel column with ethyl acetate/petroleum ether (7:3) as eluent to give ferrocene-linked nucleobases **1a**,**b**, which were recrystallized from the appropriate solvent.

1,1′-Bis(4-(thyminyl)butyl)ferrocene (1a): Yellow needle, mp 208−209 °C (DCM/methanol). Yield 90%. IR (thin film) 3174, 1670 cm^{-1}. ^1H NMR ($CDCl_3$ +2 drops DMSO-d_6, 200 MHz) δ 1.45−1.30 (m, 4H), 1.65−1.48 (m, 4H), 1.78 (s, 6H), 2.23−2.07 (m, 4H), 3.55 (t, 4H, $J = 7.1$ Hz), 3.96 (br s, 8H), 6.86 (s, 2H), 9.79 (s, 2H). ^{13}C NMR (DMSO-d_6, 50 MHz) δ 12.1, 27.7, 28.5, 28.5, 47.2, 67.7, 68.6, 88.6, 108.6, 141.7, 151.1, 164.5; MS (LC-MS) (*m*/*z*) calcd for $C_{28}H_{34}N_4O_4Fe$ 546.44 [M^+], found 546.14 [M^+], 569.14 [$M^+ + Na$]. Anal. Calcd for $C_{28}H_{34}N_4O_4Fe$: C, 61.54; H, 6.27; N, 10.25. Found: C, 61.15; H, 6.04; N, 10.01.

1,1′-Bis(4-(uracyl)butyl)ferrocene (1b): Orange solid, mp 165−167 °C (DCM/methanol/toluene). Yield 71%. IR (thin film) 3020, 1681 cm^{-1}. ^1H NMR ($CDCl_3$ + 2 drops DMSO-d_6, 200 MHz) δ 1.53−1.28 (m, 4H), 1.77−1.54 (m, 4H), 2.38−2.20 (m, 4H), 3.64 (t, 4H, $J = 6.6$ Hz), 3.97 (s, 8H), 5.60 (d, 2H, $J = 7.2$ Hz), 7.07 (d, 2H, $J = 7.4$ Hz), 9.61 (br s, 2H). ^{13}C NMR (DMSO-d_6, 50 MHz) δ 27.7, 28.5, 47.5, 67.7, 68.6, 88.6, 101.0, 145.9, 151.2, 164.0. MS (LC-MS) (*m*/*z*) calcd for $C_{26}H_{30}N_4O_4Fe$ 518.39 [M^+], found 518.21 [M^+], 541.21 [$M^+ + Na$]. Anal. Calcd for $C_{26}H_{30}N_4O_4Fe$: C, 60.24; H, 5.83; N, 10.81. Found: C, 60.33; H, 5.86; N, 10.88.

1,1′-Bis[4-(5-bromouracyl)butyl]ferrocene (1c). To a stirred solution of compound **7c** (0.1 g, 0.11 mmol) dissolved in a THF/methanol mixture (3:2, 54 mL) was added LiOH (2 N) solution in water. The reaction was monitored by checking TLC. After 6 h the solvent was removed under reduced pressure and the residual material was treated with ice cold water, acidified with dil. HCl, and extracted with ethyl acetate/methanol (50:1, 3 × 40 mL). The combined organic phases were washed with water, 5% $NaHCO_3$, and brine solution, dried over Na_2SO_4, and concentrated. The crude product was chromatographed on a silica gel column using petroleum ether/ethyl acetate (3:7) as eluent to give compound **1c** (35 mg, 45%). Yellow needle, mp 228 °C ignited (THF/methanol). Yield 45%. IR (thin film) 3188, 1693, 1674 cm^{-1}. ^1H NMR ($CDCl_3$ + 2 drops of DMSO-d_6, 200 MHz) δ 1.41−1.21 (m, 4H), 1.62−1.43 (m, 4H), 2.21−2.05 (m, 4H), 3.55 (t, 4H, $J = 7.1$ Hz), 3.91 (br s, 8H), 7.41 (s, 2H), 11.08 (br s, 2H). MS (MALDI-TOF) (*m*/*z*) calcd for $C_{26}H_{28}N_4Br_2O_4Fe$ 676.18 [M^+], found 676.98 [M^+]. Anal. Calcd for $C_{26}H_{28}N_4Br_2O_4Fe$: C, 46.18; H, 4.17; N, 8.28. Found: C, 46.37; H, 4.23; N, 8.36.

1-(3-Carboxypropionyl)ferrocene (8). For the experimental procedure see the Experimental Section in the Supporting Information. Orange powder, mp 164−165 °C (water). Yield 58%. ^1H NMR ($CDCl_3$, 200 MHz) δ 2.75 (m, 2H), 3.07 (m, 2H), 4.22 (s, 5H), 4.50 (s, 2H), 4.80 (s, 2H). MS (LC-MS) (*m*/*z*) calcd for $C_{14}H_{14}O_3Fe$ 286.11 [M^+], found 287.07 [$M^+ + 1$], 309.07 [$M^+ + Na$]. Anal. Calcd for $C_{14}H_{14}O_3Fe$: C, 58.74; H, 4.89. Found: C, 58.38; H, 4.94.

1-(3-Carboxypropyl)ferrocene (9). The experimental procedure is the same as that for **5**. The only difference is here we have used acetic acid instead of ethanol. Yellow powder, mp 115−116 °C (ethyl acetate/pet ether). Yield 90%. ^1H NMR ($CDCl_3$, 200 MHz) δ 1.78−1.92 (m, 2H), 2.36−2.43 (m, 4H), 4.06 (s, 4H), 4.11 (s, 5H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 25.9, 28.8, 33.7, 67.3, 68.1, 68.5, 88.0, 179.9; MS (LC-MS) (*m*/*z*) calcd for $C_{14}H_{16}O_2Fe$ 272.12 [M^+], found 272.13 [M^+], 295.04 [$M^+ + Na$]. Anal. Calcd for $C_{14}H_{16}O_2Fe$: C, 61.76; H, 5.88. Found: C, 61.88; H, 5.94.

1-(3-Carbethoxypropyl)ferrocene (10). The experimental procedure and setup are the same as those for **4** (procedure B). Reddish-yellow oil. Yield 95%. ^1H NMR ($CDCl_3$, 200 MHz) δ 1.27 (t, 3H, $J = 6.7$ Hz), 1.77−1.92 (m, 2H, 2.29−2.42 (m, 4H), 4.07 (br s, 4H), 4.11 (s, 5H), 4.16 (m, 4H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 14.1, 25.9, 28.7, 33.7, 59.9, 67.1, 68.0, 68.4, 88.1, 173.1. MS (LC-MS) (*m*/*z*) calcd for $C_{16}H_{20}O_2Fe$ 300.17 [M^+], found 300.24 [M^+], 323.25 [$M^+ + Na$]. Anal. Calcd for $C_{16}H_{20}O_2Fe$: C, 64.0; H, 6.67. Found: C, 64.21; H, 6.35.

1-(4-Hydroxybutyl)ferrocene (11). The experimental procedure and setup are the same as those for **6**. Reddish-yellow oil. Yield 93%. ^1H NMR ($CDCl_3$, 200 MHz) δ 1.56−1.62 (m, 4H), 2.38 (t, 2H, $J = 7.3$ Hz), 3.64 (t, 2H, $J = 6.7$ Hz), 4.07 (s, 4H), 4.12 (s, 5H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 27.1, 29.2, 32.5, 62.5, 67.1, 68.1, 68.5, 89.1. MS (LC-MS) (*m*/*z*) calcd for $C_{14}H_{18}OFe$ 258.14 [M^+], found 258.15 [M^+]. Anal. Calcd for $C_{14}H_{18}OFe$: C, 65.11; H, 6.97. Found: C, 64.73; H, 7.19.

1-(4(*N*3-Benzoylthyminyl)butyl)ferrocene (12a). For the experimental procedure see the Experimental Section in the Supporting Information. Yellow needles, mp 142−143 °C. Yield 68%. IR (thin film) 1745, 1697, 1650 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ 1.55 (m, 2H), 1.74 (m, 2H), 1.97 (s, 3H), 2.41 (t, 2H), 3.73 (t, 2H), 4.10 (s, 4H), 4.14 (s, 5H), 7.10 (s, 1H), 7.52 (t, 2H, $J = 8$ Hz), 7.68 (t, 1H, $J = 8$ Hz), 7.95 (d, 2H, $J = 8$ Hz). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 12.2, 27.9, 28.6, 29.0, 48.4, 67.3, 68.1, 68.6, 88.3, 110.4, 129.0, 130.2, 131.7, 134.7, 140.1, 149.7, 163.0, 169.1;. MS (LC-MS) (*m*/*z*) calcd for $C_{26}H_{26}N_2O_3Fe$ 470.34 [M^+], found 470.34 [M^+]. Anal. Calcd for $C_{26}H_{26}N_2O_3Fe$: C, 66.38; H, 5.53; N, 5.95. Found: C, 65.75; H, 5.47; N, 5.85.

1-(4-(*N*3-Benzoyluracil)butyl)ferrocene (12b): Brown oil. Yield 57%. IR (thin film) 1747, 1703, 1660 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ 1.55−1.43 (m, 2H), 1.84−1.66 (m, 2 H), 2.46−2.27 (m, 2H), 3.72 (t, 2H, $J = 6.4$ Hz), 4.12 (s, 9H), 5.78 (d, 1H, $J = 7.2$ Hz), 7.19 (d, 2H, $J = 7.4$ Hz), 7.52−7.45 (m, 2H), 7.68 −7.61 (m, 1 H) , 7.92 (d, 2H, $J = 7.2$ Hz). ^{13}C NMR($CDCl_3$, 50 MHz) δ 28.0, 28.6, 29.1, 48.9, 67.2, 68.1, 68.5, 88.0, 101.9, 129.1, 130.3, 131.5, 135.0, 144.1, 149.7, 162.4, 168.8. MS (LC-MS) (*m*/*z*) calcd for $C_{26}H_{26}N_2O_3Fe$ 456.32 [M^+], found 456.10 [M^+], 479.09 [$M^+ + Na$].

General Procedure for Debenzoylation 2a,b. The experimental procedure and setup were the same asthose for **1a**,**b**.

1-(4-(Thyminyl)butyl)ferrocene (2a): Yellow needle, mp 199−200 °C (ethyl acetate/petroleum ether). Yield 94%. IR (thin film) 3149, 1704, 1666 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ 1.42−1.52 (m, 2H), 1.61−1.76 (m, 2H), 2.35 (t, 2H), 3.66 (t, 2H), 4.12 (s, 9H), 6.92 (s, 1H), 8.71 (s, 1H). MS (LC-MS) (*m*/*z*) calcd for $C_{19}H_{22}N_2O_2Fe$ 366.24 [M^+], found 366.14 [M^+]. Anal. Calcd for $C_{19}H_{22}N_2O_2Fe$: C, 62.29; H, 6.01; N, 7.65. Found: C, 62.00; H, 6.06; N, 7.66.

1-(4-(Uracyl)butyl)ferrocene (2b): Orange needles, mp 146−147 °C (ethyl acetate/petroleum ether). Yield 95%. IR (thin film): 1747, 1703, 1665 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ 1.43−1.55 (m, 2 H), 1.64−1.75 (m, 2H), 2.31−2.42 (m, 2H), 3.65−3.72 (m, 2H), 4.13 (s, 9H), 5.66 (d, 1H, $J = 8$ Hz), 7.09 (d, 1H, $J = 8$ Hz), 8.49 (s, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 28.0, 28.7, 29.2, 48.6, 67.2, 68.1, 68.4, 88.1, 102.1, 144.3, 150.9, 164.0. MS (LC-MS) (m/z) calcd for $C_{18}H_{20}N_2O_2Fe$ 352.21 [M^+], found 352.05 [M^+]. Anal. Calcd for $C_{18}H_{20}N_2O_2Fe$: C, 61.36; H, 5.68; N, 7.95. Found: C, 61.53; H, 5.52; N, 7.62.

1-(4-Hydroxybutyl)-1′-(4-(*tert*-butyldimethylsilyloxy)butyl)-ferrocene (13). Compound **6** (0.68 g, 2.06 mmol), imidazole (0.42 g, 6.18 mmol), and $AgNO_3$ (0.17 g, 1.03 mmol) were dissolved in 20 mL of DCM and the resulting mixture was stirred at 0 °C. Then TBDMSCl (0.34 g, 2.266 mmol) in 10 mL of DCM was added dropwise and the reaction mixture was allowed to come to rt and stirred overnight, then extracted with DCM (3 × 20 mL), and the combined organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated. The crude product was chromatographed on a silica gel column, packing with petroleum ether/triethylamine (98:2) and eluted with ethyl acetate/petroleum ether (1:19) to give compound **13** (515 mg, 56%). Reddish-yellow oil. Yield 56%. ^1H NMR ($CDCl_3$, 200 MHz) δ 0.04 (s, 6H), 0.89 (s, 9H), 1.27 (br s, 1H), 1.69−1.37 (m, 8H), 2.39−2.16 (m, 4H), 3.70−3.51 (m, 4H), 4.01 (s, 8H). ^{13}C NMR($CDCl_3$, 50 MHz) δ −5.3, 18.3, 26.0, 27.4, 29.2, 29.2, 32.6, 32.7, 62.8, 63.1, 67.66, 67.72, 68.6, 88.8, 89.2. MS (LC-MS) (m/z) calcd for $C_{24}H_{40}O_2SiFe$ 444.51 [M^+], found 444.30 [M^+].

1-(4-(*N*3-Benzoylthyminyl)butyl)-1′-(4-(*tert*-butyldimethylsilyloxy)butyl)ferrocene (14). For the experimental procedure and setup see the Experimental Section in the Supporting Information. Brown oil. Yield 69%. IR (KBr) 1747, 1697, 1658 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ 0.04 (s, 6H), 0.88 (s, 9H), 1.57−1.45 (m, 6H), 1.78−1.64 (m, 2H), 1.94 (s, 3H), 2.43−2.21 (m, 4H), 3.60 (t, 2H, J = 5.4 Hz), 3.69 (t, 2H, J = 7 Hz), 3.97 (s, 8H), 7.02 (s, 1H), 7.51−7.43 (m, 2H), 7.67−7.59 (m, 1H), 7.90 (d, 2H, J = 7.3 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz) δ −5.3, 12.3, 18.3, 21.9, 25.9, 27.4, 28.2, 28.6, 29.0, 29.1, 32.7, 48.6, 63.0, 67.7, 67.9, 68.6, 87.9, 89.2, 110.5, 129.1, 130.3, 131.6, 134.9, 140.1, 149.7, 163.1, 169.1. MS (LC-MS) (m/z) calcd for $C_{36}H_{48}N_2O_4SiFe$ 656.71 [M^+], found 656.25 [M^+], 679.24 [M^+ + Na].

1-(4-(*N*3-Benzoylthyminyl)butyl)-1′-(4-hydroxybutyl)ferrocene (15). To a stirred, cooled (0−5 °C) solution of **14** (0.29 g, 0.44 mmol) in THF (5 mL) was added 1 M solution of TBAF (1.3 mL, 1.32 mmol) in THF and the resulting mixture was stirred at 0−5 °C for 3 h. Solvent was removed under reduced pressure and extracted with DCM (3 × 10 mL). The combined organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated. The crude product was chromatographed on a silica gel column, packed with petroleum ether/triethylamine (98:2), and eluted with ethyl acetate/petroleum ether (1:1) to give compound **15** (170 mg, 71%). Brown oil. Yield 71%. IR (KBr) 3431, 1747, 1697, 1650 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ 1.56−1.34 (m, 4H), 1.81−1.61 (m, 4H), 1.93 (s, 3H), 2.34−2.16 (m, 4H), 3.61−3.47 (m, 2H), 3.67 (t, 2H, J = 6.95 Hz), 4.10 (s, 8H), 7.02 (s, 1H), 7.51−7.43 (m, 2H), 7.67−7.60 (m, 1H), 7.89 (d, 2H, J = 7.7 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 12.3, 27.3, 28.1, 28.6, 28.9, 29.1, 32.5, 48.5, 62.6, 67.7, 67.9, 68.6, 88.0, 89.0, 110.5, 129.1, 130.3, 131.6, 134.9, 140.1, 149.8, 163.1, 169.1. MS (LC-MS) (m/z) calcd for $C_{30}H_{34}N_2O_4Fe$ 542.46 [M^+], found 542.14 [M^+], 565.14 [M^+ + Na].

1-(4-(*N*3-Benzoylthyminyl)butyl)-1′-(4-(*N*3-benzoyluracyl)butyl)ferrocene (16). For the experimental procedure and setup see the Experimental Section in the Supporting Information. Yellow foam. Yield 68%. IR (thin film) 1747, 1699, 1660 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ 1.53−1.38 (m, 4H), 1.77−1.62 (m, 4H), 1.93 (s, 3H), 2.36−2.15 (m, 4H), 3.76−3.62 (m, 4H), 4.06 (br s, 8H), 5.76 (d, 1H, J = 7.8 Hz), 7.03 (s, 1H), 7.20 (d, 2H, J = 7.8 Hz), 7.54−7.41 (m, 4H), 7.69−7.58 (m, 2H), 7.96−7.85 (m, 4H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 12.2, 27.9, 28.5, 28.6, 28.8, 48.4, 48.8, 68.0, 68.8, 88.2, 88.3, 101.8, 110.4, 129.1, 129.1, 130.3, 131.4, 131.6, 134.9, 135.0, 140.2, 144.3, 149.7, 149.7, 162.4, 163.1, 168.9, 169.2. MS (MALDI-TOF) (m/z) calcd for $C_{41}H_{40}N_4O_6Fe$ 740.63 [M^+], found 740.03 [M^+].

1-(4-(Thyminyl)butyl)-1′-(4-(uracyl)butyl)ferrocene (1d). The experimental procedure and setup are the same as those for **1a**,**b**. Yellow needle, mp 162−164 °C (DCM/methanol/toluene). Yield 82%. IR (thin film) 3184, 1697, 1674 cm^{-1}. ^1H NMR ($CDCl_3$ + 3−4 drops of DMSO-d_6, 200 MHz) δ 1.52−1.42 (m, 4H), 1.75−1.60 (m, 4H), 1.88 (s, 3H), 2.33−2.20 (m, 4H), 3.70−3.61 (m, 4H), 4.04 (br s, 8H), 5.62 (dd, 1H, J = 2, 7.8 Hz), 6.95 (s, 1H), 7.13 (d, 1H, J = 7.8 Hz), 9.93 (br s, 1H), 10.06 (br s, 1H). ^{13}C NMR (DMSO-d_6, 50 MHz) δ 12.1, 27.7, 28.5, 47.2, 47.5, 67.7, 68.6, 88.56, 88.60, 101.0, 108.6, 141.7, 145.9, 151.1, 151.2, 164.0, 164.5. MS (LC-MS) (m/z) calcd for $C_{27}H_{32}N_4O_4Fe$ 532.42 [M^+], found 532.13 [M^+], 555.13 [M^+ + Na]. Anal. Calcd for $C_{27}H_{32}N_4O_4Fe$: C, 60.90; H, 6.05; N, 10.52. Found: 60.58, 6.05, 10.33.

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Supporting Information Available: Experimental procedures, spectroscopic details of new compounds, and data for single crystal X-ray analysis of **1a**−**d** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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