Short Note

4,4’-Bis(4-octylphenoxy)-2,2’-bipyridine

Ru Liu, Yan Xu, Jun-Ru Wang and Zhen-Ting Du *

College of Sciences, Northwest A&F University, Yangling, Shanxi 712100, China

* Author to whom correspondence should be addressed; E-Mail: duzt@nwsuaf.edu.cn.

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Abstract: 4,4’-Bis(4-octylphenoxy)-2,2’-bipyridine which can be used in complexes of ruthenium was synthesized. This ligand bears a long chain for the purpose of increasing the solubility of the final complex. The synthesis was achieved through a nucleophilic aromatic substitution reaction of 4,4’-bromo-2,2’-bipyridine and 4-octylphenol.

Keywords: bipyridine; nucleophilic aromatic substitution

Much attention is currently devoted to the search for new molecular materials for optoelectronics due to their potential applications in photovoltaic [1] or light-emitting devices [2–4]. Especially, derivatives of 2,2’-bipyridine [5–14] have received much attention due to their potential for metal coordination to form polypyridyl metal complexes, particularly of ruthenium. The complex of 4,4’-dicarboxylbipyridine with ruthenium showed very promising potential in dye-sensitized solar cells (DSSC) [15–17]. The photochemical and redox properties of these complexes can be varied through appropriate substitution on the pyridine rings. The derivatization of a 2,2’-bipyridine ligand with electron donating/withdrawing groups in the 4,4’-positions has been a popular means of controlling the redox potential of transition metal bipyridyl complexes. The 4,4’-disubstitution pattern is desirable, not only because it is the synthetically simplest to prepare but also because substitution at these positions offers no steric complications on complexation. Herein, we wish to report the synthesis of 4,4’-bis(4-octylphenoxy)-2,2’-bipyridine with a long chain which can be used to increase the solubility of the complex of ruthenium in common solvents for DSSC research.
Preparation of 4,4′-bromo-2,2′-bipyridine 2 [18]

To a solution of 2,2′-bipyridyl (15.6 g, 0.1 mol) in 15 mL AcOH was introduced 30% AcOOH (140 mL, 0.6 mol) below 25 °C. Then the mixture was heated to 50 °C and stirred for 5 h. The mixture was cooled, neutralized with 25% NaOH, and extracted with dichloromethane. The organic phase was dried over MgSO₄ and evaporated to give crude 2,2′-bipyridine 1,1′-dioxide (16.0 g, 88%).

\[ \text{1H-NMR (DMSO-}d_6\text{): 7.90 (m, 4H), 7.85 (dd, } J = 6.8 \text{ Hz, } J = 1.2 \text{ Hz, 2H), 8.50 (d, } J = 6.8 \text{ Hz, 2H).} \]

\[ \text{13C-NMR (DMSO-}d_6\text{): 129.44, 129.95, 132.73, 140.63, 142.58.} \]

To a mixture of fuming H₂SO₄ and fuming HNO₃ (4:3; 70 mL) was added 2,2′-bipyridine 1,1′-dioxide (10.0 g, 53 mmol). Then the mixture was heated at 80–90 °C for 12 h. After cooling, the mixture was poured into ice-water, and a yellowish precipitate formed. The precipitate was collected and the cake was washed with water. The cake was dried to give 4,4′-dinitro-2,2′-bipyridine 1,1′-dioxide as a yellowish solid (7.0 g, 48%).

A mixture of 4,4′-dinitro-2,2′-bipyridine 1,1′-dioxide (5.5 g, 20 mmol), AcOH (20 mL) and AcBr (6.1 g, 50 mmol) was refluxed for 6 h. After completion, the mixture was poured into ice-water, and the white solid was collected and dried to give 4,4′-bromo-2,2′-bipyridine 1,1′-dioxide as a yellowish solid (7.0 g, 30% for two steps).

\[ \text{1H-NMR (CDCl}_3\text{): 7.48 (dd, } J = 5.2 \text{ Hz, } J = 1.6 \text{ Hz, 2H), 8.46 (d, } J = 4.4 \text{ Hz, 2H), 8.60 (d, } J = 1.2 \text{ Hz, 2H).} \]

\[ \text{13C-NMR (CDCl}_3\text{): 128.57, 129.06, 132.00, 139.75, 141.64.} \]

Preparation of 4,4′-bis(4-octylphenoxy)-2,2′-bipyridine 3

Under argon, a mixture of 4,4′-bromo-2,2′-bipyridine (3.0 g, 10 mmol), 4-octylphenol (5.0 g, 24 mmol), anhydrous K₂CO₃ (5.5 g, 40 mmol), DMF (50 mL) was refluxed for several h. The reaction
was monitored by TLC. After completion, the mixture was poured into water (70 mL), and it was extracted with dichloromethane. The combined organic phases were washed with water, brine, and dried over MgSO₄. After evaporation, the residue was purified by column chromatography on silica gel with petroleum ether and ethyl acetate (30/1, v/v) to give the title compound (5.1 g, 90%).

$$\text{1H-NMR (CDCl}_3\text{): } 0.88 \text{ (t, } J = 6.8 \text{ Hz, 6H), 1.28–1.32 (m, 20H), 1.61–1.64 (m, 4H), 2.62 (t, } J = 7.6 \text{ Hz, 4H), 6.80 (dd, } J = 6.0 \text{ Hz, } J = 2.8 \text{ Hz, 2H), 7.02 (d, } J = 8.4 \text{ Hz, 4H), 7.21 (d, } J = 8.4 \text{ Hz, 4H), 7.94 (d, } J = 2.4 \text{ Hz, 2H), 8.44 (d, } J = 5.6 \text{ Hz, 2H). 13C-NMR (CDCl}_3\text{): } 14.57, 23.06, 29.61, 29.80, 30.04, 31.85, 32.21, 35.65, 109.47, 111.89, 120.18, 129.57, 139.56, 150.07, 151.48, 157.40, 165.38. HR-MS (FAB+H): Found 565.3792. C₃₈H₄₉O₂N₂ requires 565.3794.

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References and Notes

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