Supporting Information

β-Cyclodextrin Modified Imidazole Probe Specific Recognition of Organic Acids Based on Nuclear Magnetic Resonance

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1. Experimental

1.1 Chemicals and instruments

Ultrapure H_2O and HPLC grade CH_3CN were supplied from Tianjin Concord Technology Company (Tianjin, China). All the other Chemicals were purchased from Heowns (Tianjin, China). ^1H NMR was performed on a Varian Infinityplus 400 NMR spectrometer (400 MHz, 7.0 T; USA).

1.2 Preparation of allyl-imidazole CD

The cationic CD (AICD) was prepared according to the synthetic method of our group.[1,2]

1.3 Preparation of samples for NMR test

AMIMCl (5 mg, 0.03 mmol) and Gn (0.03 mmol) were dissolved in a beaker containing the solution CD_3OD/D_2O（v/v = 40:60, 0.6 mL）. Ultrasonicate the mixture to a clear solution. Wait to the desired time and go for the NMR test.

AICD (15 mg, 0.012 mmol) and Gn (0.012 mmol) were dissolved in a beaker containing the solution CD_3OD/D_2O（v/v = 40:60, 1 mL）. Ultrasonicate the mixture to a clear solution. Wait to the desired time and go for the NMR test.

1.4 Preparation of mixed samples (G1+Gn+AICD) for NMR test

AICD (30 mg, 0.024 mmol) and G1 (21.626 mg, 0.12 mmol) were dissolved in a beaker containing the solution of CH_3CN (5 mL) and H_2O (5 mL) to form a clarified solution. Subsequently, Gn (0.12 mmol) was added, and a bright yellow solution was formed by magnetic stirring at r.t. for 12 h. Then the solvent was distilled under reduced pressure. Finally, the crude solid product can be obtained by filtration after being washed with CH_3CN (5 mL×3). The solid product should be dried at 60℃ in vacuum oven before doing the nuclear magnetic resonance (NMR) test.

The mixture of G1 and AICD exhibits a distinctive peak characteristic (one single peak at approximately 7.54 ppm) as previously described. G1 was employed as an internal standard substance, and G2, G3, G4, G5, and G6 were added to the aforementioned mixture of G1+ AICD (Fig.S-13). After 24 h of stirring at room temperature, the solvent was removed under a low pressure. The guest molecules who didn't interact with AICD were then washed away with CH_3CN, and the resulting products were dried and characterized by ^1H NMR. The Fig. S-3 illustrates that G1+G2+AICD, G1+G3+AICD, G1+G5+AICD, and G1+AICD all exhibit the same characteristic peaks, indicating that they are all G1+AICD. This indicates that G1 is capable of occupying all the available cavities of the CD, resulting in its ultimate retention. When the same molar amounts of G1 and G2 are mixed with positively charged cyclodextrin probes, the characteristic peaks are observed to manifest as AICDG1. It can thus be postulated that adamantyl groups are more prone to forming complexes with CDs than phenyl groups. In contrast, the G1+G4+AICD and G1+G6+AICD samples display the characteristic peaks that are not a single peak at approximately 7.54 ppm (Fig. S-3). It can be reasonably inferred that sulfonic acid groups are more prone to forming complexes with positively charged cyclodextrin probes in comparison to carboxylic acid groups. Given that sulfonic acids are more acidic than carboxylic acids, the combined effect of electrostatic interactions on host-guest interactions is greater than that of inclusion interactions.

1.5 Preparation of AICD+G1 with different chemical equivalents

AICD (30 mg, 0.024 mmol) were dissolved in a beaker containing the solution of D_2O (0.6 mL) and CD_3OD (0.4 mL) to form a clarified solution. Subsequently, G1 (n mmol, n=0.012, 0.024, 0.048 respectively) was added and ultrasound the mixture for 30 min. Then do the nuclear magnetic resonance (NMR) test.

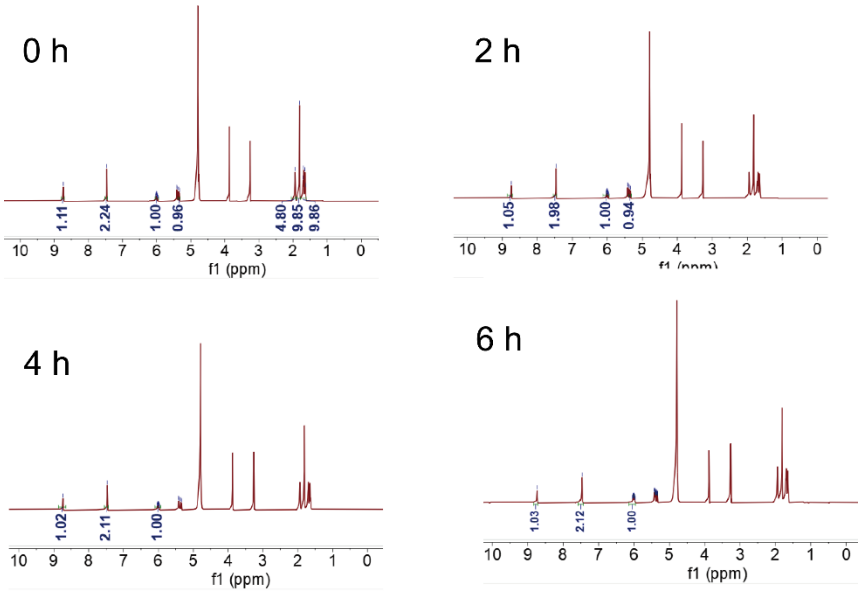

Fig. S-1 The ^{1}H NMR spectrum of AMMCl and G1 at different time.

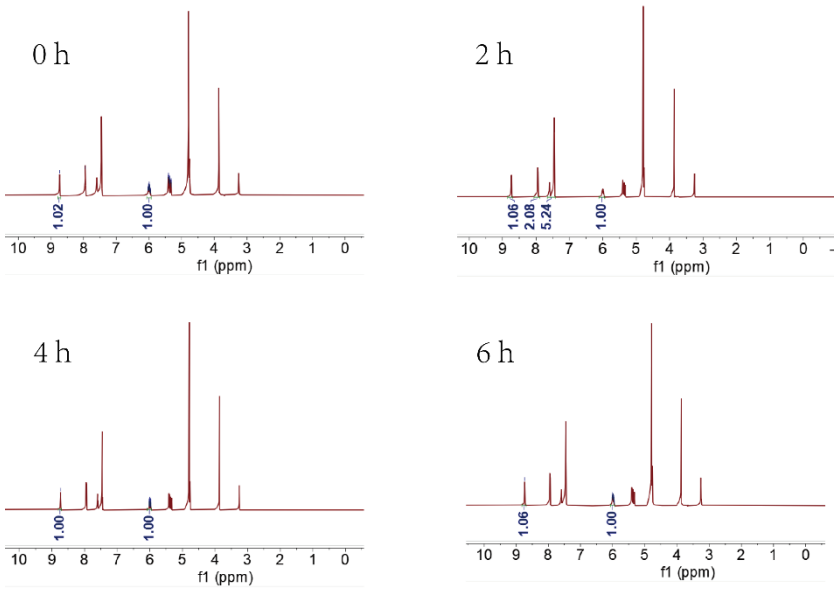

Fig. S-2 The ^{1}H NMR spectrum of AMMCl and G2 at different time.

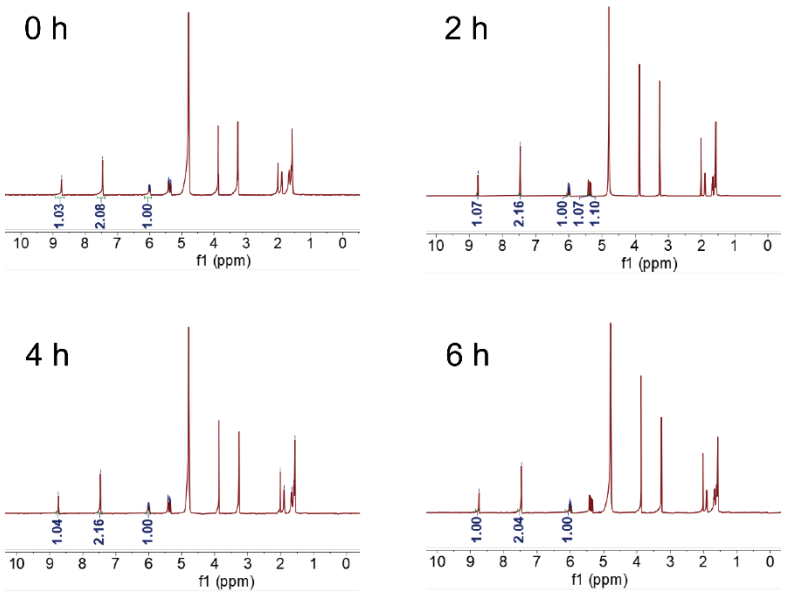

Fig. S-3 The ^{1}H NMR spectrum of AMMCl and G3 at different time.

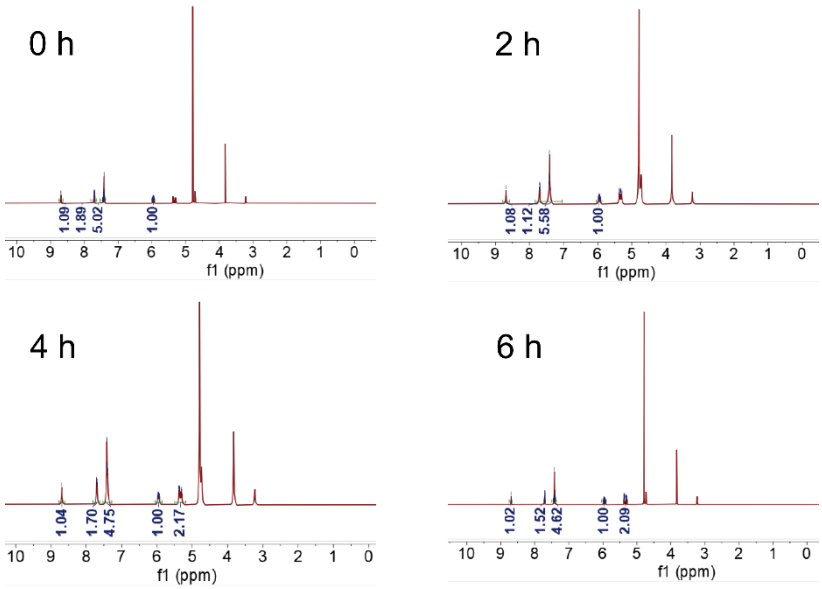

Fig. S-4 The ^{1}H NMR spectrum of AMMCl and G4 at different time.

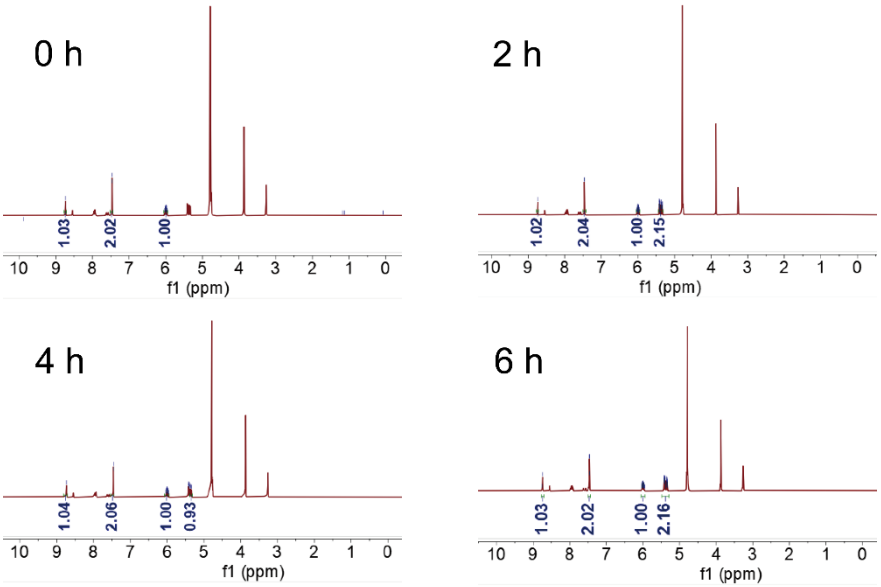

Fig. S-5 The ^{1}H NMR spectrum of AMMCl and G5 at different time.

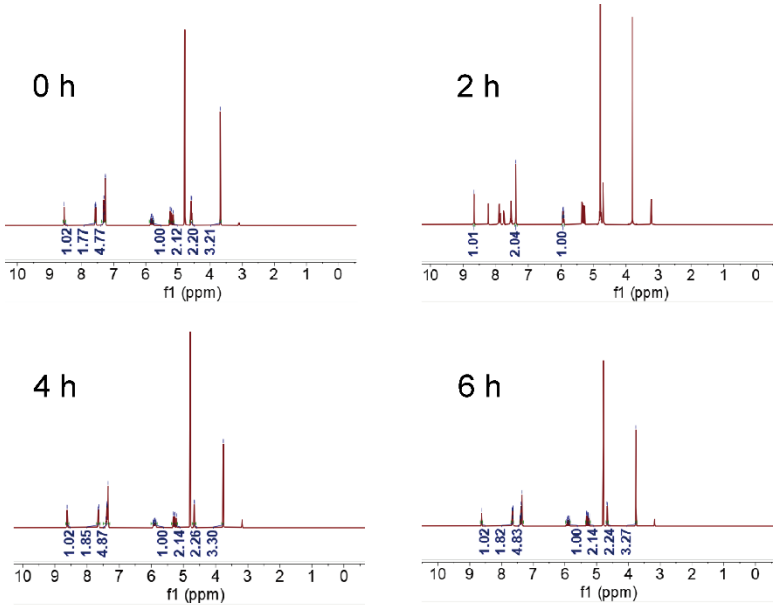

Fig. S-6 The ^{1}H NMR spectrum of AMMCl and G6 at different time.

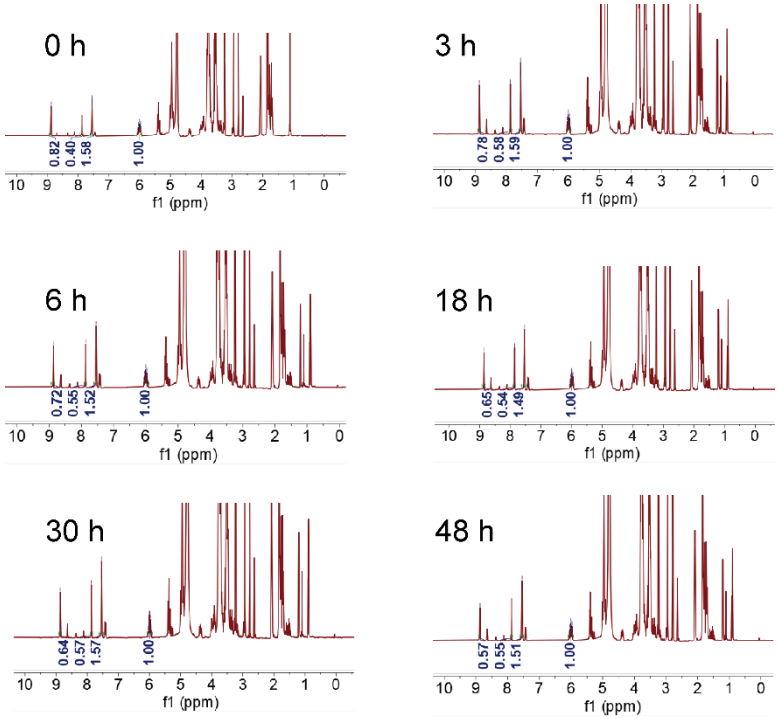

Fig. S-7 The ^{1}H NMR spectrum of AICD and G1 at different time.

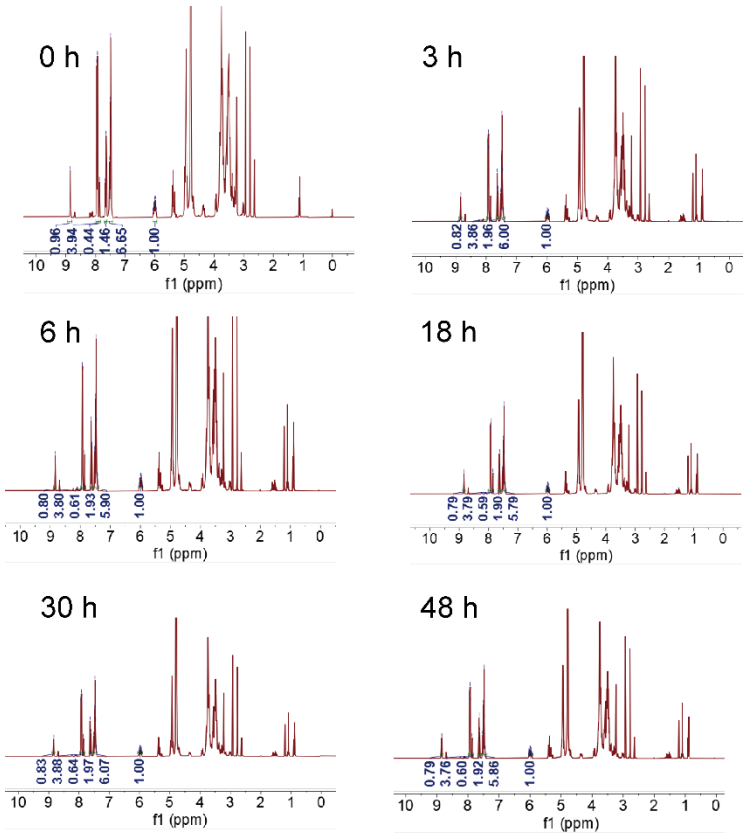

Fig. S-8 The ^{1}H NMR spectrum of AICD and G2 at different time.

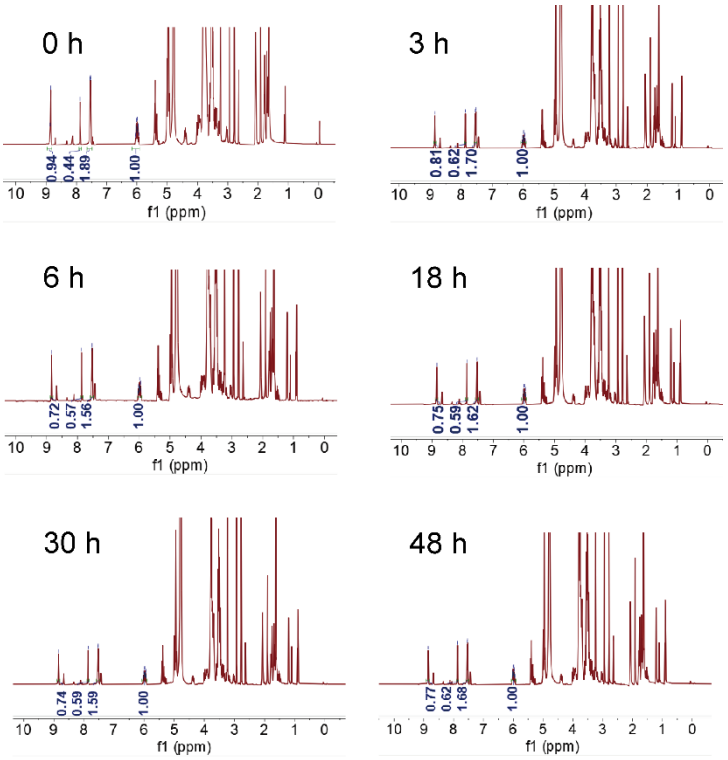

Fig. S-9 The ^{1}H NMR spectrum of AICD and G3 at different time.

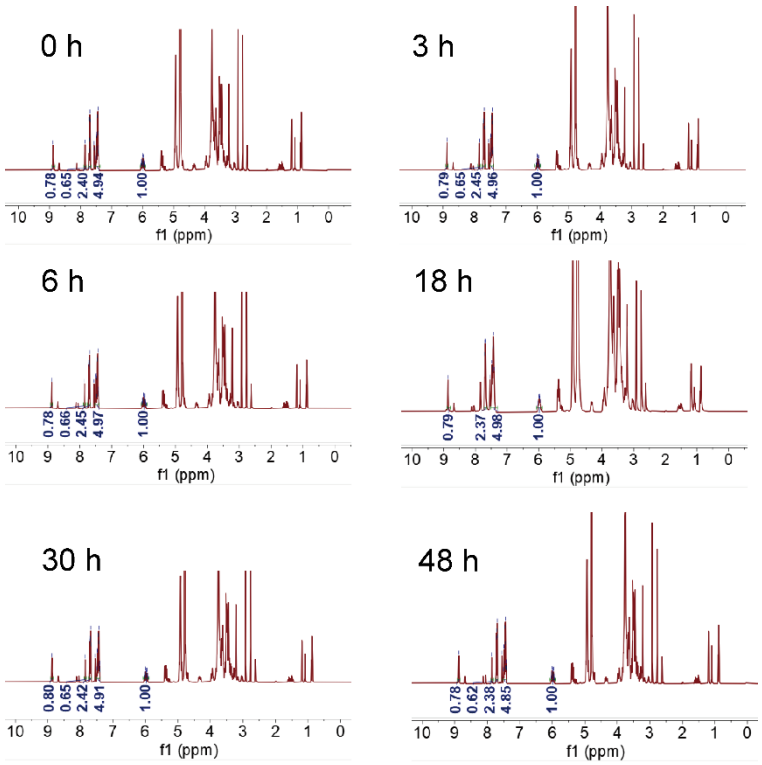

Fig. S-10 The ^{1}H NMR spectrum of AICD and G4 at different time.

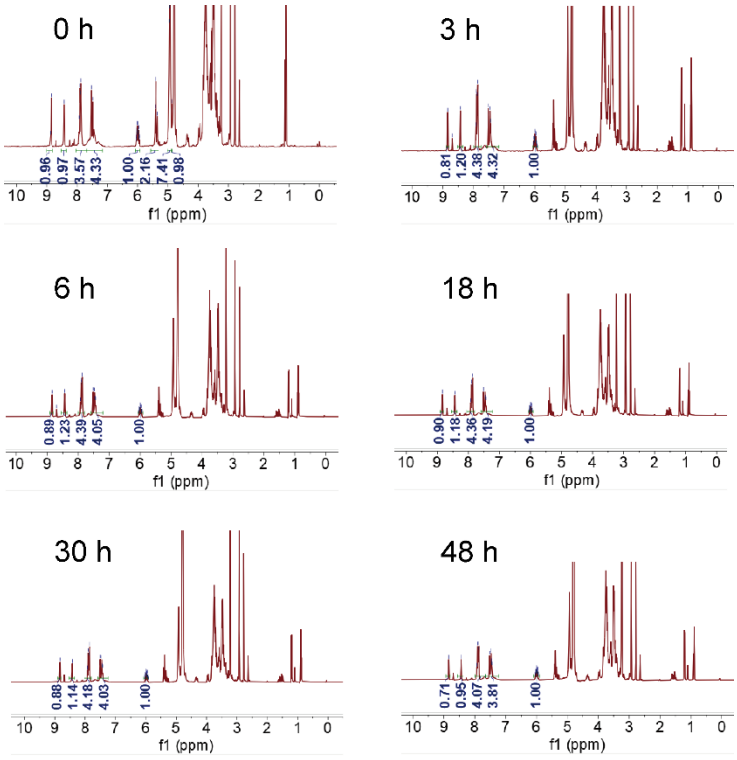

Fig. S-11 The ^{1}H NMR spectrum of AICD and G5 at different time.

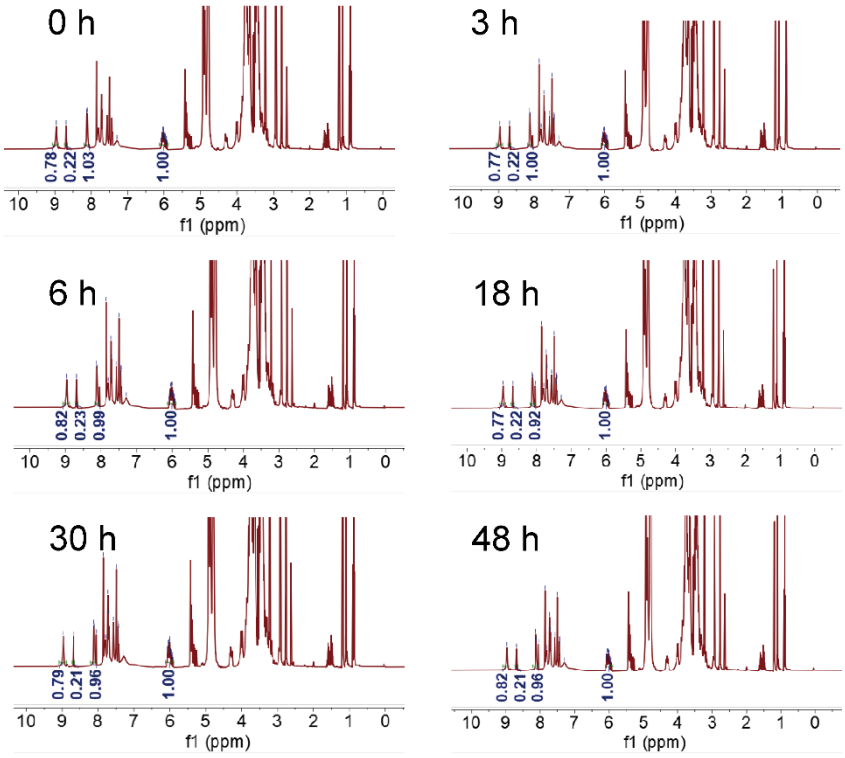

Fig. S-12 The ^{1}H NMR spectrum of AICD and G6 at different time.

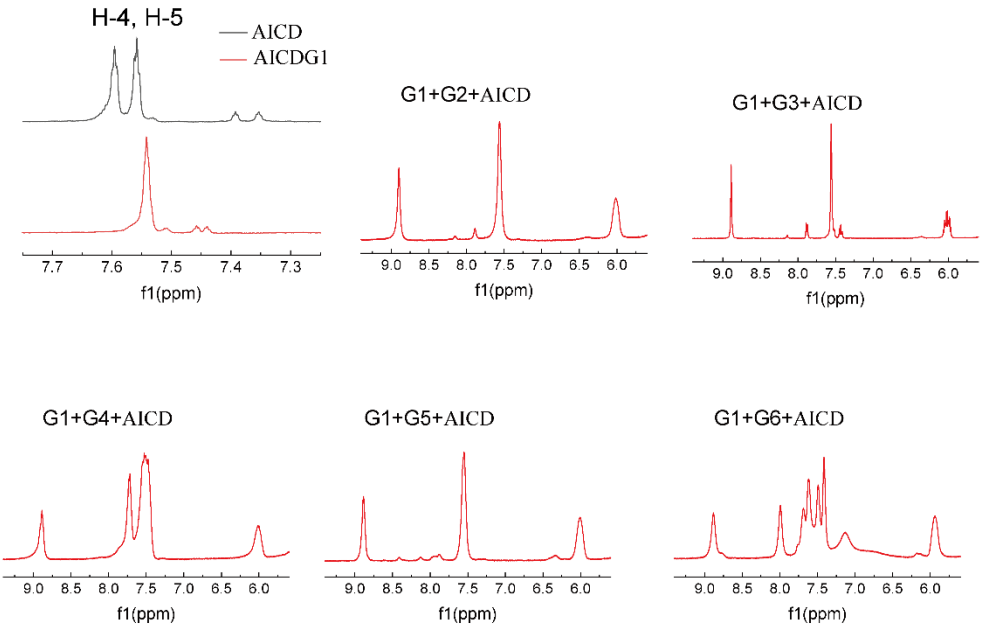

Fig. S-13. ^{1}H NMR spectra of the mixed samples were obtained after a dissolution period of 6 h in CD_3OD/D_2O (40/60, v/v).

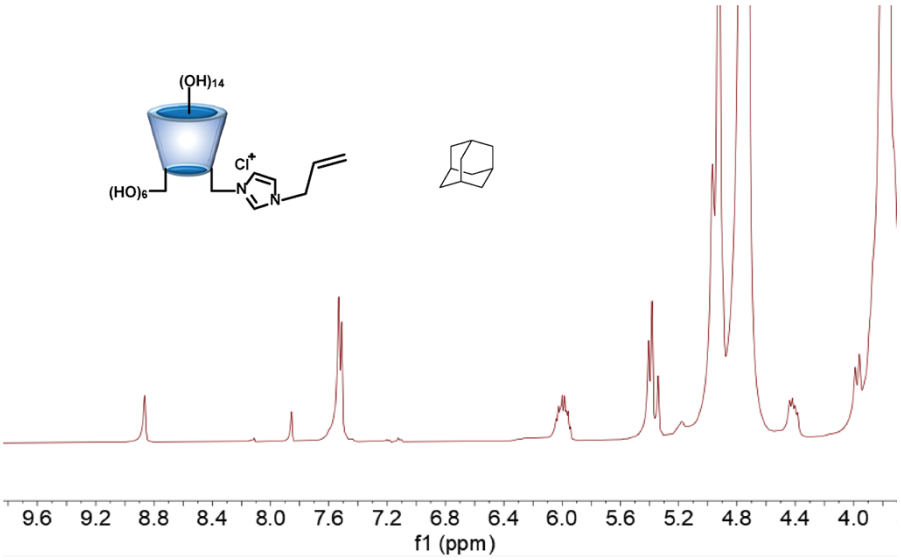

Fig. S-14. ^{1}H NMR spectra of the AICD mixed with adamantane were obtained after a dissolution period of 24 h in CD_3OD/D_2O (40/60, v/v).

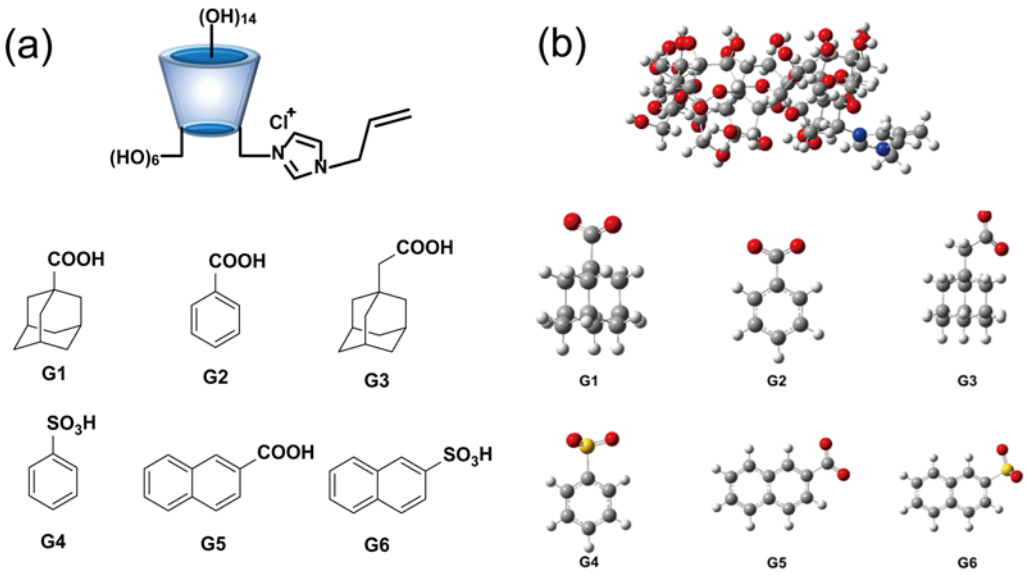

Fig. S-15 The structure of cationic CD and guest molecule.

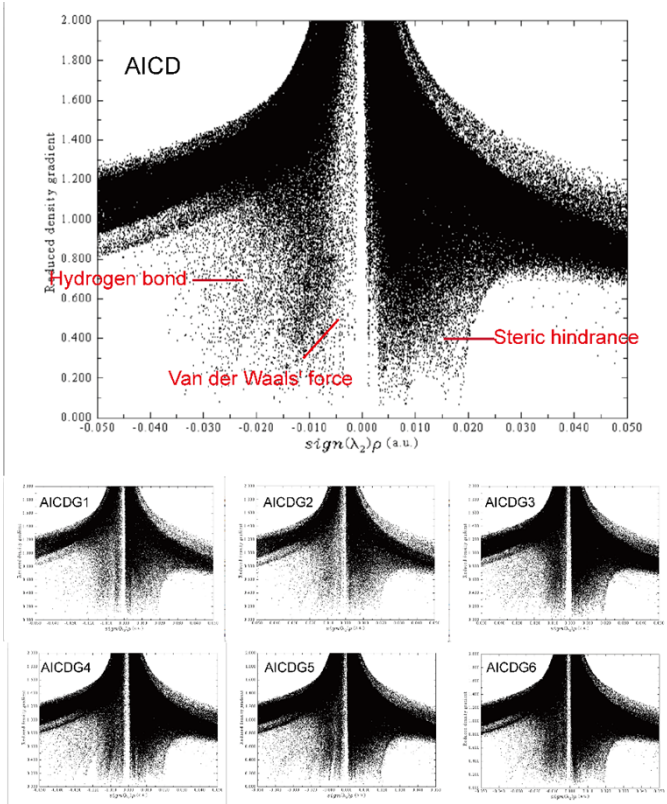

Fig. S-16. Scatterplots of S-sign(λ2)ρ for each system.

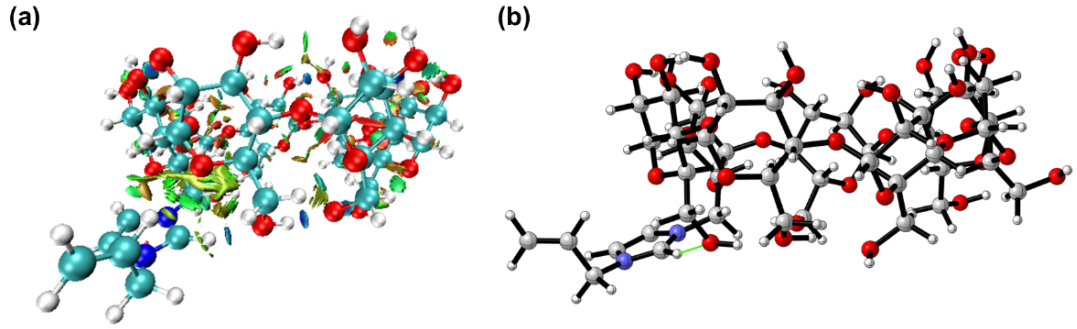

Fig. S-17 (a) Color-filled view of RDG isosurfaces for AICD; (b) Schematic of H-2 hydrogen bonding for AICD.

References

1. X. Lu, H. Xu, Y. Cheng, W. Liu and Y. Wang, *Langmuir*, 2023, **39**, 2779-2786.
2. Y. Li, X. Jin, Y. Xiao, X. Ma and Y. Wang, *Analyst*, 2023, **148**, 4987-4994.