

*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.

Received: 16 November 2009 / Accepted: 26 November 2009 / Published: 2 December 2009

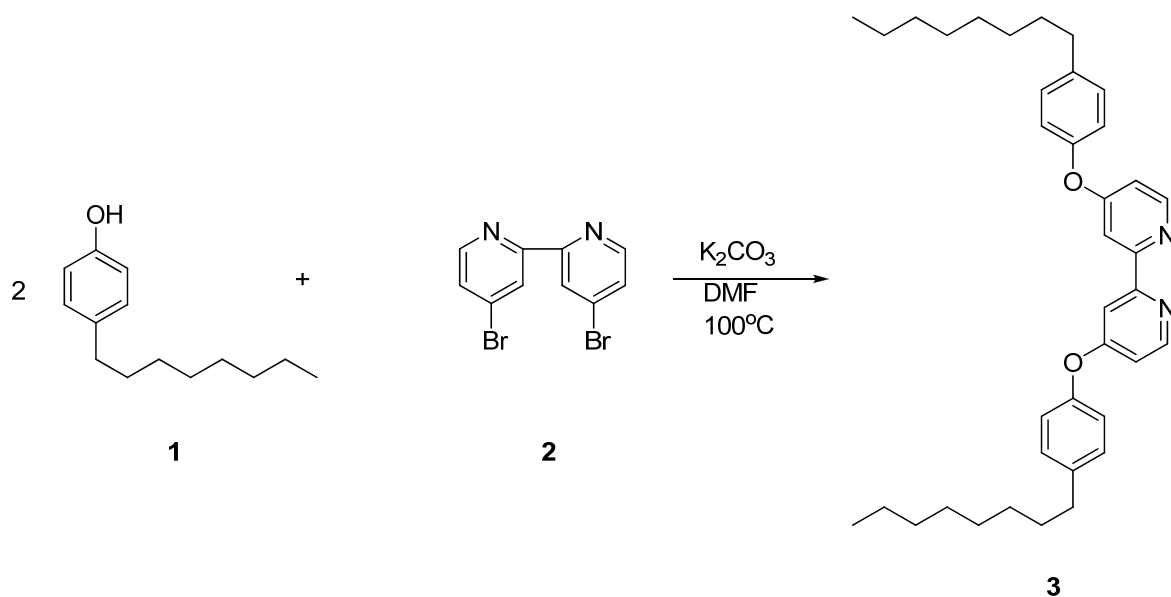
---

**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  $25^\circ C$ . Then the mixture was heated to  $50^\circ C$  and stirred for 5 h. The mixture was cooled, neutralized with 25% NaOH, and extracted with dichloromethane. The organic phase was dried over  $MgSO_4$  and evaporated to give crude 2,2'-bipyridine 1,1'-dioxide (16.0 g, 88%).  $^1H$ -NMR ( $DMSO-d_6$ ): 7.90 (m, 4H), 7.85 (dd,  $J = 6.8$  Hz,  $J = 1.2$  Hz, 2H), 8.50 (d,  $J = 6.8$  Hz, 2H).  $^{13}C$ -NMR ( $DMSO-d_6$ ): 129.44, 129.95, 132.73, 140.63, 142.58.

To a mixture of fuming  $H_2SO_4$  and fuming  $HNO_3$  (4:3; 70 mL) was added 2,2'-bipyridine 1,1'-dioxide (10.0 g, 53 mmol). Then the mixture was heated at  $80$ – $90^\circ C$  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.

A mixture of above solution of 4,4'-bromo-2,2'-bipyridine 1,1'-dioxide, toluene (20 mL) and  $PBr_3$  (10.8 g, 40 mmol) was refluxed for 4 h. The mixture was poured into ice-water, and the pH of the water phase was adjusted to 10 with saturated  $Na_2CO_3$ . The water phase was extracted with toluene, and the organic phases were combined. Evaporation of the solvent gave 4,4'-bromo-2,2'-bipyridine (1.88 g, 30% for two steps).

$^1H$ -NMR ( $CDCl_3$ ): 7.48 (dd,  $J = 5.2$  Hz,  $J = 1.6$  Hz, 2H), 8.46 (d,  $J = 4.4$  Hz, 2H), 8.60 (d,  $J = 1.2$  Hz, 2H).  $^{13}C$ -NMR ( $CDCl_3$ ): 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  $K_2CO_3$  (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  $\text{MgSO}_4$ . 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%).

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 0.88 (t,  $J = 6.8$  Hz, 6H), 1.28–1.32 (m, 20H), 1.61–1.64 (m, 4H), 2.62 (t,  $J = 7.6$  Hz, 4H), 6.80 (dd,  $J = 6.0$  Hz,  $J = 2.8$  Hz, 2H), 7.02 (d,  $J = 8.4$  Hz, 4H), 7.21 (d,  $J = 8.4$  Hz, 4H), 7.94 (d,  $J = 2.4$  Hz, 2H), 8.44 (d,  $J = 5.6$  Hz, 2H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ): 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.  $\text{C}_{38}\text{H}_{49}\text{O}_2\text{N}_2$  requires 565.3794.

## Acknowledgements

Financial support from Program for Excellent Young Talents in Northwest A&F University (2111020712) as well as the National Natural Science Foundation of China (20802058) is greatly appreciated.

## References and Notes

1. Burland, D.M. Optical nonlinearities in chemistry: Introduction. *Chem. Rev.* **1994**, *94*, 1–2.
2. Segura, J.L.; Martin, N. Functionalized oligoarylenes as building blocks for new organic materials. *J. Mater. Chem.* **2000**, *10*, 2403–2435.
3. Martin, R.E.; Diederich, F.; Hide, F. Linear monodisperse-conjugated oligomers: Model compounds for polymers and more. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350–1377.
4. Kraft, A.; Grimsdale, A.C.; Holmes, A.B. Electroluminescent conjugated polymers seeing polymers in a new light. *Angew. Chem., Int. Ed.* **1998**, *37*, 402–408.
5. Garcia, M.A.D.; Schwartz, B.J.; Heeger, A.J. New developments in the photonic applications of conjugated polymers. *Acc. Chem. Res.* **1997**, *30*, 430–436.
6. Case, F.H. The synthesis of certain substituted 2,2'-bipyridyls. *J. Am. Chem. Soc.* **1946**, *68*, 2574–2577.
7. Bos, K.D.; Kraaijkamp, J.G.; Noltes, J.G. Improved synthesis of 4,4'-disubstituted-2,2'-bipyridines. *Synth. Commun.* **1979**, *9*, 497–504.
8. Connor, J.A.; Overton, C. Substituted 2,2'-bipyridines as ligands. Preparation and characterization of 4,4'-disubstituted 2,2'-bipyridine derivatives of the hexacarbonyls of chromium, molybdenum and tungsten. *J. Organomet. Chem.* **1983**, *249*, 165–174.
9. Takeuchi, K.; Thompson, M.S.; Pipes, D.W.; Meyer, T.J. Redox and spectral properties of monooxo polypyridyl complexes of ruthenium and osmium in aqueous media. *Inorg. Chem.* **1984**, *23*, 1845–1851.
10. Della Ciana, L.; Hamachi, I.; Meyer, T.J. Synthesis of side-chain derivatives of 2,2'-bipyridine. *J. Org. Chem.* **1989**, *54*, 1731–1735.
11. Della Ciana, L.; Dressick, W.J.; Sandrini, D.; Maestri, M.; Ciano, M. Synthesis and characterization of a new family of luminescent *cis*-(4,4'-X2-5,5'-Y2-2,2'-bipyridine) $_2\text{Os}(\text{CO})\text{Cl}(\text{PF}_6)$  complexes (X=NEt $_2$ , OMe, Me, H, Cl, Y=H; X=H, Y=Me;

- X=Y=Me): Control of excited-state properties by bipyridyl substituents. *Inorg. Chem.* **1990**, 29, 2792–2798.
12. Ram, M.S.; Hupp, J.T. Generalized synthesis of *cis*- and *trans*-dioxorhenium(V) (bi)pyridyl complexes. *Inorg. Chem.* **1991**, 30, 130–133.
  13. Hino, J.K.; Della Ciana, L.; Dressick, W.J.; Sullivan, P.B. Substituent constant correlations as predictors of spectroscopic, electrochemical, and photophysical properties in ring-substituted 2,2'-bipyridine complexes of rhenium(I). *Inorg. Chem.* **1992**, 31, 1072–1080.
  14. Kinnunen, T.J.; Haukka, M.; Nousiainen, M.; Patrikka, A.; Pakkanen, T.A. Electron withdrawing and electron donating effects of 4,4-bipyridine substituents on ruthenium mono(bipyridine) complexes. *J. Chem. Soc., Dalton Trans.* **2001**, 2649–2654.
  15. O'Regan, B.; Gratzel, M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO<sub>2</sub> films. *Nature* **1991**, 353, 737–739.
  16. Cherepy, N.J.; Smestad, G.P.; Gratzel, M.; Zhang, J.Z. Ultrafast electron injection: Implications for a photoelectrochemical cell utilizing an anthocyanin dye-sensitized TiO<sub>2</sub> nanocrystalline electrode. *J. Phys. Chem. B* **1997**, 101, 9342–9351.
  17. Hagfeldt, A.; Gratzel, M. Molecular photovoltaics. *Acc. Chem. Res.* **2000**, 33, 269–277.
  18. Nakashima, K.; Shinkai, S. Sugar assisted chirality control of tris(2,2'-bipyridine)-metal complexes. *Chem. Lett.* **1994**, 23, 1267–1270.

© 2009 by the authors; licensee Molecular Diversity Preservation International, Basel, Switzerland. This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/3.0/>).