Supplementary Information

Instantaneous and Reversible Gelation of Organically Grafted Polyoxometalate Complexes with Dicarboxylic acids

Zhenfeng He, Huanbing Wang, Yinglin Wang, Yue Wu, Haolong Li,* Lihua Bi, and Lixin Wu

State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, China.

*Corresponding author; E-mail address: hl_li@jlu.edu.cn.

Preparation of $C_5H_4NCONHC(CH_2OH)_3$. Pyridine–4–carboxylic acid, C_5H_4N-COOH, (10.00 g, 81.3 mmol) was dissolved in dry CH_3OH (150 mL), and several drops of 98 wt% H_2SO_4 were added as catalyst. The reaction mixture was refluxed for 12 h. After cooling to room temperature, the pH of reaction solution was adjusted to *ca.* 7 with a saturated aqueous solution of Na_2CO_3. Pyridine–4–carboxylate methyl ester was extracted with $CHCl_3$ and obtained as a light yellow solution and used in the next reaction without further purification. The obtained pyridine–4–carboxylic acid methyl ester (4.00 g, 26.5 mmol) and tris(hydroxymethyl)aminomethane (Tris) (3.21 g, 26.5 mmol) were mixed and stirred at room temperature in dry DMSO (50 mL) with the addition of anhydrous K_2CO_3 (3.66 g, 36.5 mmol) for 30 h under N_2 atmosphere. The insoluble residues were filtered off, and the filtrate was evaporated under vacuum. The obtained $C_5H_4NCONHC(CH_2OH)_3$ was purified through silica gel column chromatography (eluent: CH_2Cl_2:CH_3OH = 10:1). Yield: 3.70 g (60.9 %). ^{1}H NMR (500MHz, DMSO-d_6, 25°C, TMS): δ = 8.70 (d, J (H, H) = 4.5 Hz, 2 H; Py–CH), 7.70 (d, J = 4.5 Hz, 2H; Py–CH), 7.49 (s, 1H; –NH–), 4.66 (t, J = 5.5 Hz, 3H; –OH), 3.70 (t, J = 6.0 Hz, 6H; –CH_2–O–) ppm. FTIR (KBr): ν = 3483, 3394, 3186, 3074, 2981, 2879, 1651, 1606, 1556, 1543, 1502, 1469, 1462, 1421, 1411, 1333, 1294, 1259, 1240, 1178, 1140, 1082, 1045, 1016, 978, 941 cm^{-1}.

Preparation of $[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)_3CNHCOC_5H_4N\}_2]$ (TBA–Py–$MnMo_6$). Under N_2 atmosphere, $[N(C_4H_9)_4]_4[\alpha\text{–}Mo_8O_{26}]$ (3.00 g, 1.4 mmol), $Mn(OAc)_3$ (0.56 g, 2.1 mmol) and $C_5H_4NCONHC(CH_2OH)_3$ (1.10 g, 4.9 mmol) were mixed in 100 mL CH_3CN and stirred at 85 °C for 24 h. The reaction solution was then cooled to room temperature and the precipitate was filtered off. The orange filtrate was exposed to ether vapor for several days. Large orange crystals were obtained. Yield: 2.90 g (88%). ^{1}H NMR (500MHz, DMSO-d_6, 25°C, TMS): δ = 64.6 (br; –CH_2O–), 8.89 (br, s, 4H; Py–CH), 7.99 (br, s, 2H; –NH–), 7.67 (br, s, 4H; Py–CH), 3.18-3.15 (m, 24H;

–CH_2–), 1.60-1.54 (m, 24H; –CH_2–), 1.35-1.27 (m, 24H; –CH_2–), 0.93 (t, J = 7.4 Hz, 36H; –CH_3) ppm. FTIR (KBr): ν = 3275, 3049, 2960, 2937, 2873, 1670, 1599, 1541, 1483, 1408, 1381, 1026, 941, 920, 903, 669 cm^{-1}. ESI-MS (negative mode, CH_3CN, m/z): 1849 [$(TBA)_2MnMo_6O_{18}\{(OCH_2)_3CNHCOC_5H_4N\}_2^-$]. Elemental analysis (%) for $(TBA)_3[MnMo_6O_{18}\{(OCH_2)_3CNHCOC_5H_4N\}_2]$: C 39.03, H 6.26, N 4.69; found: C 39.21, H 6.46, N 4.28.

Additional structural characterization data.

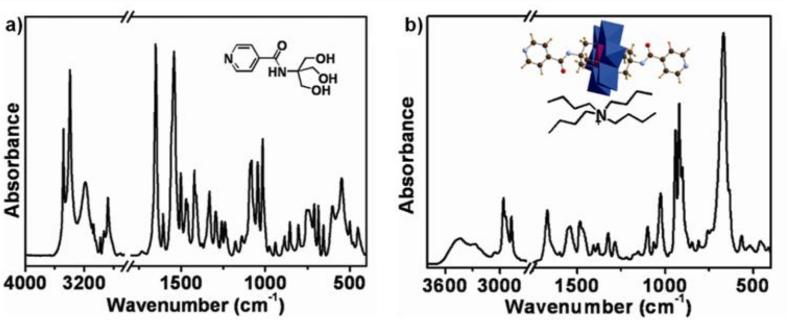

Fig. S1. FT-IR spectra of (a) $C_5H_4NCONHC(CH_2OH)_3$ and (b) TBA–Py–MnMo$_6$ in KBr pellets.

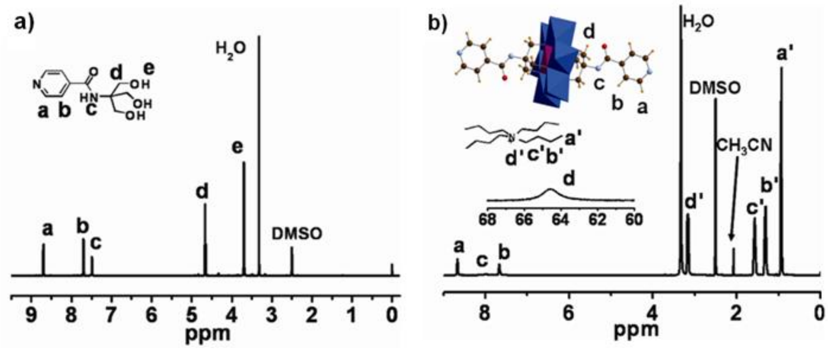

Fig. S2. ^{1}H NMR spectra of (a) $C_5H_4NCONHC(CH_2OH)_3$ and (b) TBA–Py–MnMo$_6$ in DMSO-d_6.

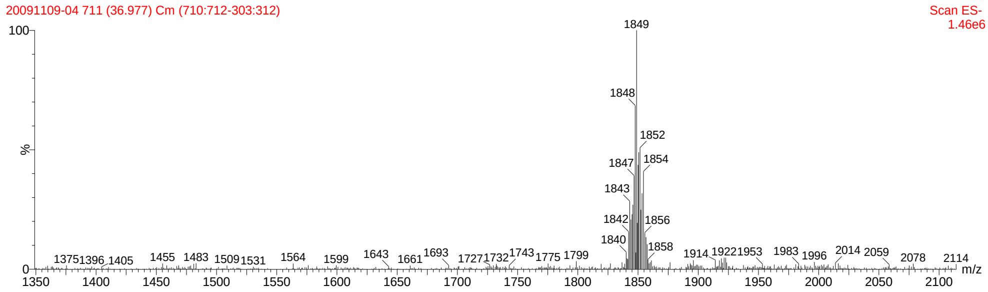

Fig. S3. ESI-MS spectrum of TBA–Py–MnMo$_6$ bearing two counterions in acetonitrile.

Characterizations of hydrogen bonding between pyridyl groups and carboxylic acids.

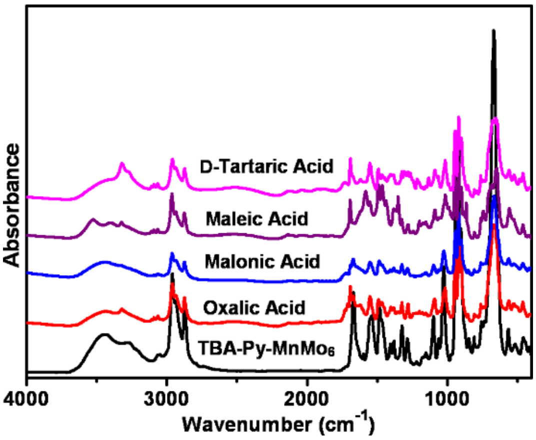

Fig. S4. IR spectra of xerogels of TBA–Py–MnMo$_6$ with different dicarboxylic acids.

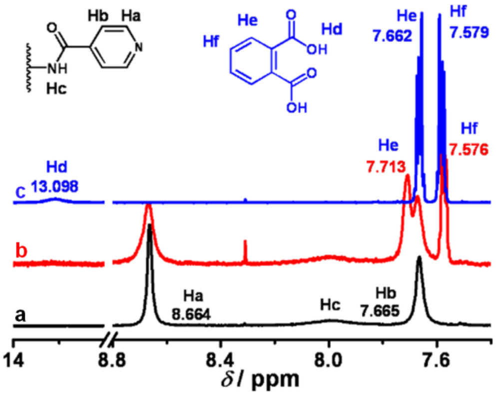

Fig. S5. ^{1}H NMR spectra of (a) TBA–Py–MnMo$_6$, (b) corresponding hydrogen bonded complex with *o*–phthalic acid, and (c) *o*–phthalic acid alone in DMSO-d_6.

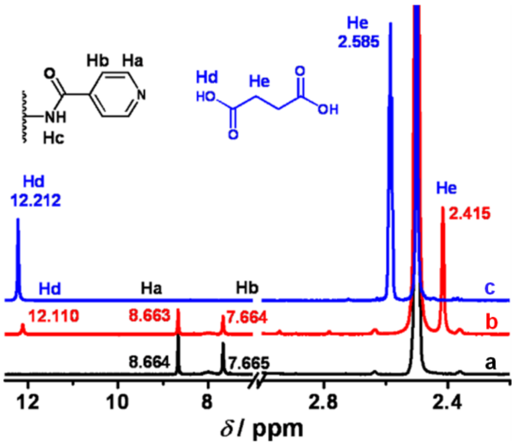

Fig. S6. ^{1}H NMR spectra of (a) TBA–Py–MnMo$_6$, (b) corresponding hydrogen bonding complex with succinic acid, and (c) succinic acid alone in DMSO-d_6.

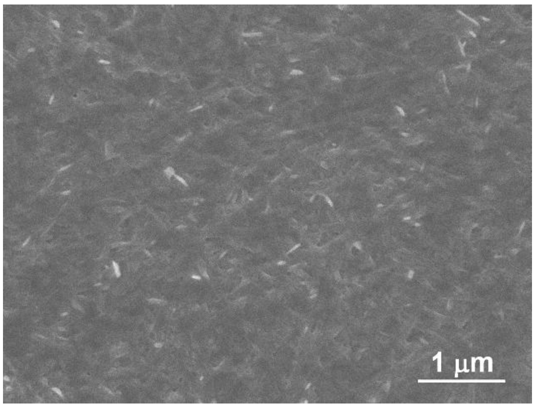

Fig. S7. SEM image of xerogel of TBA–Py–MnMo$_6$ and L–tartaric acid.

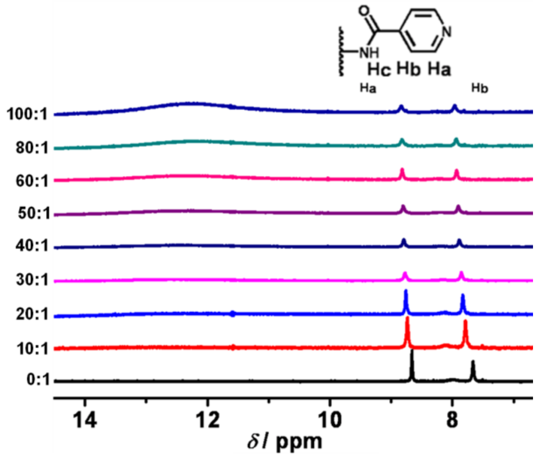

Fig. S8. ^{1}H NMR spectra of TBA–Py–MnMo$_6$ versus the addition of maleic acid in DMSO-d_6 in molar ratio from 0:1 to 100:1.