

Use of Boolean and Fuzzy Logics in Lactose Glycoclusters Research

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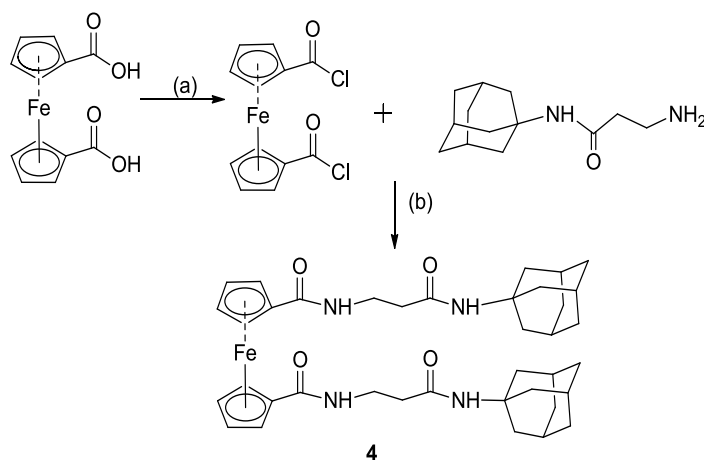
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 1. General Information

All chemicals were reagent grade and used as supplied except where noted. Analytical thin layer chromatography (TLC) was performed on Merck silica gel 60 F254 plates (0.25 mm). Compounds were visualized by UV irradiation or dipping the plate in CAM solution followed by heating. Column chromatography was carried out using force flow of the indicated solvent on Fluka Kieselgel 60 (230–400 mesh). ¹H and ¹³C NMR spectra were recorded on Jeol 400 MHz using residual solvents signals as an internal reference (CDCl₃ δ H, 7.26 ppm, δ c 77.3 ppm and CD₃OH δ H 3.31 ppm, δ c 49.0 ppm). The chemical shifts (δ) are reported in *ppm* and coupling constants (*J*) in Hz. ITC spectra were recorded by using isothermal titration calorimeter (ITC 200, USA).

2. Synthesis of ferrocene derivative



Scheme 1: Synthesis of comp : (a) (COCl)₂; DCM; (b) DIPEA; DCM

Synthesis of ferrocene-adamantyl complex (4).

1, 1-Ferrocene dicarboxylic acid (300 mg, 1.1 mmol) was dissolved in DCM (10 mL). Then oxalyl chloride (0.6 ml, 5.5 mmol) was added and stirred at room temperature for 4 h. Completion of reaction was monitored by TLC. After completion, the reaction mixture was evaporated and directly added to adamantyl derivative (0.6 g, 2.75 mmol) followed by addition of DIPEA (1 mL). The reaction mixture was allowed to stir at room temperature for overnight. After that reaction mixture extracted with DCM: H₂O (1:1) and dried over anhydrous Na₂SO₄. Organic layer was concentrated under reduced pressure to give crude product, which was further purified by silica gel column chromatography using MeOH/DCM (95:5-92:8) to get pure final product **4** (0.23 g, 31%). ¹H NMR (400 MHz, CDCl₃) δ 7.27 (br, 2H), 5.9 (bs, 2H), 4.57 (s, 4H), 4.3 (s, 4H), 3.61 (q, *J* = 7.0 Hz, 4H), 2.49 (t, *J* = 7.0 Hz, 4H), 2.03 (s, 6H), 2.02 (s, 12H), 1.58 (s, 12H) ¹³C NMR (100 MHz, CDCl₃) δ 171.2, 169.9, 78.1, 71.2, 70.5, 52.2, 41.7, 39.4, 29.4. . HRMS *m/z* calc'd for C₃₈H₅₀FeN₄O₄ (M+H)⁺: 683.3259; found:682.3181.

3. ITC measurements

The thermodynamic studies of carbohydrate-protein interaction were estimated by using isothermal titration calorimeter (ITC 200, USA). The stock solution (0.05 mmol) was kept in the titration cell and was titrated by PNA (0.01 mmol). Each experiment consisted of 18 injections with a successive time gap of 200 s between two injections. For proper mixing of the solutions the stirring speed was maintained at 1000 rotations/min. Cell temperature was kept fixed at 298

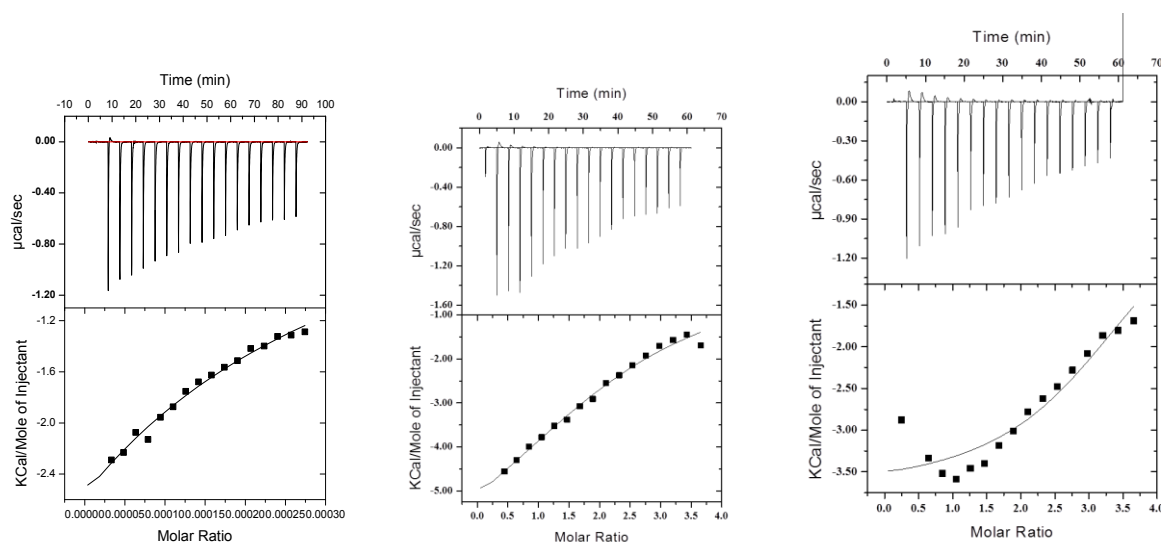


Figure 1. ITC profile for **3** in the presence of CaCl_2 , PNA and PNA + CaCl_2 together at 298 K in H_2O . The top panels represent the energy ($\mu\text{cal s}^{-1}$) required to maintain isothermal conditions with respect to the reference cells and the lower panels represent the heat evolved from each injection per mole of Ca^{2+} versus the molar ratio of (a) Conc of **3** = 0.05 mM in water and CaCl_2 solution = 20 mM in water; (b) Conc of **2** = 0.05 mM in water and PNA = 0.01 mM (c) Conc of **2** = 0.05 mM in water, CaCl_2 = 20 mM PNA = 0.01 mM in Phosphate buffer pH 7.4 in water.

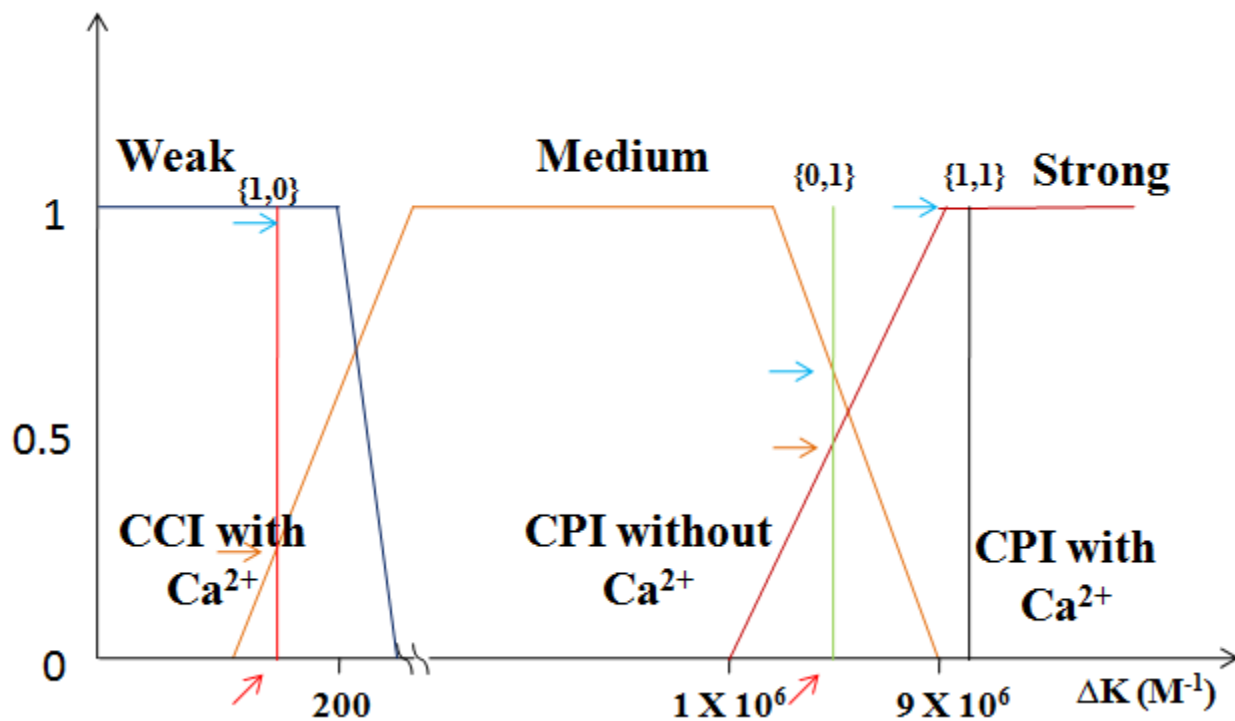
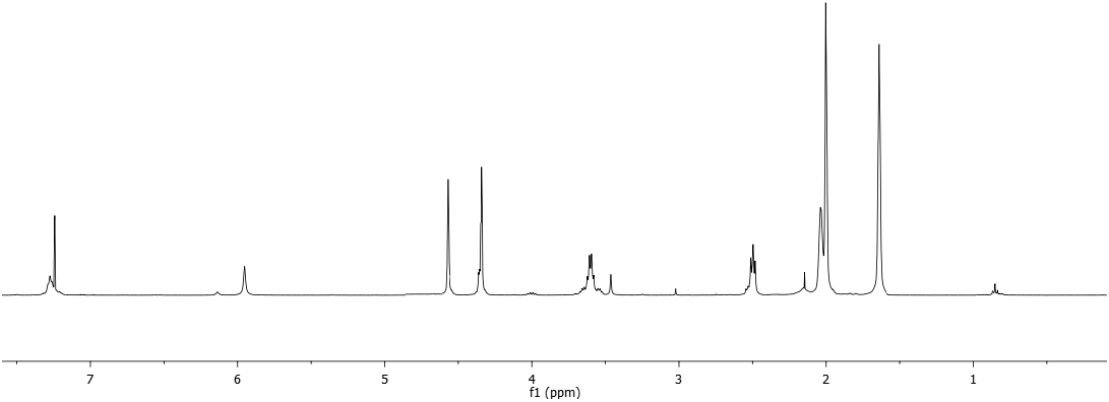
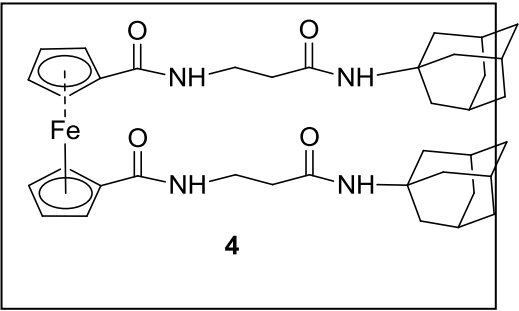


Figure 2. FLS rules: $\Delta K \leq 200 \text{ M}^{-1}$ - weak interaction, $100 \leq \Delta K \leq 9 \times 10^6 \text{ M}^{-1}$ - medium interaction and for $\Delta K \geq 1 \times 10^6 \text{ M}^{-1}$ - strong binding. SM (slightly medium); W (weak); SS (slightly strong); FM (fairly medium)

4. NMR datas :

180213-12-PB-K-FD



180213-12-PB-K-FD

