Supplementary information for

Chemo- and Size-Selective Molecule Association of a Bowl-Type Dodecavanadate Cage

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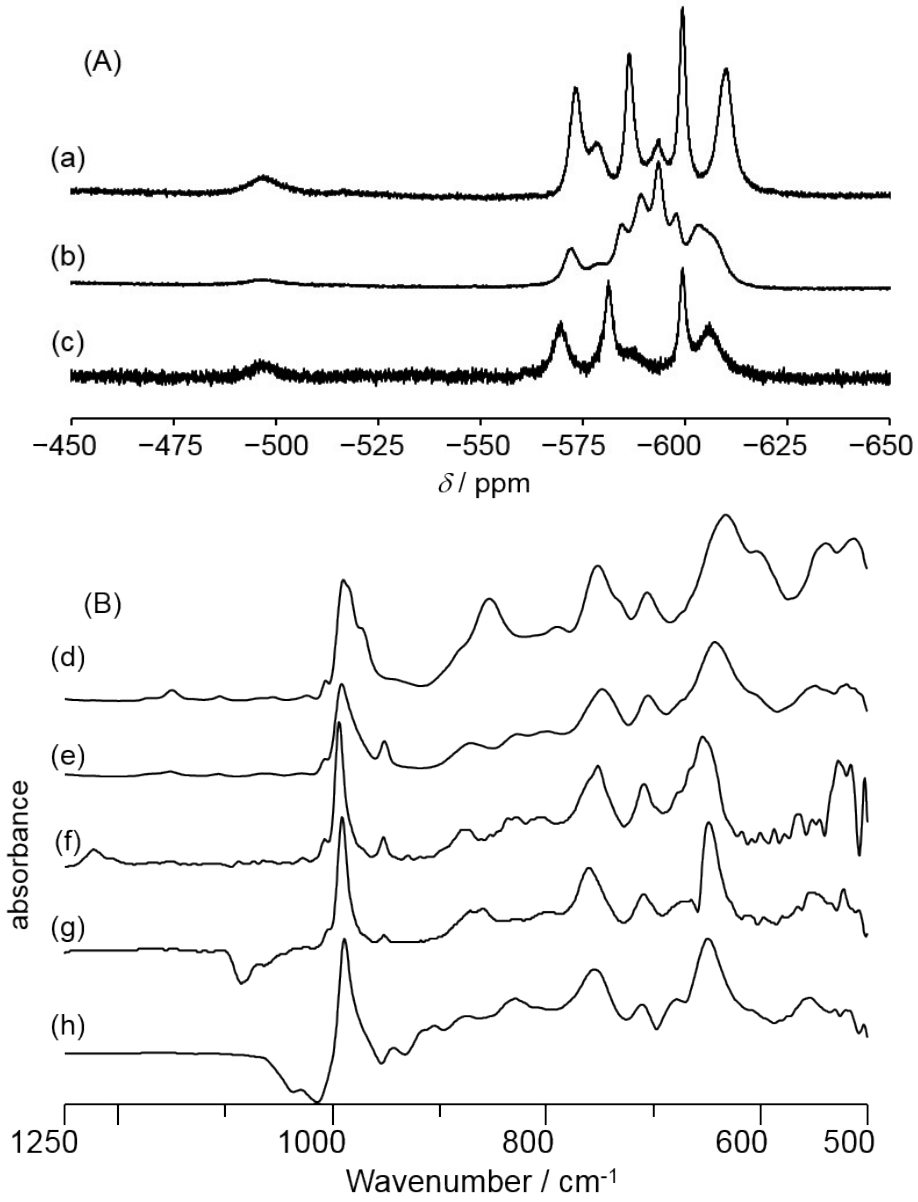

Figure S1. (A) ^{51}V NMR spectra of **V12-free** in (a) acetone, (b) DMF, and (c) DMSO. (B) IR spectra of (d) **V12(AN)** and (e) **V12-free** in the solid state, and **V12-free** in (f) acetone, (g) DMF, and (h) DMSO.

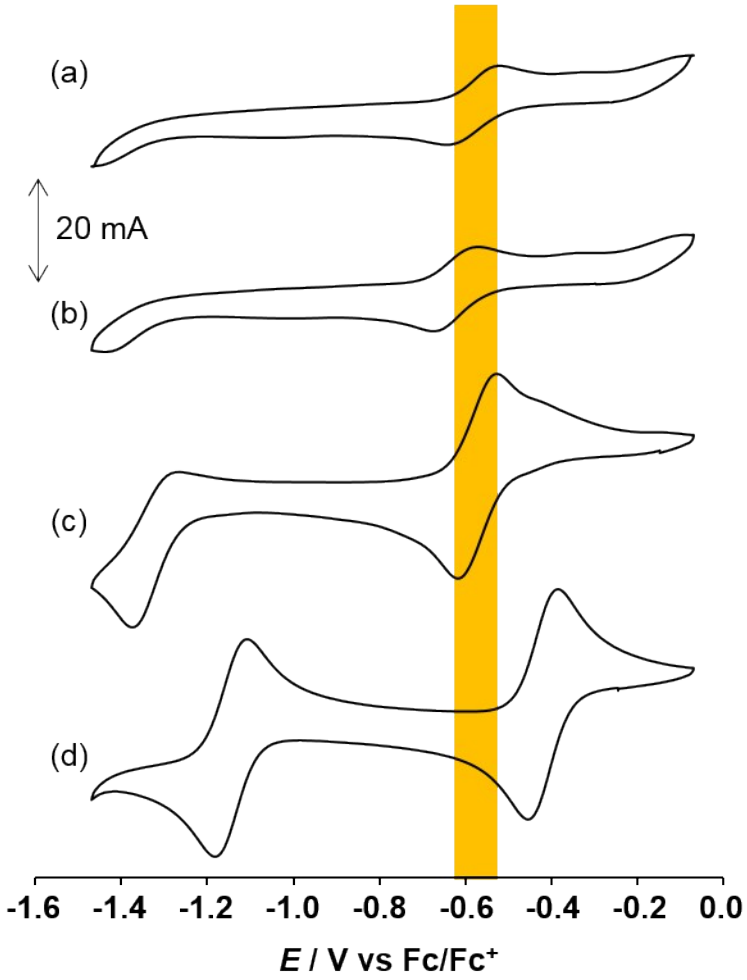

Figure S2. Cyclic voltammograms of **V12-free** in DMF (a) absent from AN and (b) in the presence of AN, (c) **V12-free** in acetone, and (d) **V12(AN)** in AN. Scan rate was 200 mV/sec. The supporting electrolyte was $\{n\text{-}Bu_4N\}PF_6$.

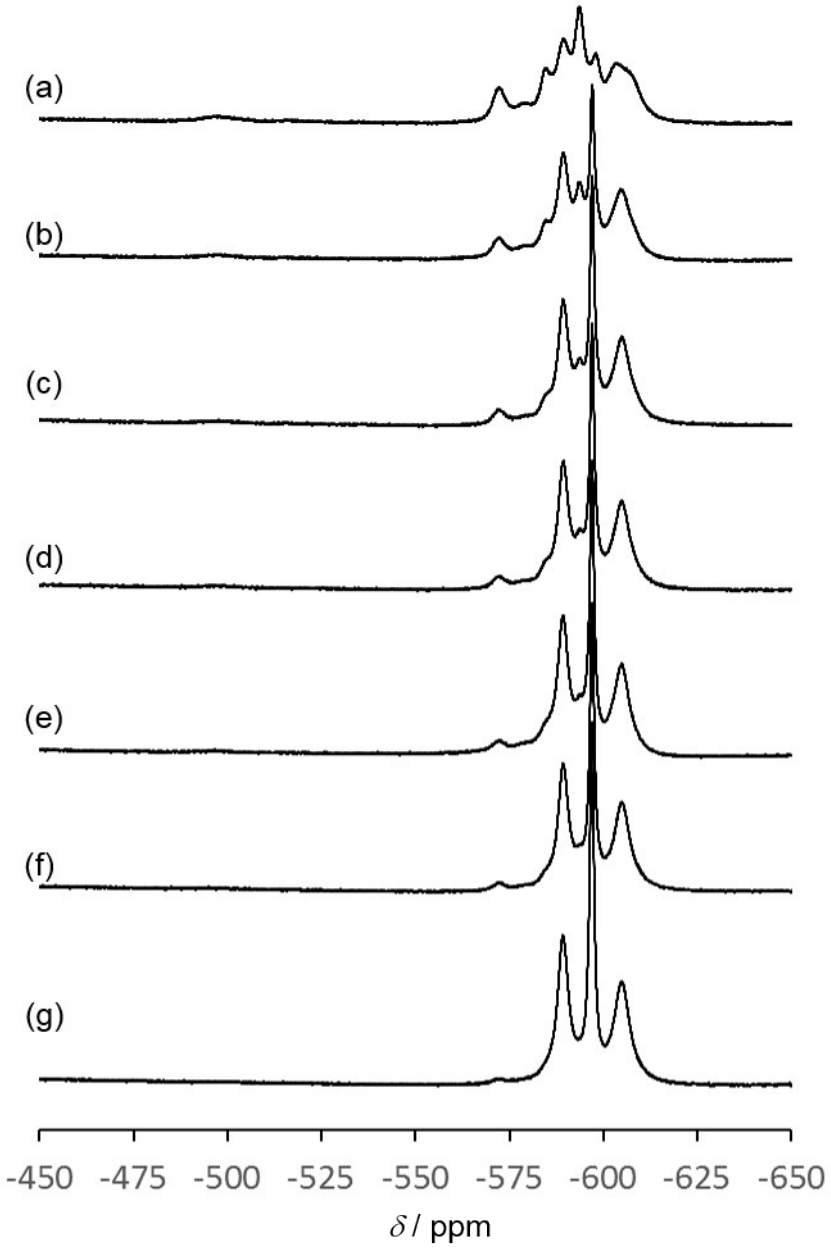

Figure S3. ^{51}V NMR spectra of **V12** in DMF in the presence of (a) 0, (b) 5, (c) 10, (d) 15, (e) 20, (f) 25, and (g) 50 equivalents of BN. From the spectra, the molar ratio of **V12-free** of (b) 55%, (c) 30%, (d) 20%, (e) 16%, (f) 12% , and (g) <1%, were determined.

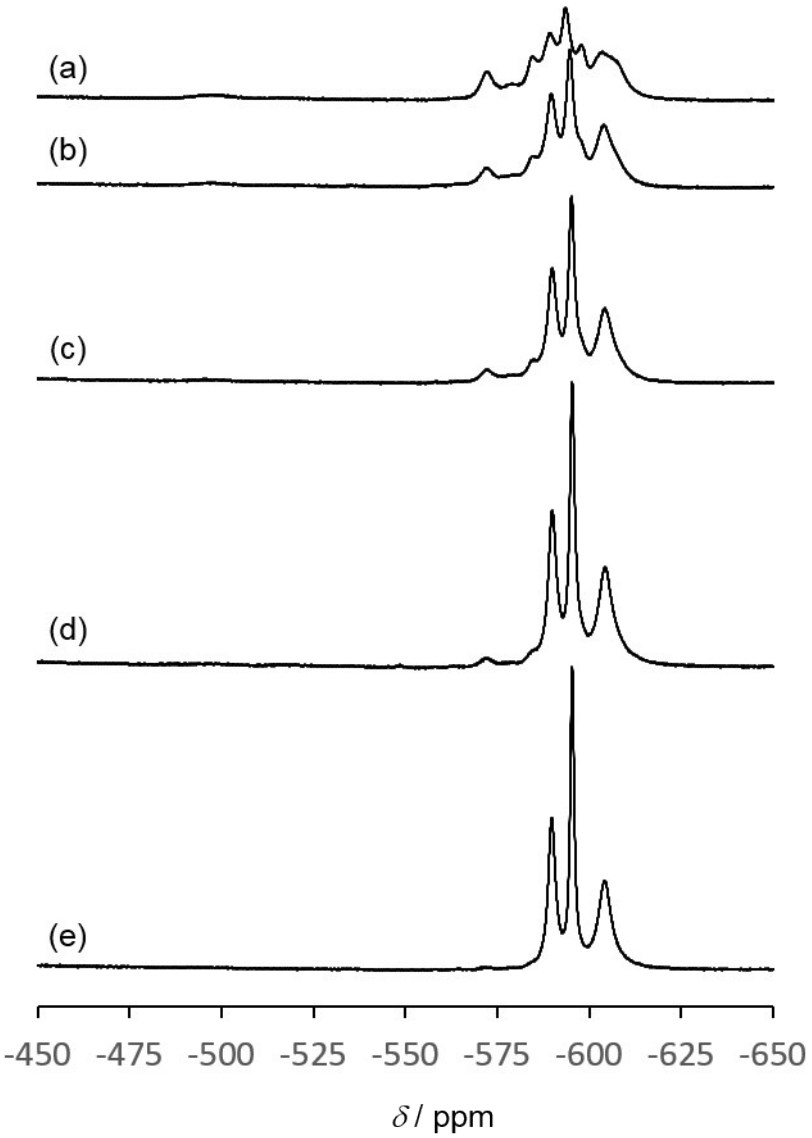

Figure S4. ^{51}V NMR spectra of **V12** in DMF in the presence of (a) 0, (b) 1, (c) 2, (d) 3.8, and (e) 15 equivalents of DCE. From the spectra, the molar ratio of **V12-free** of (b) 62%, (c) 42%, (d) 25%, and (e) <1%, were determined.

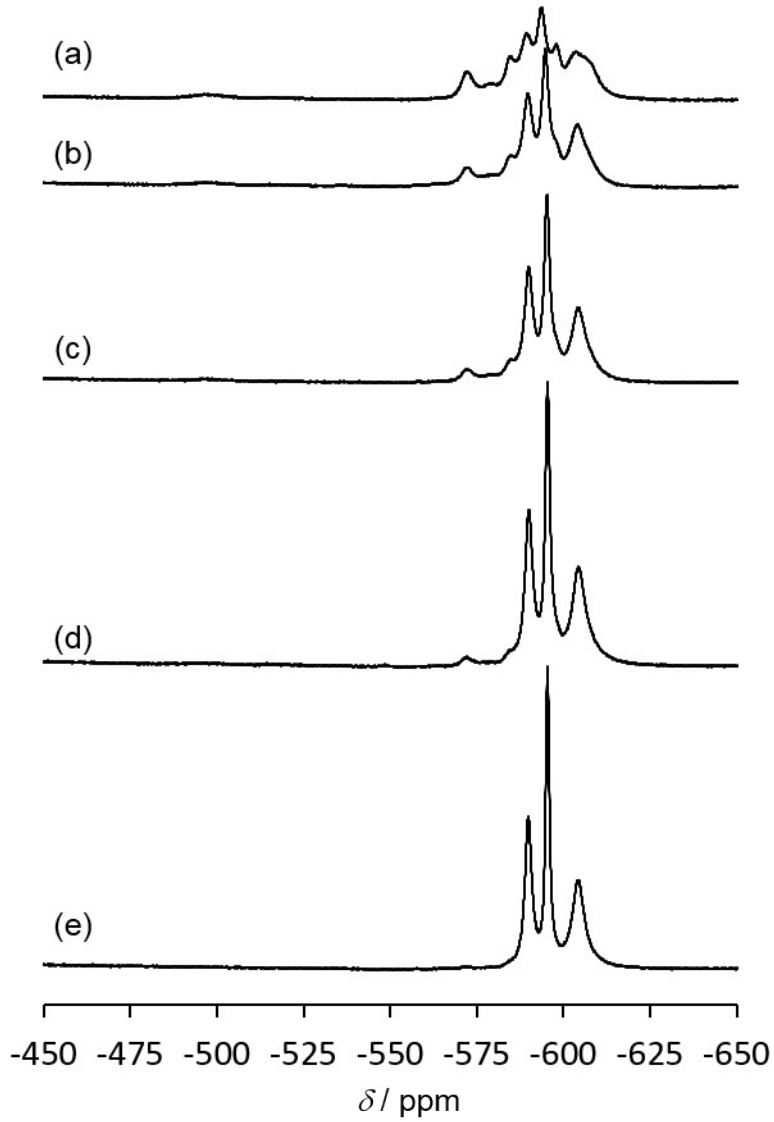

Figure S5. ^{51}V NMR spectra of **V12** in DMF with the total concentration of NM of (a) 0, (b) 3.7, (c) 7.5, and (d) 11, and (e) 30 M. From the spectra, the molar ratio of **V12-free** of (b) 70%, (c) 45%, (d) 40%, and (e) 20%, were determined.

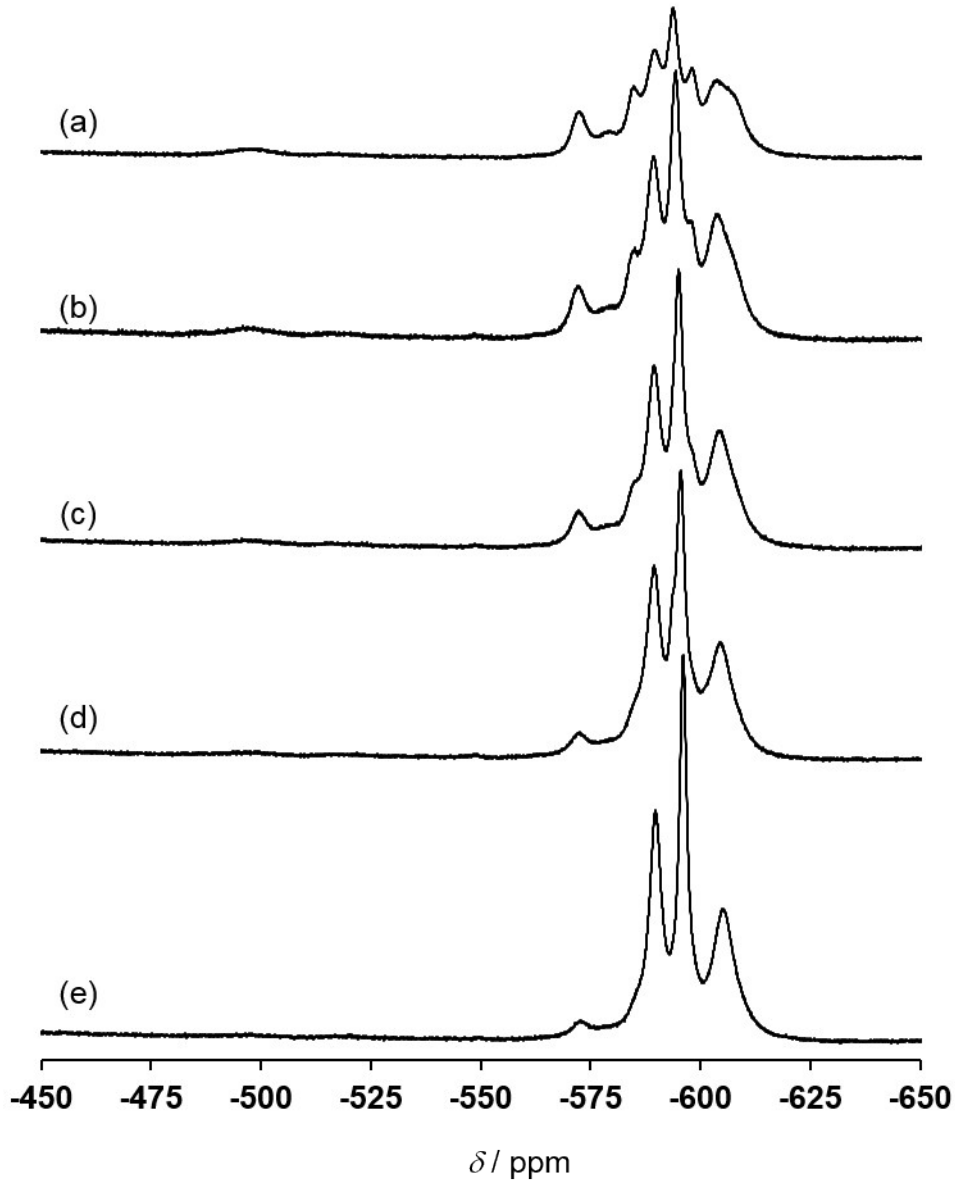

Figure S6. ^{51}V NMR spectra of **V12** in DMF with the total concentration of DCM of (a) 0, (b) 2.3, (c) 4.7, (d) 7.0, and (e) 9.4 M. From the spectra, the molar ratio of **V12-free** of (b) 65%, (c) 45%, (d) 36%, and (e) 30%, were determined.

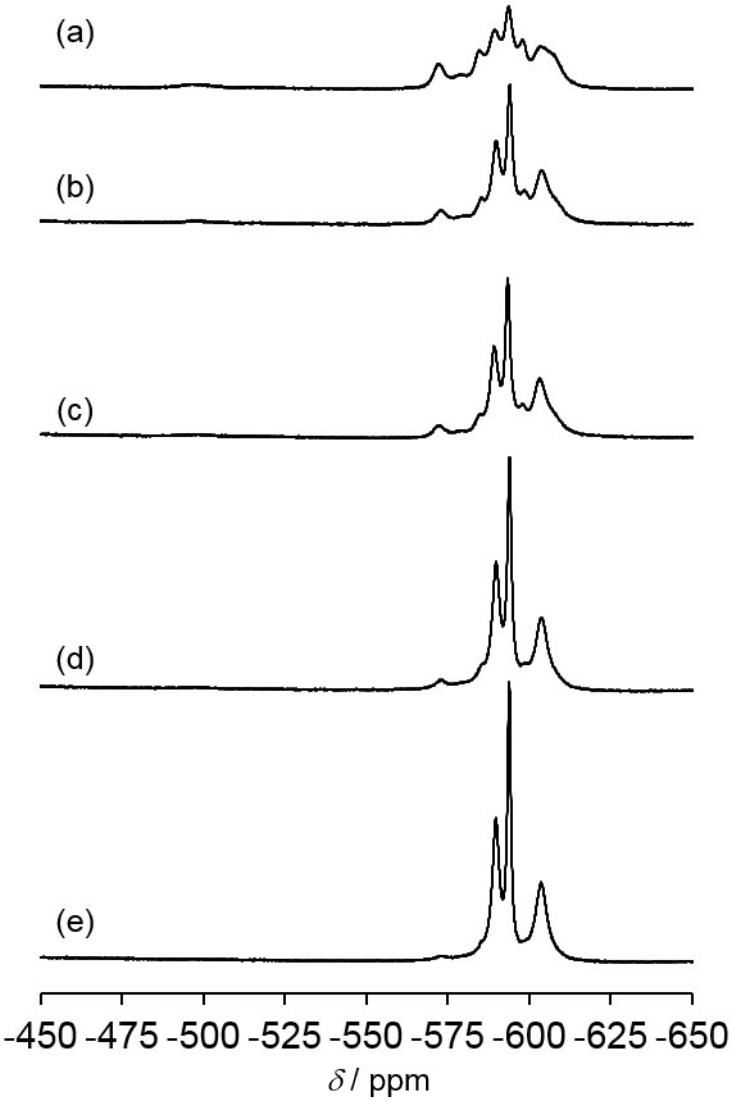

Figure S7. ^{51}V NMR spectra of **V12** in DMF in the presence of (a) 0, (b) 1, (c) 2, (d) 3, and (e) 5 equivalents of DBE. From the spectra, the molar ratio of **V12-free** of (b) 55%, (c) 43%, (d) 20%, and (e) <1%, were determined.

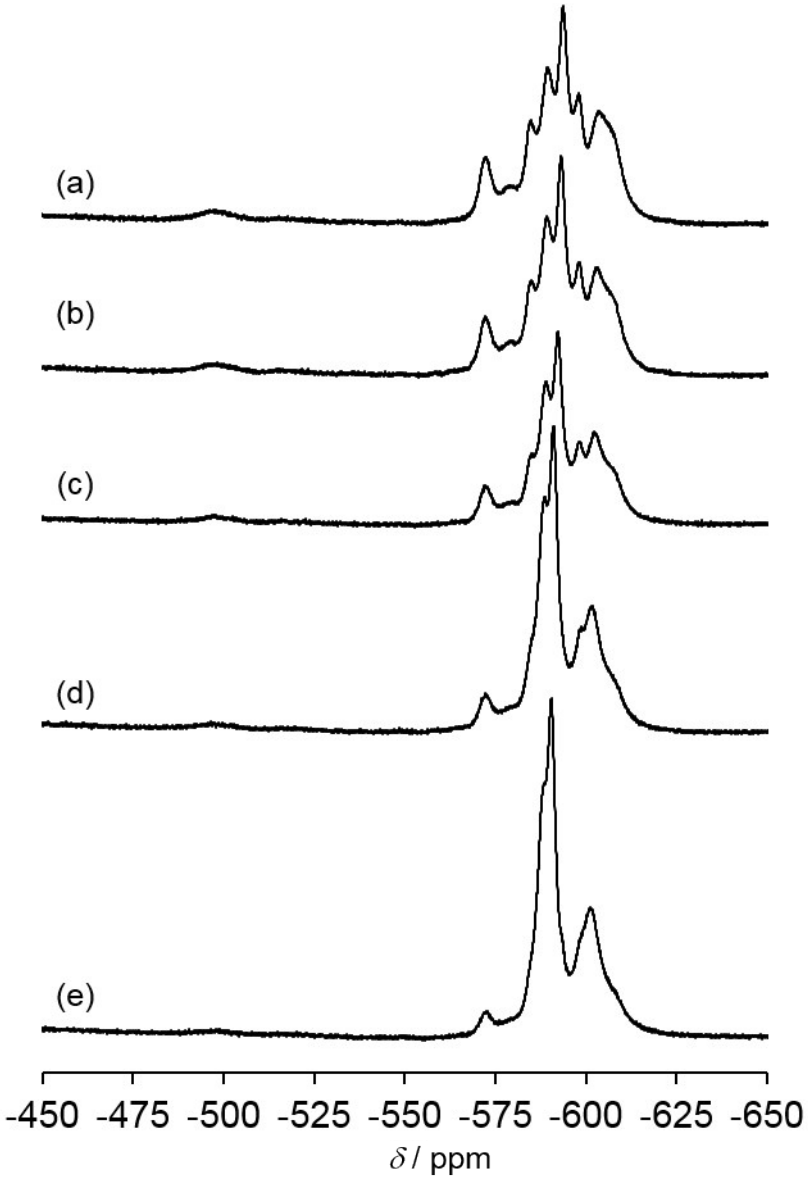

Figure S8. ^{51}V NMR spectra of **V12** in DMF in the presence of (a) 0, (b) 5, (c) 10, (d) 25, and (e) 50 equivalents of DIE. From the spectra, the molar ratio of **V12-free** of (b) 85%, (c) 65%, (d) 40%, and (e) 25%, were determined.

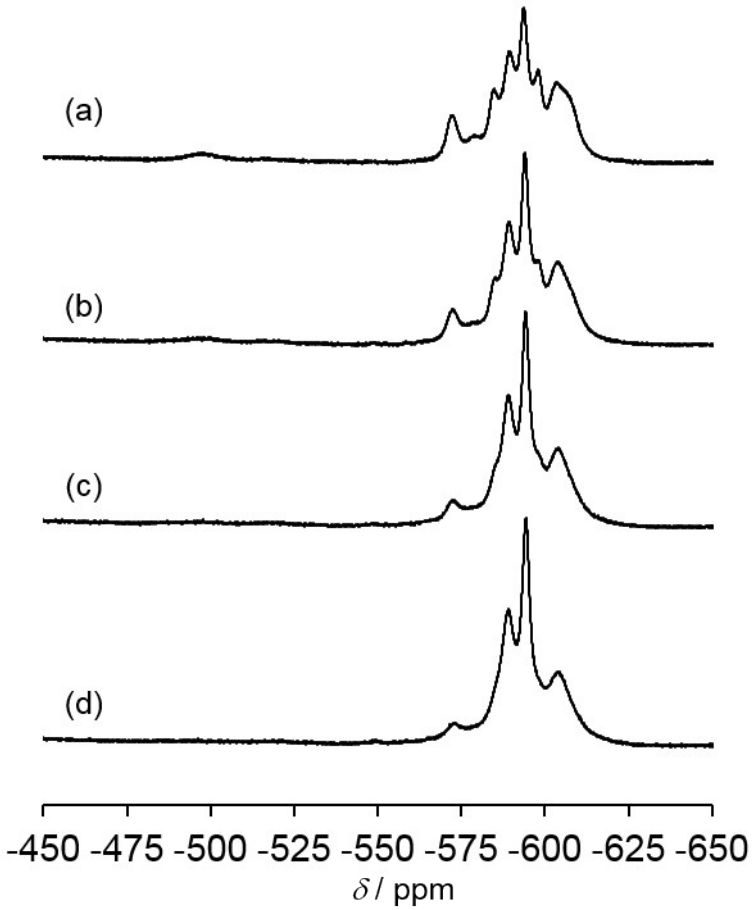

Figure S9. ^{51}V NMR spectra of **V12** in DMF with the total concentration of DBM of (a) 0, (b) 2.9, (c) 5.8, and (d) 8.6 M. From the spectra, the molar ratio of **V12-free** of (b) 63%, (c) 43%, and (d) 33%, were determined.

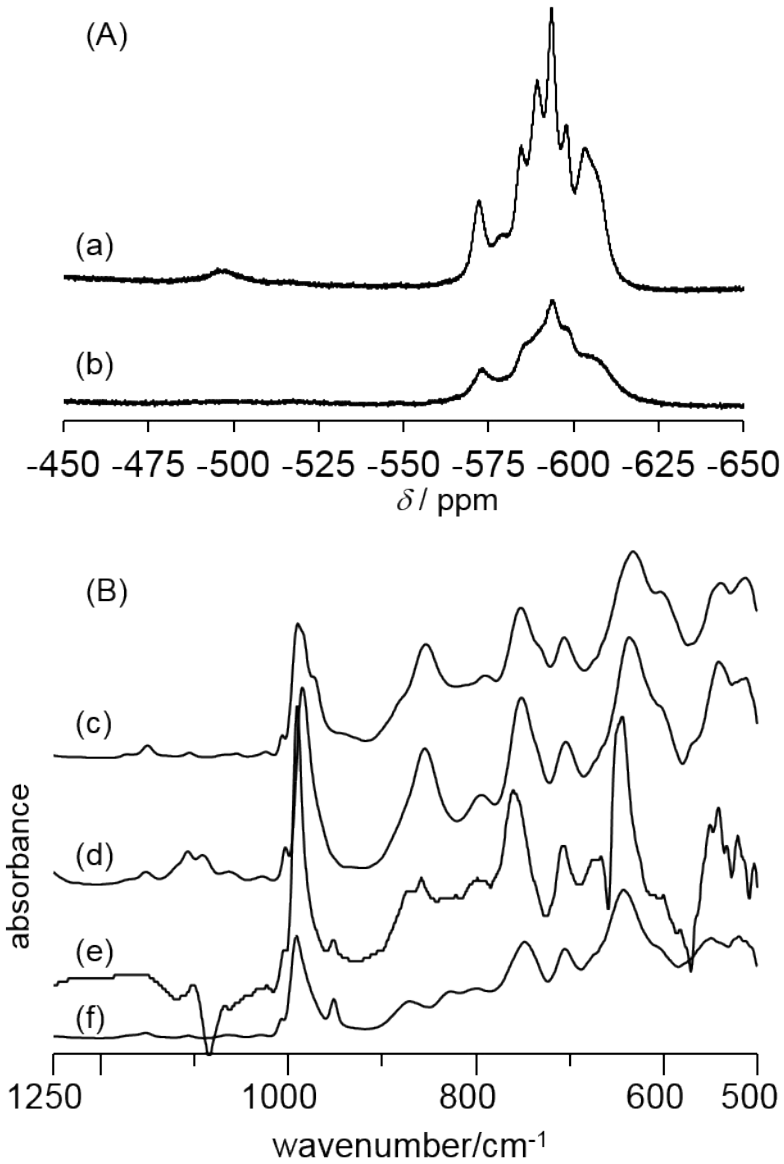

Figure S10. (A) ^{51}V NMR spectra of **V12** in (a) DMF and (b) in the mixed solvent of DMF and DIM (1:1, v/v) after the filtration. (B) IR spectra of (c) the precipitates, (d) **V12(AN)**, (e) the filtrate (solution state IR), and (f) **V12-free**.

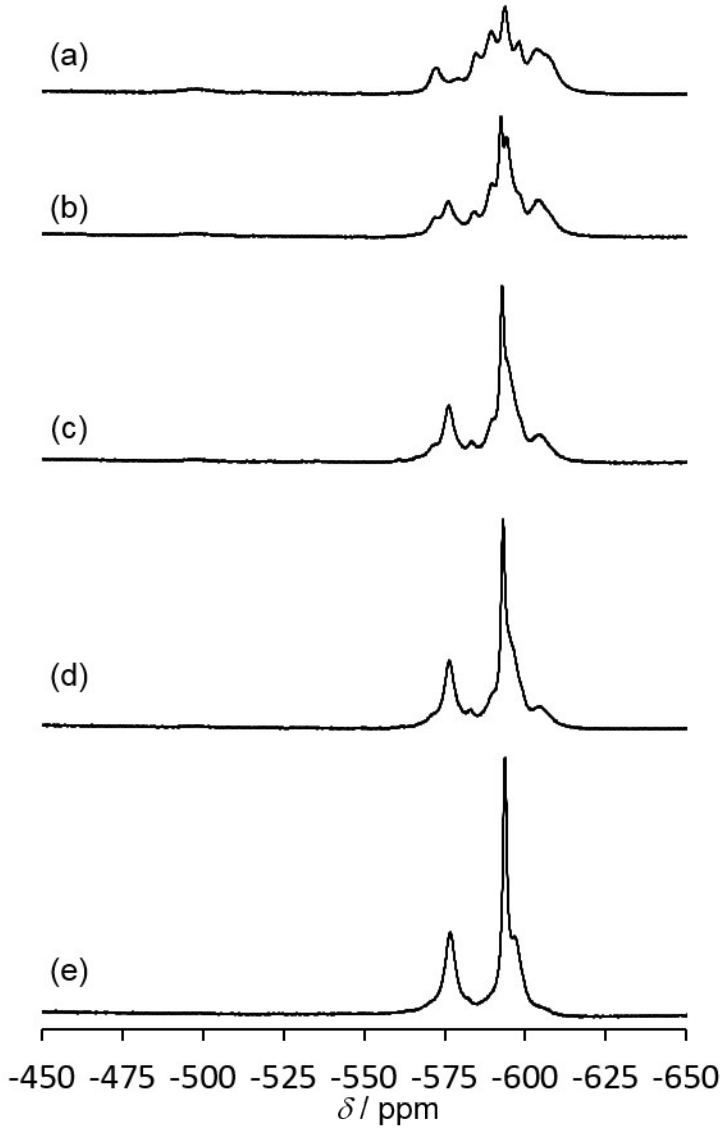

Figure S11. ^{51}V NMR spectra of **V12** in DMF with the total concentration of EC of (a) 0, (b) 0.75, (c) 1.5, (d) 2.25, and (e) 9.0 M. From the spectra, the molar ratio of **V12-free** of (b) 73%, (c) 55%, (d) 44%, and (e) <1% were determined.

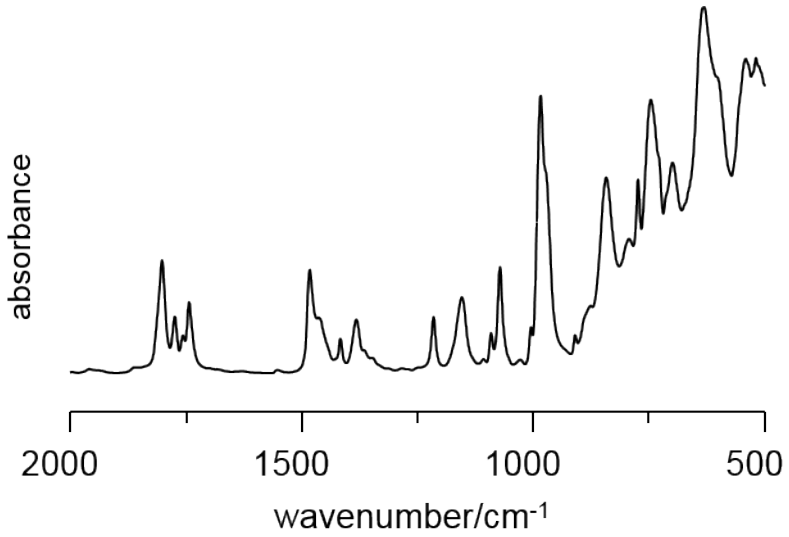

Figure S12. IR spectrum of **V12(EC)**.

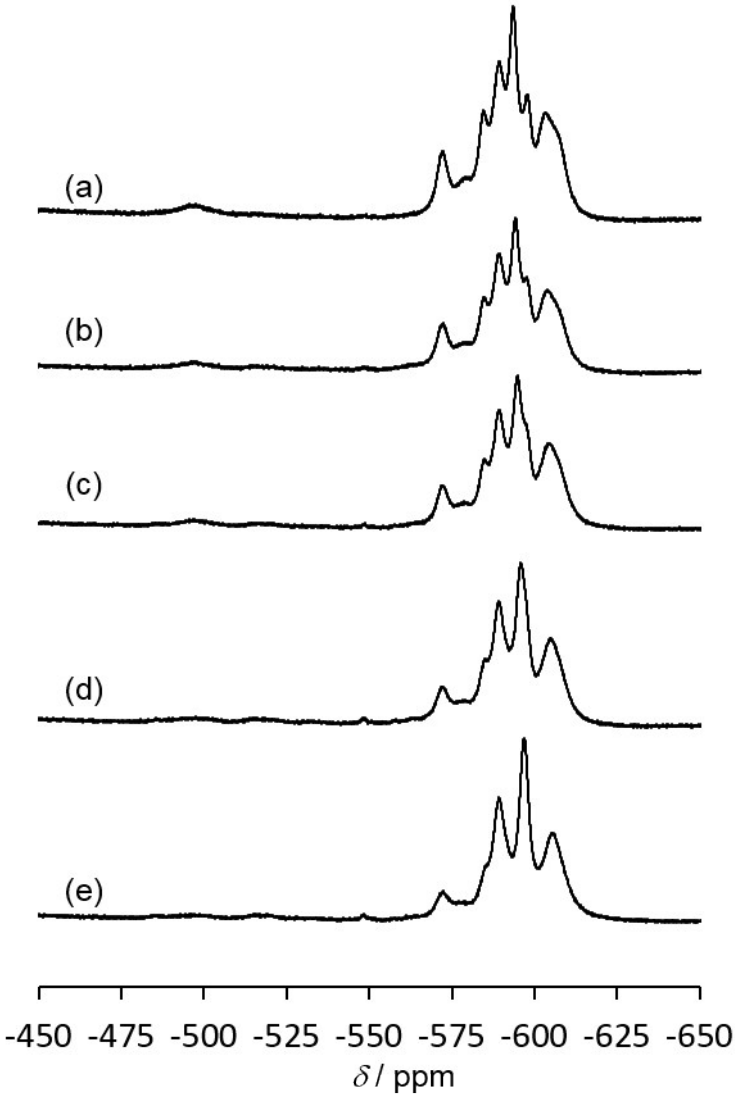

Figure S13. ^{51}V NMR spectra of **V12** in DMF with the total concentration of CB of (a) 0, (b) 1.4, (c) 2.7, (d) 5.4, and (e) 8.2 M. From the spectra, the molar ratio of **V12-free** of (b) 80%, (c) 66%, (d) 51%, and (e) 43%, were determined.

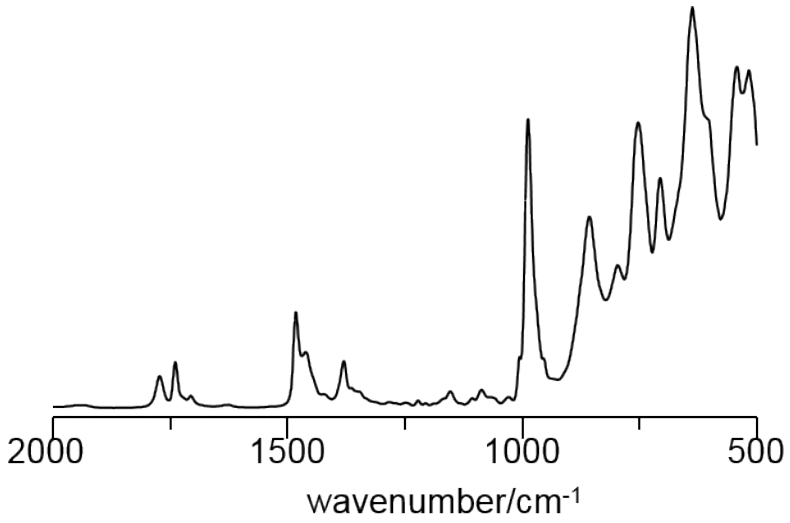

Figure S14. IR spectra of (a) **V12(CB)**.

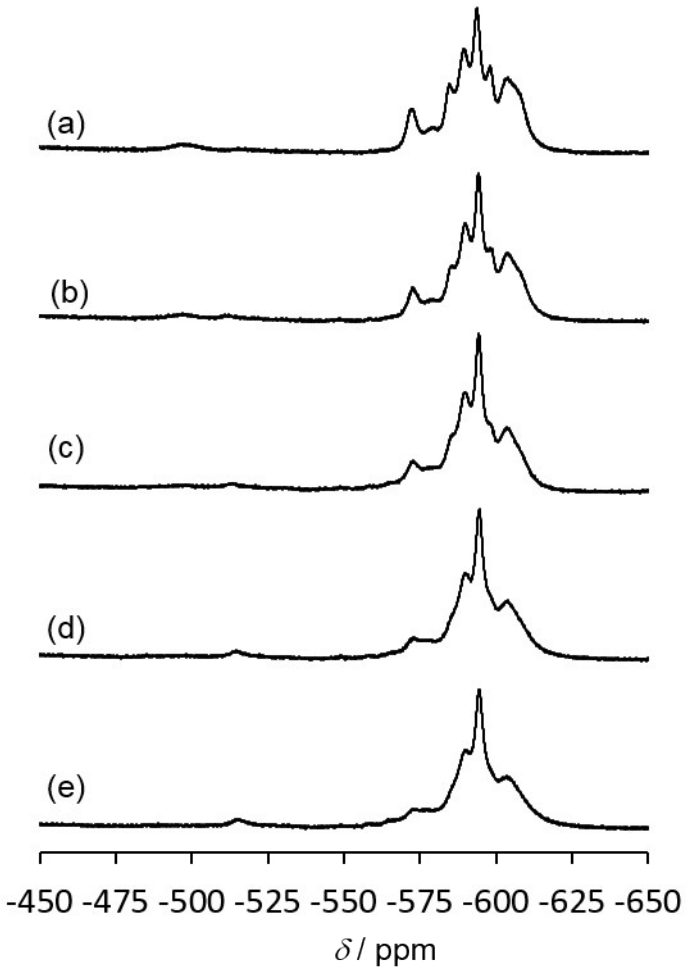

Figure S15. (A) ^{51}V NMR spectra of **V12** in DMF with the total concentration of HA of (a) 0, (b) 1.6, (c) 3.3, (d) 4.9, and (e) 5.7 M. From the spectra, the molar ratio of **V12-free** of (b) 87%, (c) 76, (d) 67%, and (e) 63%, were determined.