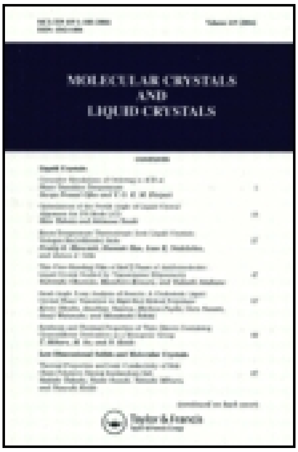


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis and Properties of Transition Metal Complexes Assembled by Coordination to Rigid π-Conjugated Aryleneethynylene Ligands

Hiroki Fukumoto [a] & Takakazu Yamamoto [a]
[a] Chemical Resources Laboratory, Tokyo Institute of Technology, 4259, Nagatsuta, Midori-ku, Yokohama, 226-8503, Japan

To cite this article: Hiroki Fukumoto & Takakazu Yamamoto (2003): Synthesis and Properties of Transition Metal Complexes Assembled by Coordination to Rigid π-Conjugated Aryleneethynylene Ligands, Molecular Crystals and Liquid Crystals, 379:1, 437-442

To link to this article: http://dx.doi.org/10.1080/713738631

Mol. Cryst. Liq. Cryst., Vol. 379, pp. 437-442
Copyright © 2002 Taylor & Francis
1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290090859

Synthesis and Properties of Transition Metal Complexes Assembled by Coordination to Rigid π-Conjugated Aryleneethynylene Ligands

HIROKI FUKUMOTO and TAKAKAZU YAMAMOTO

Chemical Resources Laboratory, Tokyo Institute of Technology,
4259, Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

A new π-conjugated aryleneethynylene compound with pyrimidine moieties, 2,5-bis(pyrimidine-5-yl-ethynyl)-1,4-didodecyloxybenzene (**1**) , has been prepared using Sonogashira reaction. **1** reacts with Ag (OSO_2CF_3) to give a polymeric complex **2** in moderate yields.

Keywords: π-conjugated ligand; aryleneethynylene; pyrimidine; metal assembled complex

INTRODUCTION

Synthesis and the properties of transition metal complexes assembled by coordination to π-conjugated ligands are actively investigated due to their high potential in material science[1]. Molecular design of π-conjugated ligands is of importance to control dimensional structures of assembled metal complexes. To generate ordered structures of assembled metal complexes, linear rod-like ligands such as 4,4'-bipyridine or 1,4-bis(2-pyridyl)butadiyne[2], has been utilized as a spacer to combine plural transition metals and their complexation with transition metal compounds have been investigated. Herein we report preparation of a rod-like π-conjugated aryleneethynylene compound **1** with pyrimidine moieties and synthesis of its transition metal complexes.

EXPERIMENTAL

Preparation

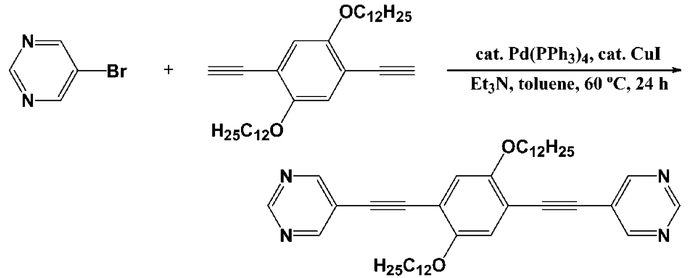
2,5-Bis(pyrimidine-5-yl-ethynyl)-1,4-didodecyloxybenzene (**1**) was prepared as follows. Dry toluene (15 mL) was added to a mixture of 2,5-didodecyloxy-1,4-diethynylbenzene (0.99 g, 2.0 mmol), 5-bromopyrimidine (0.64 g, 4.0 mmol) and triethylamine (10 mL) in a Schlenk tube under nitrogen. CuI (65 mg, 0.06 mmol) and $Pd(PPh_3)_4$ (6 mg, 0.06 mmol) were then added to the mixture, and the reaction mixture was stirred at 60 °C for 24 h to obtain a deep red suspension. The solvent was removed by evaporation. The residue was purified by column chromatography on silica gel using chloroform as an eluent. Yield: 0.44 g (34%). ^{1}H NMR ($CDCl_3$, 400 MHz): 0.87 (t, 6H), 1.29 (m, 32H), 1.52 (m, 4H), 1.85 (m, 4H), 4.04 (t, 4H), 7.00 (s, 2H), 8.86 (s, 4H), 9.15 (s, 2H). Anal. Calcd. for $C_{42}H_{58}N_4O_2$: C, 77.50; H, 8.98; N, 8.61. Found: C, 76.80; H, 8.79; N, 8.48. Preparation of Ag(I) complex **2** was carried out as follows. To a THF solution of an excess amount of $Ag(OSO_2CF_3)$ (70 mg, 0.27 mmol) was added **1** (38 mg, 0.057 mmol). The reaction mixture was stirred at room temperature and a green powder precipitated within 10 min. The precipitation was collected and then washed with THF. The precipitation was not soluble in any organic solvents and thereby characterized by elemental analysis. Anal. Calcd. for $(C_{43}H_{58}AgF_3N_4O_5S)_n$: C, 56.89; H, 6.44; F, 6.28; N, 6.17; S, 3.53. Found: C, 55.57; H, 6.43; F, 5.91; N, 6.05; S, 3.12.

X-ray Structure of 1

The crystal structure of **1** suitable for X-ray diffraction studies was mounted on a Rigaku AFC-5R four-circle data collection instrument using Mo-Kα radiation. The units cell parameters at 25 °C were determined by a least-squares fit to 2θ values of 20 strong higher reflections. Crystallographic data for **1**; $C_{42}H_{58}N_4O_2$, F.W. = 650.92, triclinic, $P\bar{1}$, a = 8.6313(12), b = 22.358(3), c = 5.3626(10) Å, α = 93.693(13), β = 104.743(13), γ = 81.147(11)°, V = 988.5(3) Å^3, Z = 1, D = 1.093 g/cm^3, 3668 measured reflections with $2.51° < 2\theta < 27.49°$ = 27.5 collected, 3477 unique reflections, reflections with $I > 2\sigma(I)$ used refinement, R = 0.0573, R_w = 0.1447.

RESULTS AND DISCUSSION

Sonogashira reaction of 1,4-diethynyl-2,5-didodecyloxybenzene with 5-bromopyrimidine afforded a new π-conjugated ligand, 2,5-bis(pyrimidine-5-yl-ethynyl)-1,4-didodecyloxybenzene (**1**) as bright yellow crystals (Scheme 1). The structure of **1** was determined by analytical and spectroscopic data as well as by X-ray crystallography.



Scheme 1

An ORTEP drawing of **1** is shown in Figure 1 and a packing diagram of **1** is displayed in Figure 2. The dodecyloxy side chains are extended in an all-*trans* conformation. The torsion angle for C(1)- C(4)- C(5)- C(6) (3°) shows that the backbone of **1** is slightly tilted. As shown in Figure 2, **1** is stacked with the neighboring molecule along c-axis in the lattice[3].

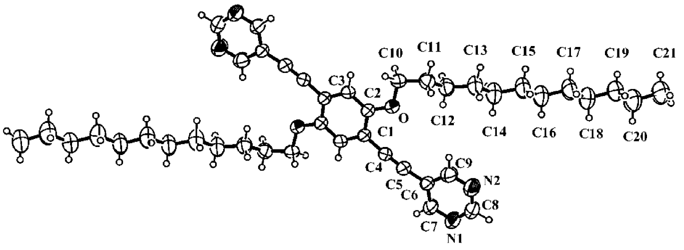


FIGURE 1 Crystal Structure of **1** with selected bond distance (Å) and angles (deg): C(1)-C(2) 1.405(4), C(1)-C(4) 1.436(4), C(4)-C(5) 1.184(3), C(5)-C(6) 1.426(4), C(2)-O(1) 1.359(3), O(1)-C(10) 1.431(3), C(1)-C(4)-C(5) 175.6(3), C(4)-C(5)-C(6) 175.0(3), C(2)-O(1)-C(10) 118.5(2), O(1)-C(10)-C(11) 107.6(2).

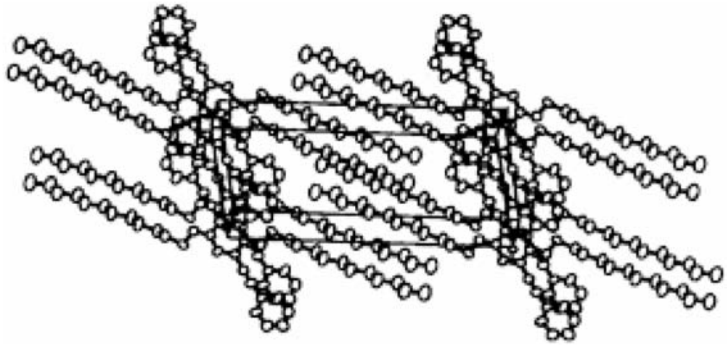
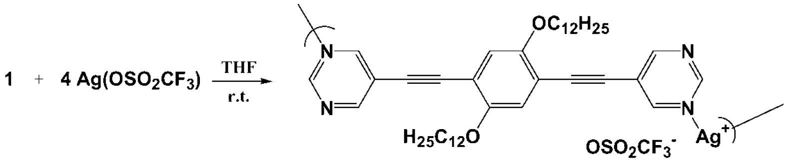


FIGURE 2 Packing Structure of **1**.

The π-π* absorption bands of **1** are observed at 305 and 373 nm. **1** shows a strong luminescence in organic solvents. A $CHCl_3$ solution of **1** emits 423 nm light on irradiation with 373 nm light and the quantum yield of **1** is 0.77 (Quinine sulfate was used as the standard).

Ligand **1** easily reacts with various transition metal compounds. For example, complexation of **1** with an excess amount of $Ag(OSO_2CF_3)$ in THF gives a yellowish green luminescent precipitate of complex **2**.



2

Scheme 2

Complex **2** is insoluble to organic solvents, indicating **2** has a polymeric structure. Elemental analysis of **2** indicates that **2** is comprised of the π-conjugated ligand **1** and Ag(I) in a molar ratio of 1:1. The structural characterization of **2** is now under progress.

Acknowledgements

We appreciate Dr. Yamagata (Osaka University) for his kind guidance on the X-ray diffraction study of **1**.

References

[1.]For reviews: J.-M. Lehn, *Supramolecular Chemistry: Concept and Perspectives*, VCH, Weinheim (1995); B. Olenyuk, A. Fechtenkötter, and P. J. Stang, *J. Chem. Soc., Dalton Trans.*, 1707 (1998); M. D. Ward, *Chem. Soc. Rev.*, 121 (1995); H. L. Bozec, and T. Renouard, *Eur. J. Inorg. Chem.*, 229 (2000);

[2.]M. Maekawa, H. Konaka, Y. Suenaga, T. Kuroda-Sowa, and M. Munakata, *J. Chem. Soc., Dalton Trans.*, 4160 (2000).

[3.]H. Li, D. R. Powell, R. K. Hayashi, and R. West, *Macromolecules*, **31**, 52 (1998).