

Supporting Information

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Contents list

1. Experimental	S2
2. Synthesis and characteristics of compounds	S2-S7
3. Gelation properties of compounds in various solvents	S8
4. Characteristics about the response to anions	S9-S10
5. Characteristics about the response to cations	S10-S15

1. Experimental

Materials:

D-Gluconic acid, 3,4-dichlorobenzaldehyde, 1,6-hexanediamine, salicylaldehyde, DMAP (4-dimethylaminopyridine) were purchased from Shanghai Jingchun Scientifical Co., Ltd. Ferrocenyl Aldehyde was purchased from Tianjin Xi'ensi Aupu Technology Co., Ltd. The chemical reagents were commercially available and directly utilized without further purification.

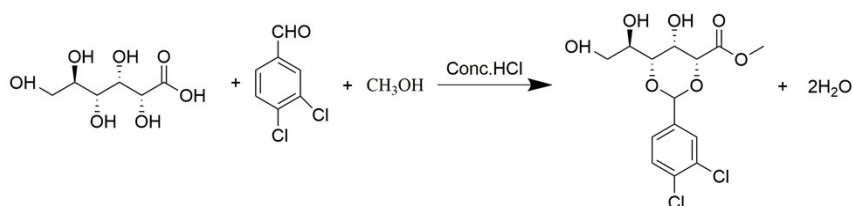
2. Synthesis and characteristics of compounds

2.1 Synthesis of compounds

(1) Synthesis of ferrocene derivative F_n (Take F-6 as example)

Synthesis of 2, 4-(3, 4-dichloro) benzylidene Methy-D-Gluconate

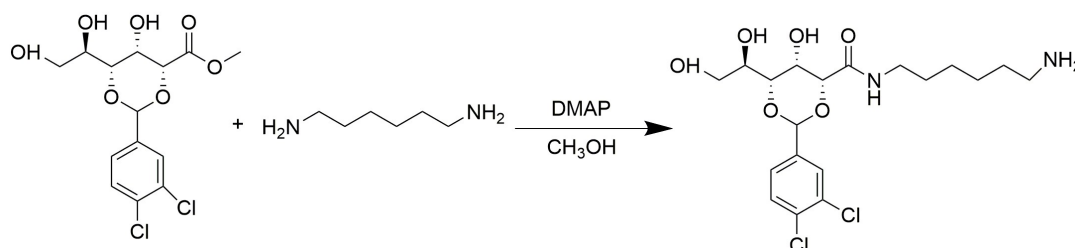
279.0g (0.71mol) 50wt% aqueous solution of D-gluconic acid was dissolved in 100 mL methanol and 200 mL hydrochloride acid was added to the solution under vigorously stirring at 10°C. 80.0 g (0.46mol) 3, 4-dichlorobenzaldehyde was added after 15 minutes. The reaction mixture was stirred by 36 h and white solid was collected by filtration. The filter cake was washed with water for 5 times until pH was 7. Then it was washed with hot dichloromethane for twice. ¹H NMR (400MHz, DMSO-d₆): δ 7.81(d, J=1.56Hz, 1H,Ar-H), 7.69(d, J=8.28Hz,1H,Ar-H), 7.48(dd, J=1.68Hz, 8.32Hz, 1H,Ar-H), 5.65(s, 1H, OCHO), 5.06(d, J=8.88Hz, 1H, OH), 4.79(d, J=6.08Hz, 1H, OH), 4.72(s, 1H, CH₂), 4.47(t, J=5.76Hz, 1H, OH), 4.00(d, J=8.8Hz, 1H, CH), 3.80(d, J=8.84Hz, 1H, CH₂), 3.69(s, 3H, CH₃), 3.64-3.65(m, 1H, CH), 3.56-3.52(m, 1H, CH), 3.41(dd, J=5.44Hz, 11.04Hz, 1H, CH), 3.17(d, J=5.24Hz, 1H, CH).



Scheme S1. Synthesis of 2, 4-(3, 4-dichloro) benzylidene Methy-D-Gluconate

Synthesis of N-(6-aminohexyl)-2, 4-(3, 4-chlorobenzylidene)-D-glucose amide

19.03 g(0.052mol) 2,4-(3,4-dichloro) benzylidene methy-D-Gluconate was dissolved in 150 mL methanol and 0.03 g DMAP was added as catalyst under vigorously stirring at 10°C. 18.07 g 1, 6-hexanediamine was added after 10 minutes. The reaction mixture was stirred by 24 h and white solid was collected by filtration. The filter cake was washed with water for 3 times and recrystallized from ethanol for twice. ¹H NMR(400MHz, DMSO-d₆): δ 7.88(d, J=1.68Hz, 1H, CONH), 7.67(d, J=8.28Hz, 1H,Ar-H), 7.56(d, J=1.68Hz, 1H,Ar-H), 7.47(s, 1H,Ar-H), 5.65(s, 1H, OCHO), 4.33(s, 2H, OH), 3.99(s, 1H, OH), 3.75(d, J=8.68Hz, 1H, CH), 3.63-3.66(m, 1H, CH), 3.57(d, J=2.48Hz, 1H, CH), 3.54(d, J=2.28Hz, 1H, CH₂), 3.41(d, J=5.32Hz, 1H, CH₂), 3.40(d, J=5.28Hz, 1H, CH), 3.29(s, 2H, NH₂), 3.09-3.17(m, 4H, CH₂), 2.86(m, 2H, CH₂), 1.41-1.44(m, 2H, CH₂), 1.32(d, J=5.96Hz, 2H, CH₂), 1.25-1.26(m, 4H, CH₂).



Scheme S2.Synthesis of N-(6-aminohexyl)-2, 4-(3, 4-chlorobenzylidene)-D-glucose amide

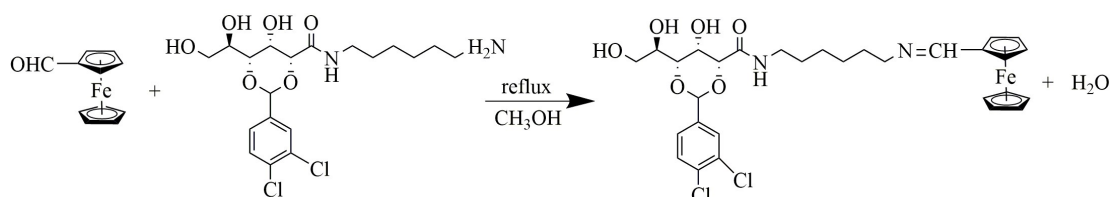
Synthesis of ferrocenyl derivate F-6

0.25 g ferrocenyl aldehyde (0.0012mol) dissolved in 10 mL methanol was added drop wise to a solution of 0.45 g N-(6-aminohexyl)-2,4-(3,4-chlorobenzylidene)-D-glucose amide (0.001mol) and 0.1 g magnesium sulfate dissolved in 30 mL methanol. The mixture was heated to reflux for 6 hours under stirring. The resulting solution was washed with water and orange precipitate was obtained. Orange solid was collected by filtration. The filter cake was washed with petroleum ether for 2 times and recrystallized from methanol for twice. Orange solid; m. p.= 157.8°C-159.2°C; ¹H NMR (400MHz, DMSO-d₆): δ 8.08(s, 1H, CH=N), 7.88(s, 1H, CONH), 7.65(d, J=7.20Hz, 1H,Ar-H), 7.54(d, J=6.00Hz, 1H,Ar-H), 7.47(d, J=4.01Hz, 1H,Ar-H), 5.65(s, 1H, OCHO), 4.72(m, 2H, OH), 4.59(s, 2H, Fc-H), 4.46(s, 1H, OH), 4.32(d,

$J=12.50\text{Hz}$, 2H, Fc-H), 4.31(s, 1H, CH), 4.15(s, 5H, Fc-H), 3.99(d, $J=6.80\text{Hz}$, 1H, CH), 3.73(d, $J=6.40\text{Hz}$, 1H, CH), 3.62(s, 1H, CH), 3.51(s, 2H, CH_2), 3.42(m, 2H, CH_2), 3.12(m, 2H, CH_2), 1.50-1.00(m, 8H, CH_2).

^{13}C NMR (100MHz, DMSO- d_6): δ 168.5, 160.2, 139.3, 131.9, 131.4, 130.7, 129.2, 127.6, 98.5, 81.6, 80.7, 79.8, 70.3, 69.5, 69.3, 68.5, 62.9, 62.8, 61.1, 39.0, 30.9, 29.7, 27.0, 26.7.

MS (ESI) m/z calculated for $\text{C}_{30}\text{H}_{36}\text{Cl}_2\text{FeN}_2\text{O}_6$ $[\text{M}+\text{H}]^+$ 647.1378, found 647.1375.

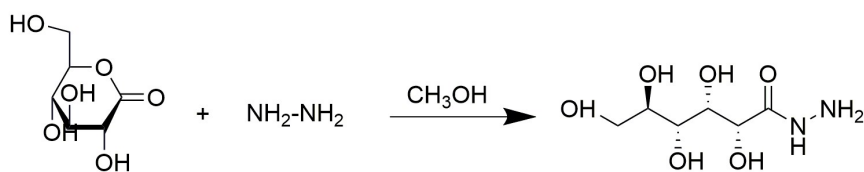


Scheme S3. Synthesis of ferrocenyl derivative F-6

(2) Synthesis of ferrocene derivative A_n (Take A-0 as example)

Synthesis of Hydrazide-D-glucose amide

0.4g (0.002mol) gluconolactone was dissolved in 20 mL methanol and 0.1g (0.002mol) hydrazine hydrate was added to the solution under vigorously stirring for 5 hours. White solid was collected by filtration. The filter cake was washed with water for 3 times. ^1H NMR (400MHz, DMSO- d_6): δ 7.90(s, 1H, CONH), 5.90 (s, 1H, OH), 4.70(s, 1H, OH), 4.22(s, 2H, NH_2), 4.21(s, 1H, OH), 3.60-3.47(m, 4H, CH), 3.45(s, 1H, OH), 3.21 (s, 1H, OH), 1.40-1.20(s, 2H, CH_2).

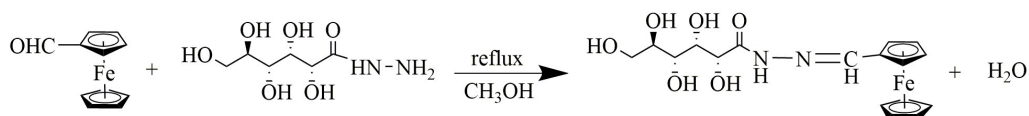


Scheme S4. Synthesis of hydrazide-D-glucose amide

Synthesis of ferrocenyl derivative A-0

0.28g ferrocenyl aldehyde (0.0013mol) dissolved in 10 mL methanol was added drop wise to a solution of 0.30 g Hydrazide-D-glucose amide (0.0013mol) dissolved in 30 mL methanol. The mixture was heated to reflux for 6 hours under stirring. Orange solid was collected by filtration. The filter cake was washed with methanol for

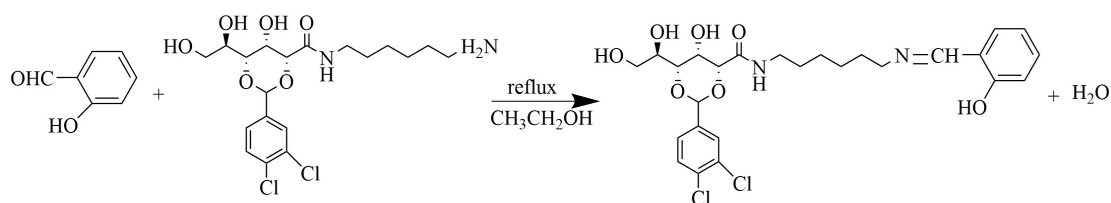
2 times. Orange solid; m. p.= 167.8-170.3°C; ¹H NMR (400MHz, DMSO-d₆): δ 8.41(s, 1H, CH=N), 6.50 (s, 1H, CONH), 5.90 (s, 1H, OH), 4.70(s, 1H, OH), 4.50(s, 2H, Fc-H), 4.30(s, 2H, Fc-H), 4.25(s, 5H, Fc-H), 2.99-2.90(m, 3H, OH), 2.65-2.60(m, 2H, CH), 2.35(s, 2H, CH), 1.40-1.20(s, 2H, CH₂).



Scheme S5.Synthesis of ferrocenyl derivate A-0

(3) Synthesis of salicylaldehyde derivate S-6

0.25 g salicylaldehyde (0.002mol) dissolved in 10 mL ethanol was added drop wise to a solution of 0.75 g N-(6-aminohexyl)-2,4-(3,4-chlorobenzylidene)-D- glucose amide (0.0016mol) dissolved in 30 mL ethanol. The mixture was heated to reflux for 6 hours under stirring. The resulting solution was washed with water and yellow precipitate was obtained. Yellow solid was collected by filtration. The filter cake was recrystallized from ethanol for twice. Yellow solid; m. p. = 185.3°C-186.2°C; ¹H NMR (400MHz, DMSO-d₆): δ 13.68(s, 1H, OH), 8.55(s, 1H, CH=N), 7.90(d, J=1.60Hz, 1H, NHCO), 7.67(d, J=8.40Hz, 1H,Ar-H), 7.55(dd, J=1.20Hz, 1.60Hz, 1H,Ar-H), 7.45(m, 2H,Ar-H), 7.32(m, 1H,Ar-H), 6.87(m, 2H,Ar-H), 5.67(s, 1H, CH), 4.72(d, J=4.12Hz, 2H, OH), 4.46(t, J=6.00Hz, OH), 4.35(s, 1H, CH), 4.00(d, J=9.20Hz, 1H, CH), 3.76(d, J=8.40Hz, 1H, CH), 3.69-3.50(m, 4H, 2CH₂), 3.42(d, J=5.20Hz, 1H, CH), 3.11(m, 2H, CH₂), 1.71-1.15(m, 8H, CH₂).



Scheme S6. Synthesis of ferrocenyl derivate S-6

2.2 Characteristics of compounds

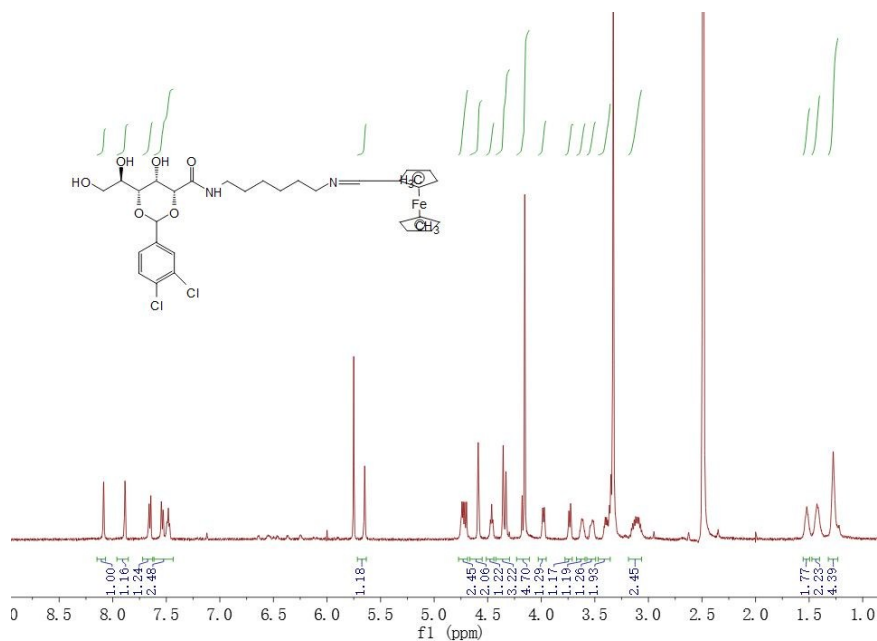


Figure S1. ¹H NMR spectrum of compound F-6 in DMSO-d₆

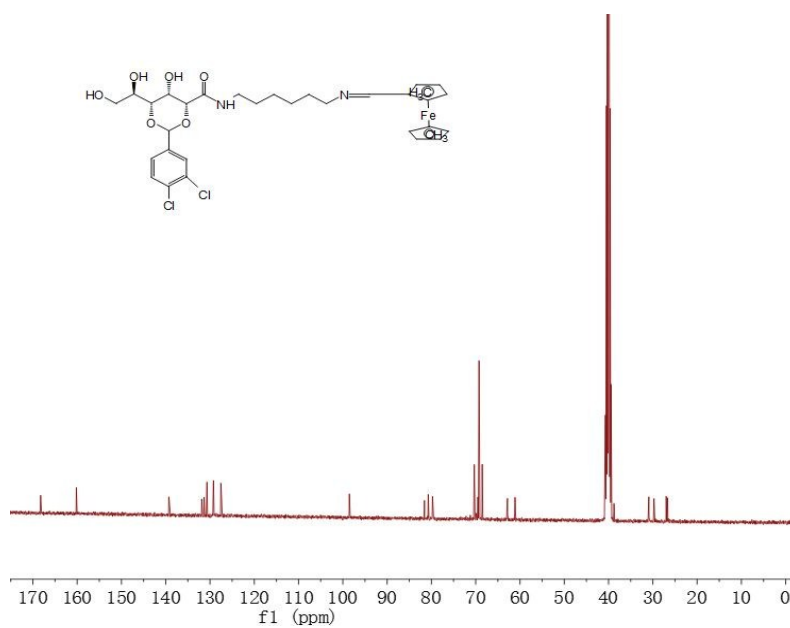


Figure S2. ¹³C NMR spectrum of compound F-6 in DMSO-d₆

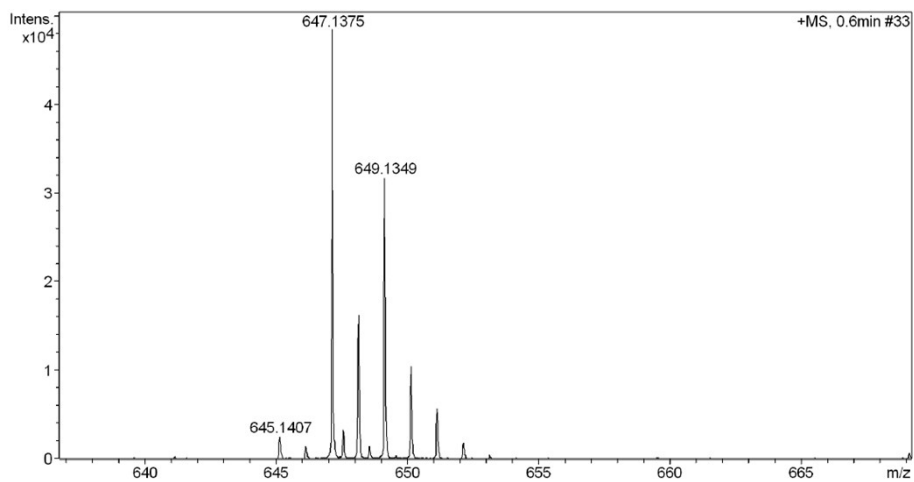


Figure S3. ESI Mass spectrum of F-6 (m/z=647.1375)

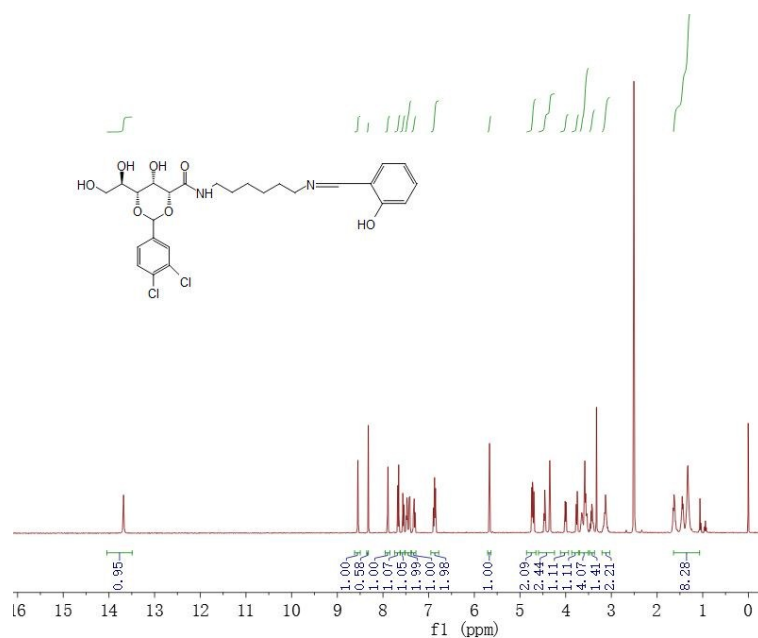


Figure S4. ¹H NMR spectrum of compound S-6 in DMSO-d₆

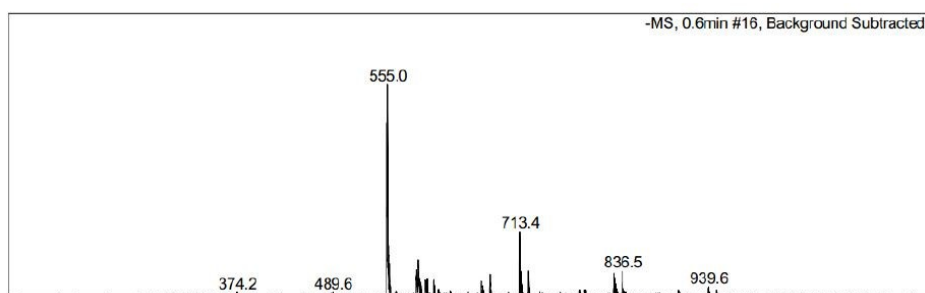


Figure S5. ESI Mass spectrum of S-6 (m/z=555.0)

3. Gelation properties of compounds in various solvents

Table S1. Gelation properties of F-0, F-6, A-0, A-6 (2%, w/v) in various solvents

Solvent	F-0	F-6	A-0	A-6
Methanol	S	S	P	S
DMSO	S	S	S	S
THF	S	S	S	S
DMF	S	S	S	S
H ₂ O	P	P	I	P
Ethyl acetate	P	P	P	P
Chloroform	S	G	S	S
Benzene	S	G	S	S
Toluene	S	G	S	S
n-octyl alcohol	S	G	P	S
o-dichlorobenzene	S	G	S	S
Acetonitrile	I	I	I	I
Acetone	I	I	I	I
Cyclohexane	I	I	I	I

G-gel, S-solution, P-precipitate, I-insoluble; gel formed by heating and cooling at room temperature.

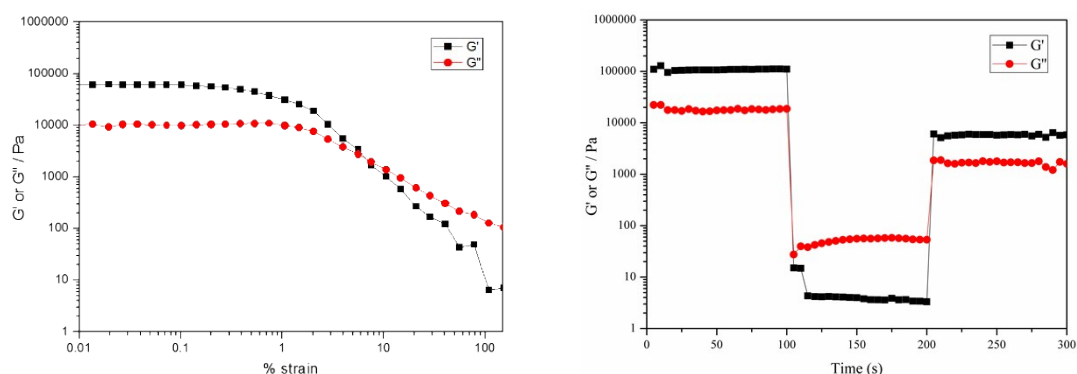


Figure S6. Rheological measurement of the (a) strain sweep at a frequency of 1Hz, (b) the process of deformation and recovery of the F-6/chloroform gel system.

4. Characteristics about the response to anions

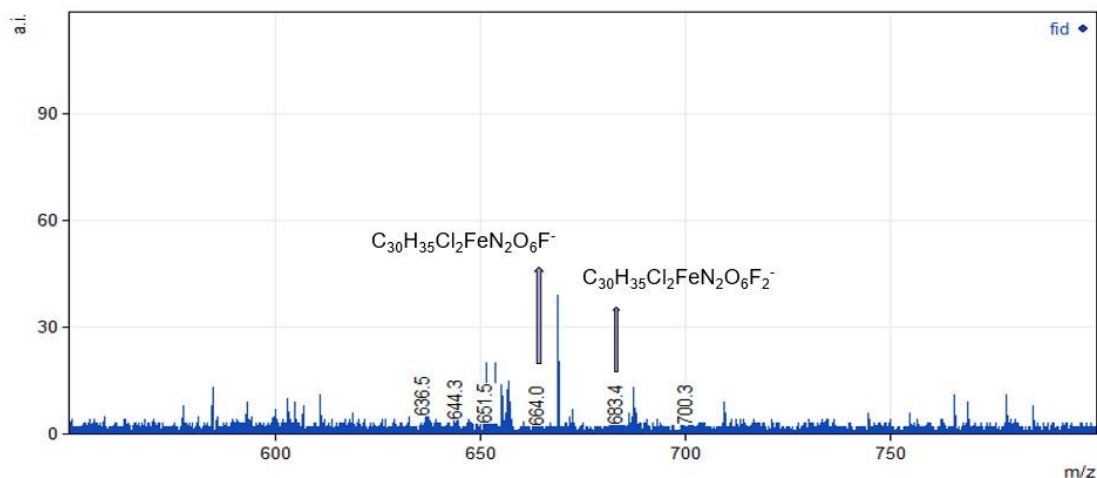


Figure S7. MALDI-TOF mass spectrum of $C_{30}H_{35}Cl_2FeN_2O_6F^-$ ($m/z=664.0$) and $C_{30}H_{35}Cl_2FeN_2O_6F_2^-$ ($m/z=683.4$)

The group of salicylaldehyde was introduced instead of ferrocene to compare the differences on the response to anions, and the interaction between S-6 and anions was also tested under the same conditions. The results showed that only F^- and Cl^- could destroy the S-6/chloroform gel with the color unchanged. It was concluded that F^- and Cl^- destroyed the original hydrogen bonding and resulted in the formation of $X \cdots HNCO$ hydrogen bonding using UV/Vis spectroscopy and 1H NMR analysis (Figure S8-S9).

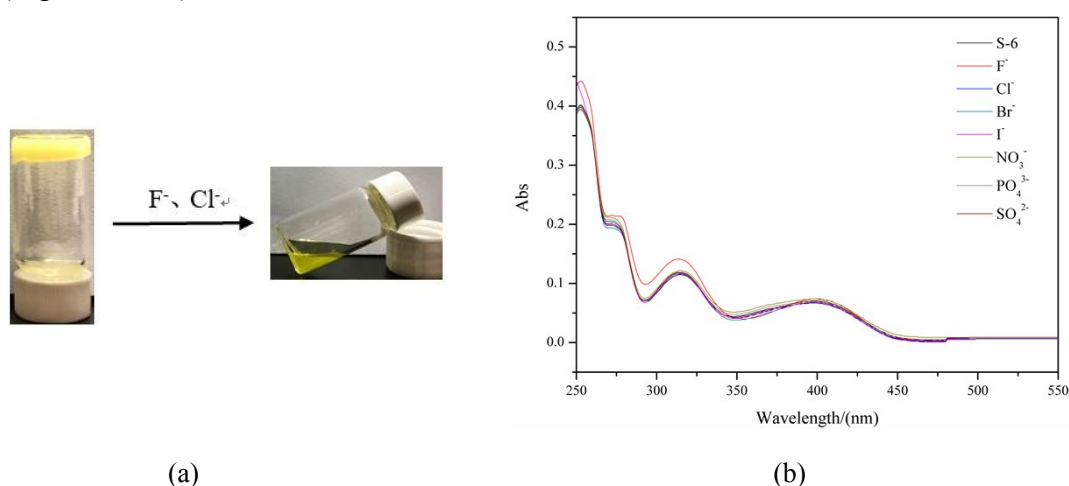


Figure S8. (a) Photographs of S-6/chloroform gel upon the addition of anions (b) UV-vis spectra of S-6 with addition of different anions in methanol

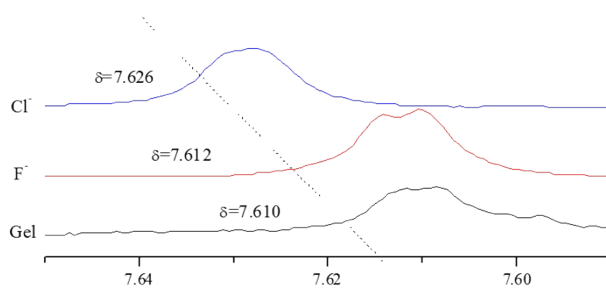


Figure S9. ^1H NMR spectra of S-6 in chloroform with different anions

5. Characteristics about the response to cations

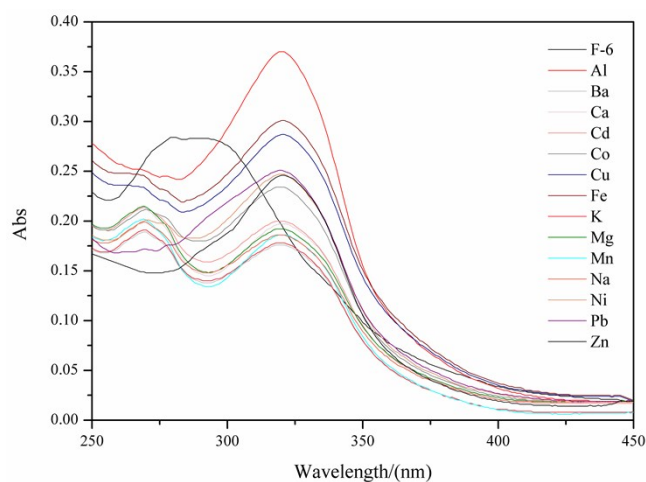


Figure S10. UV-vis spectra of F-6 with addition of different metal ions in $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (8:2)

(Na^+ , K^+ , Ba^{2+} , Mg^{2+} , Ca^{2+} , Al^{3+} , Fe^{3+} , Cu^{2+} , Pb^{2+} , Zn^{2+} , Cd^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+})

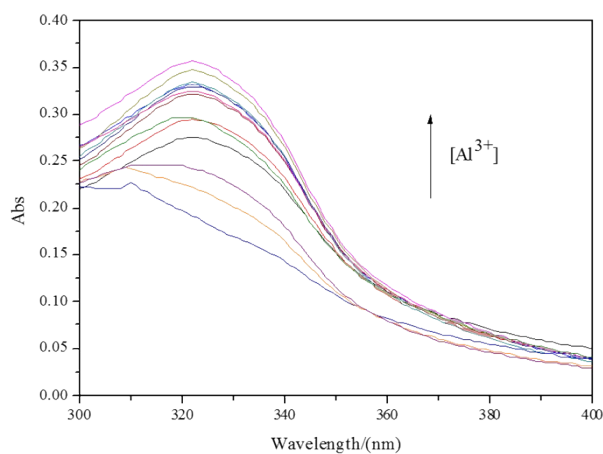


Figure S11. UV-vis spectra of F-6 after addition of increasing amounts of Al^{3+}
(from up to down: 10, 20, 30, 40, 50, 55, 60, 65, 70, 75, 80, 85, 90 μM)

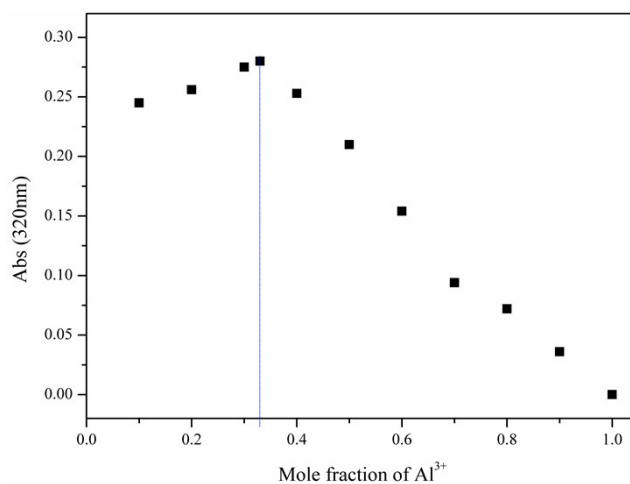


Figure S12. Job's plot for F-6 with Al³⁺

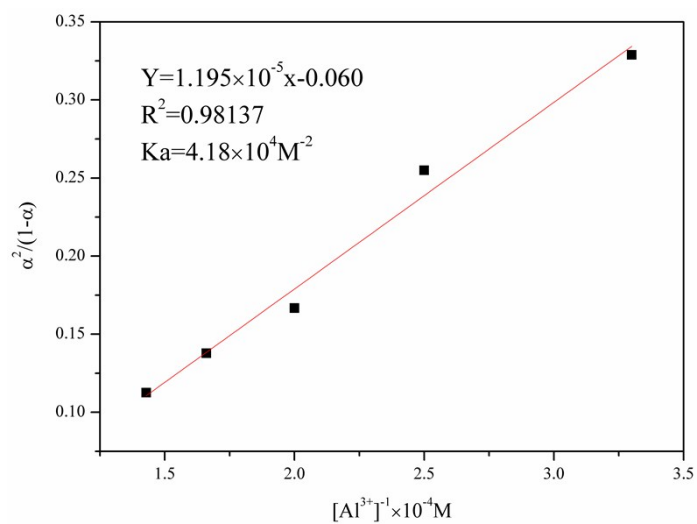


Figure S13. Association constant calculation by plotting $\alpha^2/(1-\alpha)$ vs $[\text{Al}^{3+}]^{-1}$ with linear fitting as well to find out the binding constant of F-6--Al³⁺

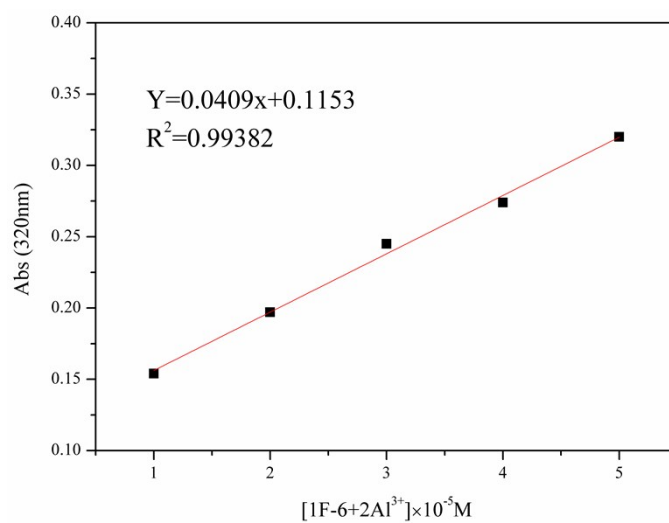


Figure S14. Calibration curve for F-6 with Al³⁺

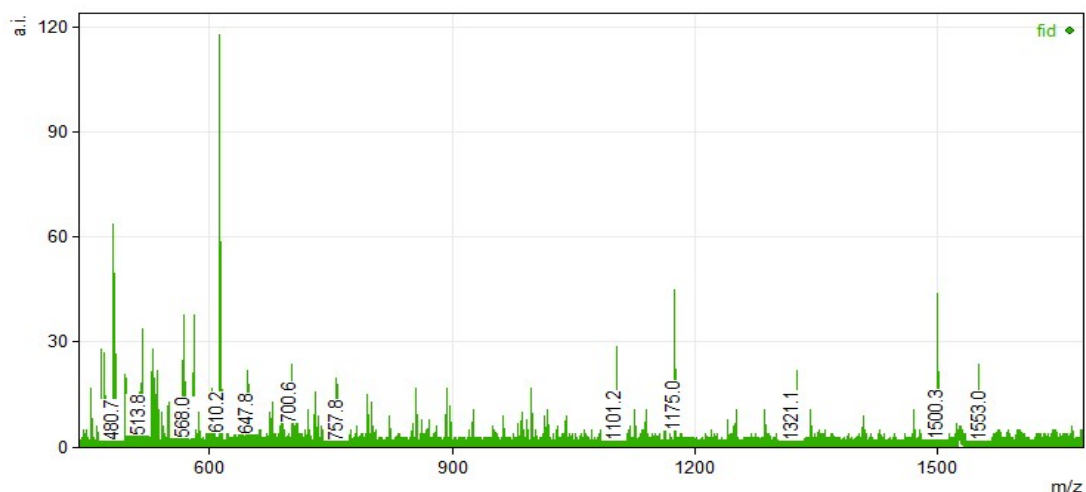


Figure S15. MALDI-TOF mass spectrum of [(F-6)₂-Al³⁺+1]⁺ (m/z=1321.1)

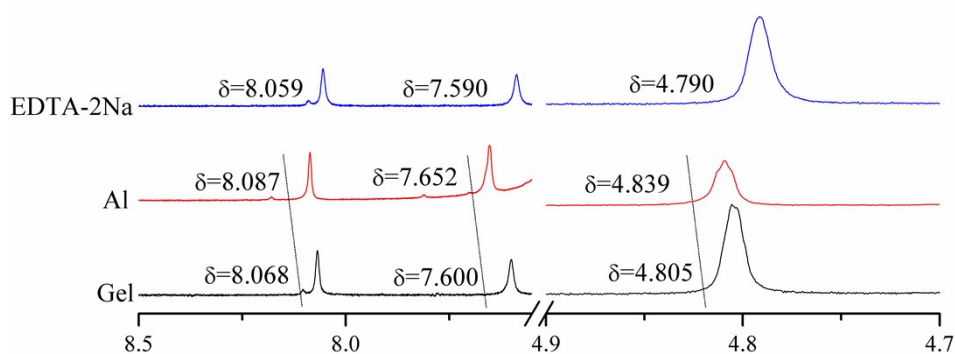


Figure S16. ¹H NMR titration of F-6 upon addition of Al³⁺ ion

In order to compare the influence of the group of ferrocene and salicylaldehyde on the response to cations, the metal binding interaction between S-6 and cations was also tested under the same conditions. The results showed that the addition of Al³⁺, Fe³⁺, Cu²⁺, Pb²⁺ converted the gel into solution without the color change. The reversible gel- sol transition was also achieved by adding an equivalent of EDTA-2Na. The absorption about 400nm nearly disappeared with Al³⁺, Fe³⁺, Cu²⁺, Pb²⁺ from UV/Vis spectroscopy in methanol/H₂O (8:2) (Figure S17). The interaction between S-6 and Al³⁺ was also investigated (Figure S18-S21). The proposed structure of S-6 and Al³⁺ was shown in Scheme S7. The conclusive stoichiometric ratio between S-6 and Al³⁺ was determined to be 2:1 and the detection limit of S-6 for the analysis of Al³⁺ was 8.71×10^{-6} M, which was higher than F-6.

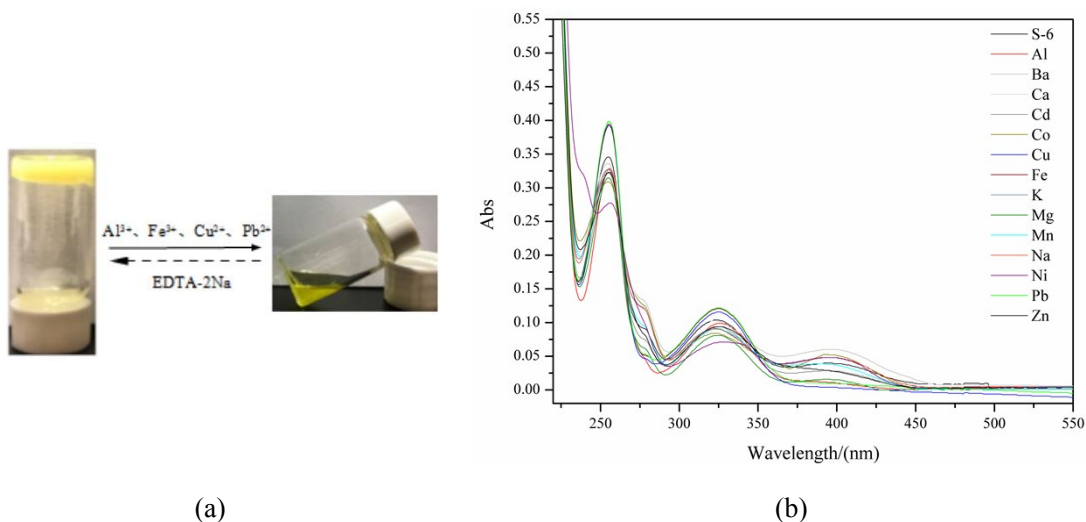


Figure S17. (a) Photographs of S-6/chloroform gel upon the addition of cations (Na^+ , K^+ , Ba^{2+} , Mg^{2+} , Ca^{2+} , Al^{3+} , Fe^{3+} , Cu^{2+} , Pb^{2+} , Zn^{2+} , Cd^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+}) (b) UV-vis spectra of S-6 with addition of different cations in methanol/ H_2O (8:2)

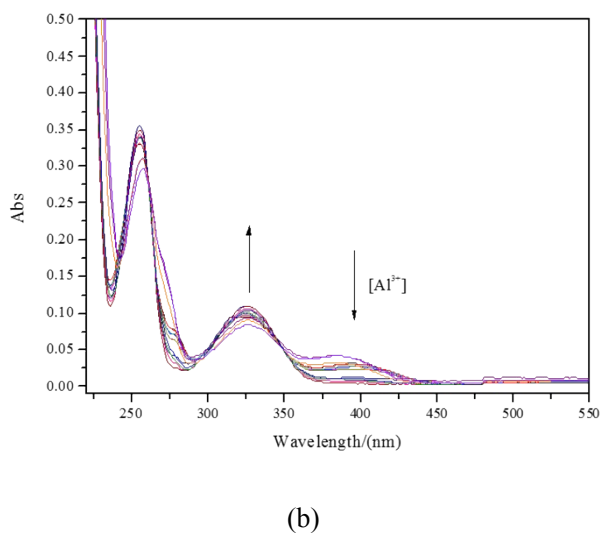
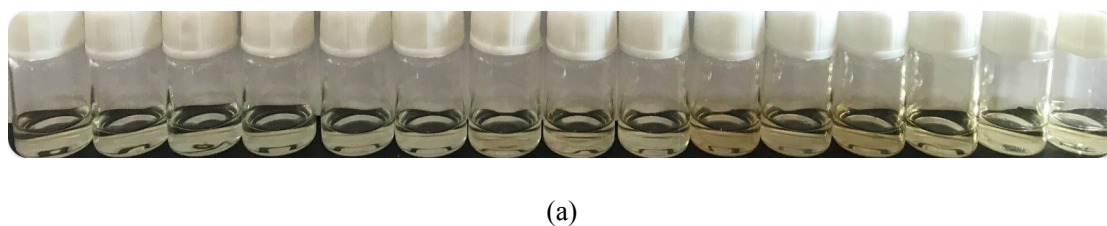


Figure S18. (a) Photographs of S-6 in methanol/ H_2O (8:2) solution and followed by the addition of metal ions (from left to right: blank sample, Na^+ , K^+ , Ba^{2+} , Mg^{2+} , Ca^{2+} , Al^{3+} , Fe^{3+} , Cu^{2+} , Pb^{2+} , Zn^{2+} , Cd^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+}) (b) UV-vis spectra of S-6 after addition of increasing amounts of Al^{3+}

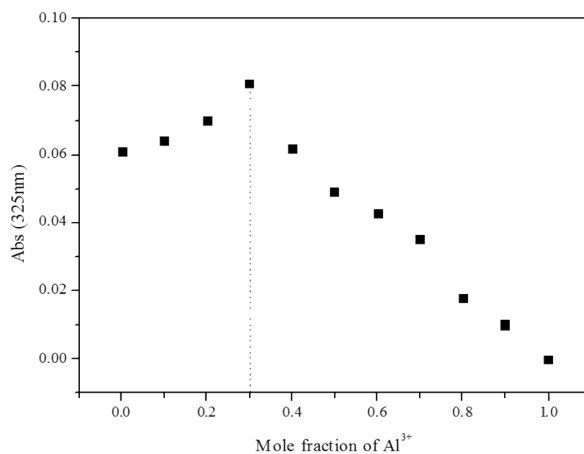


Figure S19. Job's plot for S-6 with Al^{3+}

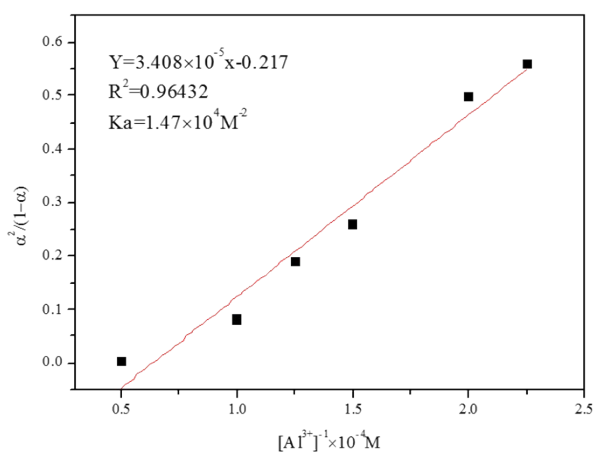


Figure S20. Association constant calculation by plotting $\alpha^2/(1-\alpha)$ vs $[\text{Al}^{3+}]^{-1}$ with linear fitting as well to find out the binding constant of S-6-- Al^{3+}

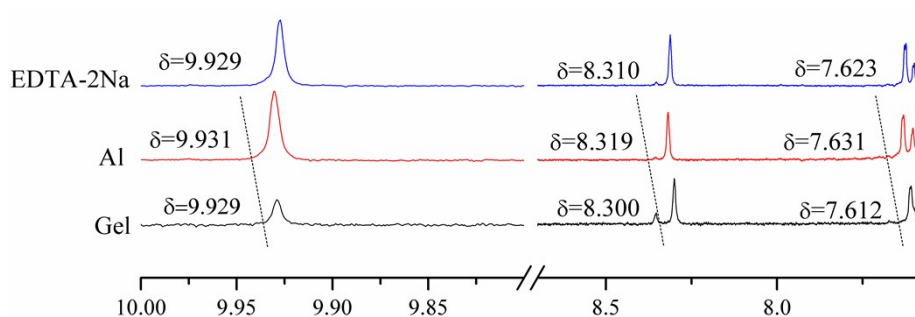
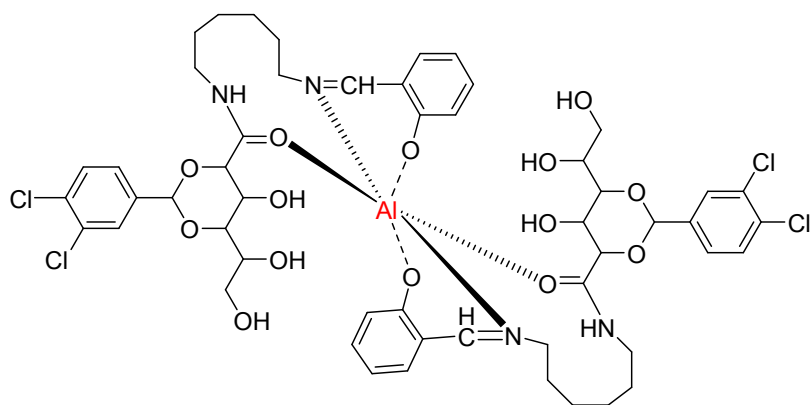


Figure S21. ^1H NMR titration of S-6 upon addition of Al^{3+} ion



Scheme S7. Proposed structure of S-6 with Al (III) complex