

The Synthesis of a New Dumbbell-shaped Compound of Bis-4, 4'-bipyridine Bridged by 2, 2'-Bipyridine

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Abstract: The title compound **5** was synthesized in 45% yield by the reaction of compound **3** with α, α' -bis (bromomethyl)-2, 2'-bipyridine in CH₃CN at 70 °C for 24 h.

Keywords: Bipyridine, molecular shuttle, dumbbell-shaped compound.

Molecular machine is a new born research field¹⁻⁵, Stoddart and co-workers firstly reported a molecular shuttles in 1991⁶. In molecular machine a cyclic (bead) moves back and forth like a shuttles between two or more groups (station) having noncovalent interaction with a bead. Dumbbell-shaped component is the key intermediate for the synthesis of molecular machines⁷. One of the approaches for control movement of the bead is based on coordination reaction intrigue. In our protocol, a ligand, which is able to bind metal ion, is incorporating into dumbbell-shaped component. The ligand can coordinate to metal ion under some circumstance and decomplex under other condition. Thus the control movement on bead can be carried out. 2, 2'-Bipyridine contains two nitrogen atoms with a pair of lone electron. We designed a dumbbell shaped compound of bis-4, 4'-bipyridine bridged by 2, 2'-bipyridine.

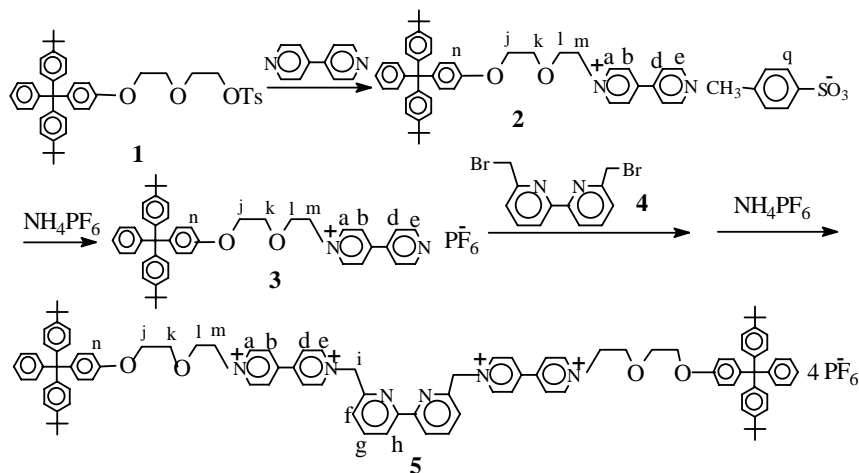
The reaction of compound **1** with 4, 4'-bipyridine (10.0 eq.) was finished in 36 h at 70°C to give bipyridinium salt **2** in very high yields. Compound **3** has better solubility in organic solvent, compound **2** was converted into compound **3** by anion exchange, and reacted with α, α' -bis(bromomethyl)-2, 2'-bipyridine in CH₃CN at 70°C for 24 h to give the dumbbell-shaped compound of bis-4, 4'-bipyridine bridged by 2, 2'-bipyridine **5** in 45% yield.

Experimental

The synthesis of compound 3: 4, 4'-Bipyridine 312 mg (20 mmol) was dissolved in dry CH₃CN (5 mL) and heated to reflux under nitrogen, the compound **1**³ 140 mg (0.2 mmol) in dry CH₃CN (5 mL) was added dropwise to this solution during 1h. The reaction mixture was stirred for 36 hs at 70°C, thus the solvent was removed in vacuum. The re-

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Scheme 1



sidue was subjected to column chromatography, using MeOH/acetate(1:4) as eluent to recover the 4, 4'-bipyridine, then eluted with MeOH/ $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (7:3:1) and MeOH/ $\text{CH}_3\text{CN}/\text{NH}_4\text{Cl}$ (7:3:0.4) as eluent to wash out compound 2. m.p.120-122°C, ^1H NMR (CD_3COCD_3 , 500 MHz, δppm), 1.29(s, 18H, 2Bu^t), 2.27(s, 3H, CH_3), 3.87(t, 2H, $J=5.0\text{Hz}$, H-k), 4.06(t, 2H, $J=5.0\text{Hz}$, H-l), 4.19(t, 2H, $J=5.0\text{Hz}$, H-j), 5.12(t, 2H, $J=5.0\text{Hz}$, H-m), 6.76(d, 2H, $J=9.15\text{Hz}$, H-n), 7.03~7.33 (m, 17H, H-Ar), 7.68(d, 2H, $J=7.95\text{Hz}$, H-q), 7.94(d, 2H, $J=6.1\text{Hz}$, H-d), 8.56(d, 2H, $J=7.0\text{Hz}$, H-b), 8.80(d, 2H, $J=6.1\text{Hz}$, H-e), 9.37(d, 2H, $J=7.0\text{Hz}$, H-a). MS. m/z 675.4(M-TsO $^-$). The compound 2 was dissolved in $\text{H}_2\text{O}-\text{Me}_2\text{CO}$ mixture, saturated aqueous NH_4PF_6 (2.0 mL) was added, the Me_2CO was evaporated off and the resulting yellowish solid was washed with H_2O , MeOH subsequently, dried under vacuum, to give the compound 3, m.p.132-134°C, yield 95%. ^1H NMR (CD_3COCD_3 , 500MHz, δppm), 1.30(s, 18H, 2Bu^t), 3.89(t, 2H, $J=4.6\text{Hz}$, H-k), 4.10(t, 2H, $J=4.6\text{Hz}$, H-l), 4.25(t, 2H, $J=4.6\text{Hz}$, H-j), 5.11(t, 2H, $J=4.6\text{Hz}$, H-m), 6.79 (d, 2H, $J=8.85\text{Hz}$, H-n), 7.05~7.32(m,15H, H-Ar), 7.95(d, 2H, $J=5.8\text{Hz}$, H-b), 8.60(d, 2H, $J=6.4\text{Hz}$, H-d), 8.83(s, 2H, H-e), 9.25(d, 2H, $J=6.1\text{Hz}$, H-a). ^{13}C NMR (CD_3COCD_3 , 500MHz, δppm), 157.568(C-a), 151.921(C-d), 149.347(C-e), 148.269(C-b), 147.105, 144.975, 132.797, 131.637, 131.349, 128.228, 126.932, 126.319, 125.098, 114.030, 70.319, 69.682, 67.885, 62.011, 34.814, 31.577, 30.265. MS. m/z 675.3(M- PF_6^-), 355.2(4),205(2). Caclcd. C, 68.8; H, 6.22; N, 3.41. Found C, 69.2; H, 6.23; N, 3.42.

Synthesis of compound 5: Compound 3 81 mg (0.1 mmol) was dissolved in dry CH_3CN (8 mL), 2, 2'-bis(bromomethyl)-2, 2'-bipyridine 4⁵ 11.4 mg (0.3 mmol) was added to the solution, the reaction mixture was stirred and heated at 70°C under nitrogen for 2 days. After cooling to room temperature, the yellowish solid was filtered off and washed with the small amounts of MeCN. The residue was then dissolved in aqueous acetone and the saturated aqueous NH_4PF_6 solution (5 mL) was added. Me_2CO was evaporated off under reduced pressure and the yellowish solid was filtered off and washed with H_2O , dried to give compound 5, m.p. 270-275°C (dec), yield 45.0%. ^1H NMR(DMSO, 500MHz, δppm), 1.25(s, 18H, 2Bu^t), 3.80 (t, 2H, $J=4.6\text{Hz}$, H-k), 4.05(m, 4H, H-l,j), 4.95(t, 2H, $J=4.6\text{Hz}$, H-m), 6.22(s, 2H, H-i), 6.86(d, 2H, $J=8.85\text{Hz}$, H-n),

7.03~7.30(m, 15H, H-Ar), 7.76(d, 1H, J=7.3Hz, H-f), 8.04(m, 2H, H-g,h), 8.85(d, 2H, J=6.8Hz, H-d), 8.90(d, 2H, J=6.2Hz, H-b), 9.34 (d, 2H, J=6.2Hz, H-e), 9.60(d, 2H, J=6.7Hz, H-a). ^{13}C NMR (CD_3COCD_3 , 500MHz, δ_{ppm}), 161.270(C-a), 158.889(C-e), 154.406(C-d), 153.168(C-b), 152.025, 147.447, 146.592, 145.827, 143.540, 139.440, 138.774, 138.296, 131.054, 130.100, 129.717, 129.586, 127.430, 126.192, 124.000, 120.089, 112.941, 69.810, 68.198, 68.010, 66.187, 62.559, 60.789, 33.651, 30.706, 23.046. MS. m/z 1532.8(M-4PF₆⁻), Calcd. C, 60.3; H, 5.30; N, 3.98. Found C, 59.9; H, 5.31; N, 3.97.

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