

Experimental

The raw materials of tetrabromocavitands and trimethyl-5-pyrimidyl stannane were prepared according to the method reported in the references of 14 and 16, respectively.

7,11,15,28-Tetrakis(5-pyrimidyl)-1,21,23,25-tetrakis(2-phenylethyl)-2,20:3,19-di-methano-1*H*,21*H*,-23*H*,25*H*-bis[1,3]dioxocino[5,4-*i*:5',4'-*i*']benzo[1,2-*d*:5,4-*d*']bis-[1,3]benzodioxocin Stereoisomer (1**)**

The mixture of trimethyl-5-pyrimidyl stannane (1.55 g, 6.39 mmol), tetrabromocavitands (1.02g, 0.80 mmol), and PdCl₂(PPh₃)₂ (0.17 g, 0.33 mmol) in anhydrous toluene (160 cm³) was refluxed under argon at 120 °C for six days. The resulting solution was poured into water and extracted from ethyl acetate. The yellow solution obtained was evaporated to dryness to leave yellow solid and it was purified by column chromatography (elute, CH₂Cl₂ : EtOH = 85 : 15). The **1** was obtained 0.54 g and the yield is 53.2%. (R_f = 0.3) ¹H-NMR (CDCl₃) δ(ppm), 2.65-2.78 (*m*, 16H, -CH₂CH₂), 4.28 (*d*, 4H, inner of OCH₂), 4.98(*t*, 4H,N -CH), 5.44 (*d*, 4H,outer of OCH₂), 7.18-7.30 (*m*, 20H, -CH₂CH₂Ph), 8.46 (*s*, 8H,NCHC), 9.13 (*s*, 4H,NCHN); FAB-mass *m/z*=1266 (M+H⁺); Anal. Calcd for C₈₀H₆₄O₈N₈•H₂O: C, 74.87%; H, 5.18%; N, 8.73%,

Found C, 75.17%; H, 5.08%; N, 8.76%.

Preparations of coordination polymers (2 ~ 5)

Mn(hfac)₂·H₂O (8 mg, 0.016mmol) and the **1** (5 mg, 0.004 mmol) was reacted in ethyl acetate (10 cm³) at 60 °C. The solution was gradually concentrated in the air. After a week, yellow prismatic crystals of **2** were formed. The crystals of **3**, **4**, and **5** were obtained in the similar way using Cu(hfac)₂·H₂O, Ni(hfac)₂·2H₂O and Co(hfac)₂·H₂O instead of Mn(hfac)₂·H₂O, respectively. The elemental analyses were carried out for all crystals of **2** to **5** treated under vacuum dried at 100 °C for 6 hours.

Anal. Calcd for **2** (MnC₉₀H₆₆N₈O₁₂F₁₂·5H₂O): Mn, 3.01%, C, 59.25%; H, 4.20%; N, 6.14%, Found: Mn, 3.43%, C, 59.55%; H, 3.92%; N, 5.88%. Calcd for **3** (Ni₂C₁₀₀H₆₈N₈O₁₆F₂₄·2H₂O): Ni, 5.22%, C, 53.45%; H, 3.23%; N, 4.99%, Found: Ni, 5.36%, C, 53.42%; H, 3.02%; N, 4.93%. Calcd for **4** (CuC₉₀H₆₆N₈O₁₂F₁₂·2H₂O): Cu, 3.57%, C, 60.47%; H, 3.97%; N, 6.30%, Found: Cu, 3.69%, C, 60.75%; H, 3.77%; N, 6.12%. Calcd for **5** (Co₂C₁₀₀H₆₈N₈O₁₆F₂₄): Co, 5.33%, C, 54.31%; H, 3.10%; N, 5.07%, Found: Co, 5.24%, C, 54.16%; H, 3.15%; N, 5.02%.