Supplementary Information

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

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Preparation of C₅H₅NCONHC(CH₂OH)₃. Pyridine–4-carboxylic acid, C₅H₅NO-COOH, (10.0 g, 81.3 mmol) was dissolved in dry CH₂OH (150 mL), and several drops of 98 wt% H₂SO₄ 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 Na₂CO₃. Pyridine–4-carboxylate methyl ester was extracted with CHCl₃ 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 K₂CO₃ (3.66 g, 36.5 mmol) for 30 h under N₂ atmosphere. The insoluble residues were filtered off, and the filtrate was evaporated under vacuum. The obtained C₅H₅NCONHC(CH₂OH)₃ was purified through silica gel column chromatography (eluent: CH₂Cl₂:CH₂OH = 10:1). Yield: 3.70 g (60.9 %). ¹H NMR (500MHz, DMSO-d₆, 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; –CH₂–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(C₄H₅)₃]₃[MnMo₄O₁₈{(OCH)₂CNHCOC(H₂)₃N}₂] (TBA–Py–MnMo₄). Under N₂ atmosphere, [N(C₄H₅)₃]₃[α–Mo₅O₂₆] (3.00 g, 1.4 mmol), Mn(OAc)₃ (0.56 g, 2.1 mmol) and C₅H₅NCONHC(CH₂OH)₃ (1.10 g, 4.9 mmol) were mixed in 100 mL CH₂CN 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%). ¹H NMR (500MHz, DMSO-d₆, 25°C, TMS): δ = 64.6 (br; –CH₂O–), 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;
\(-\text{CH}_2\)-, 1.60-1.54 (m, 24H; -\text{CH}_2-), 1.35-1.27 (m, 24H; -\text{CH}_2-), 0.93 (t, \(J = 7.4\) Hz, 36H; -\text{CH}_3) ppm. FTIR (KBr): \(\nu = 3275, 3049, 2960, 2937, 2873, 1670, 1599, 1541, 1483, 1408, 1026, 941, 920, 903, 669 \text{ cm}^{-1}\).

ESI-MS (negative mode, CH\textsubscript{3}CN, \(m/z\)): 1849 \([\text{TBA}_2\text{MnMo}_6\text{O}_{18}\{\text{OCH}_2\text{CNHCOC}_5\text{H}_4\text{N}\}_2]^{-}\). Elemental analysis (%) for \((\text{TBA})_3[\text{MnMo}_6\text{O}_{18}\{\text{OCH}_2\text{CNHCOC}_5\text{H}_4\text{N}\}_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) \(\text{C}_5\text{H}_4\text{NCONHC(CH}_2\text{OH})_3\) and (b) TBA–Py–MnMo\textsubscript{6} in KBr pellets.

**Fig. S2.** \(^1\text{H} \text{NMR spectra of (a) C}_5\text{H}_4\text{NCONHC(CH}_2\text{OH})_3\) and (b) TBA–Py–MnMo\textsubscript{6} in DMSO-\text{d}_6.

**Fig. S3.** ESI-MS spectrum of TBA–Py–MnMo\textsubscript{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\textsubscript{6} with different dicarboxylic acids.

**Fig. S5.** $^1$H NMR spectra of (a) TBA–Py–MnMo\textsubscript{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\textsubscript{6}, (b) corresponding hydrogen bonding complex with succinic acid, and (c) succinic acid alone in DMSO-$d_6$. 

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**Fig. S7.** SEM image of xerogel of TBA–Py–MnMo₆ and L–tartaric acid.

**Fig. S8.** ¹H NMR spectra of TBA–Py–MnMo₆ versus the addition of maleic acid in DMSO-d₆ in molar ratio from 0:1 to 100:1.