



ELSEVIER

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

An oxygen-sensing rhenium(I) complex with a carbazole “Shield” in its diamine ligand: Synthesis, characterization, photophysical property and sensing performance



Chuan-e Wang*

College of Chemical Engineering, Lanzhou University of Arts and Science, Lanzhou, 730000, China

ARTICLE INFO

Article history:

Received 9 April 2013

Received in revised form

7 August 2013

Accepted 14 August 2013

Available online 22 August 2013

Keywords:

Re(I) complex

Carbazole shield

Photoluminescence

Oxygen sensing

ABSTRACT

In this paper, we synthesized a novel Re(I) complex of $\text{Re}(\text{CO})_3\text{Br}(\text{PBI-Cab})$ owing a diamine ligand of 9-(4-(2-(pyridin-2-yl)-1H-benzo[d]imidazol-1-yl)butyl)-9H-carbazole (PBI-Cab), where the carbazole moiety was connected by an alkyl chain, hoping to realize an optical sensor immune to surrounding interference. The geometric and electronic structures were revealed by single crystal and density functional theory calculation, which indicated that the carbazole moiety played as a shield for the emissive center. $\text{Re}(\text{CO})_3\text{Br}(\text{PBI-Cab})$ was proved to be a promising oxygen-sensing probe owing to the immunity of emission towards surrounding interference, proper emissive energy and long excited state lifetime. By doping $\text{Re}(\text{CO})_3\text{Br}(\text{PBI-Cab})$ into a polymer host of poly(vinylpyrrolidone), the oxygen sensing performance of the resulting composite material was obtained and discussed. Finally, a high sensitivity of 20.53 was achieved, with a short response/recovery time of 6 s/28 s.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Owing to their virtues of optical and electrical features, luminescent transition metal compounds have found their application in electro-optical field such as optical sensors and light-emitting devices [1,2]. Optical sensors have shown advantages of simple, rapid and non-destructive characteristics. They have low requirement in instrumental implementation and sample pre-treatment compared with traditional techniques. In addition, optical sensors can also provide advantages in term of device size, electrical safety, low cost, needing no reference element and the fact that the sensing signals are free of electromagnetic interference [3,4]. Among the reported optical sensors, those for oxygen detection have been considered as one of the most important aspect since the quantification of oxygen concentration is an important issue in various branches of chemical and food industry, medicine, analytical chemistry, as well as environmental monitoring [5,6].

For practical optical sensors, the sensing probes should be embedded into solid matrixes so that the analytes can be transported from surroundings. Some comment matrixes include silica based molecular sieves, polymers and Langmuir–Blodgett films. In addition, the matrixes have to meet some stringent criteria to achieve desired performance [7]. For example, a quick response

needs the high diffusion coefficient, while the highly effective quenching around the sensing probe is crucial for high sensitivity. Stable sensing signal transition for long distance on-line monitoring needs a high photostability from both the probe and the matrix. As a consequence, the development for sensing probes with proper luminescence, long excited state lifetime, good photostability and compatibility with the supporting matrixes is continuous to be a challenge for optical sensor development.

It seems that the phosphorescent Re(I) complexes of $\text{Re}(\text{CO})_3(\text{N-N})\text{X}$, where N–N and X mean diamine ligand and halogen atom, respectively, can be developed as potential probe for optical sensors due to their virtues of high photoluminescence (PL) yield and good thermal/photochemical stability [8–10]. Theoretical calculations on representative $\text{Re}(\text{CO})_3(\text{N-N})\text{X}$ complexes suggest that the occupied frontier molecular orbitals (MOs) own predominant metal character, while the unoccupied frontier MOs are essentially π^* orbitals of the diamine ligands. The emission comes from the lowest triplet state and thus can be considered as a character of metal-to-ligand-charge-transfer $^3\text{MLCT} [d(\text{Re}) \rightarrow \pi^*(\text{N-N})]$. Some precursive efforts have confirmed the phosphorescent nature of such emissions and explored their response towards various oxygen concentrations, which sparks their application as oxygen sensors [11,12]. A later report by Zhang and coworkers suggests that this MLCT based emission, including both emissive energy and quantum yield, is vulnerable towards surrounding variations [13]. In addition, it has been reported that the emission from $\text{Re}(\text{CO})_3(\text{N-N})\text{X}$ complexes also vary upon different supporting matrixes [7]. Consequently, there should be a shield that blocks

* Tel.: +86 15293190769.

E-mail address: wang_chuane@163.com

the interference from surroundings, aiming at stable sensing signals and accurate results.

Guided by above results, in this paper, we design and synthesize a Re(I) complex of $\text{Re}(\text{CO})_3\text{Br}(\text{PBI-Cab})$ with a diamine ligand of PBI-Cab, where the carbazole moiety is connected by alkyl chain, hoping to achieve a promising optical sensor immune to surrounding interference.

2. Experimental section

The synthetic route for the diamine ligand PBI-Cab, its corresponding Re(I) complex $\text{Re}(\text{CO})_3\text{Br}(\text{PBI-Cab})$ and the composite fibers of $\text{Re}(\text{CO})_3\text{Br}(\text{PBI-Cab})/\text{PVP}$ is shown in Scheme 1. The starting reagents and chemicals of 2-(pyridin-2-yl)-1H-benzo[d]imidazole (PBI), $\text{Re}(\text{CO})_5\text{Br}$, 1,4-dibromobutane, poly(vinylpyrrolidone) (PVP, K30) and 9H-carbazole were purchased from Aldrich Chemical Co. and used without further purifications. Organic solvents used in this work, including cyclohexane, tetrahydrofuran (THF), *N,N'*-dimethylformamide (DMF), 1,2-dichloroethane, toluene, ethanol and CH_2Cl_2 , were purified and redistilled through standard procedures.

2.1. Synthesis of PBI-Cab

2.1.1. 9-(4-Bromobutyl)-9H-carbazole

9-(4-Bromobutyl)-9H-carbazole was synthesized according to a procedure described as follows [14]. The mixture of 0.74 g of NaH, 3.34 g of 9H-carbazole and 100 mL of anhydrous DMF was stirred at room temperature. After the solution became transparent, 3.0 mL of 1,4-dibromobutane was added. The mixture was stirred at room temperature for another 6 h. Then the solution was poured into 500 mL of cool water. The organic components were extracted with 40 mL of CH_2Cl_2 . After the evaporation of CH_2Cl_2 solvent, the crude product was purified by silica gel column chromatography with petroleum ether and acetic acid ethyl ester (*v/v* = 10: 1) to yield 3 g of white needle crystal. ^1H NMR (CDCl_3 , 500 MHz) δ [ppm] 1.90 (*m*, 2H), 2.06 (*m*, 2H), 3.36 (*t*, 2H), 4.35 (*t*, 2H), 7.24 (*m*, 2H), 7.37 (*d*, 2H, *J* = 8.0 Hz), 7.47 (*t*, 2H), 8.07 (*d*, 2H, *J* = 8.0 Hz). Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{BrN}$: C 63.59, H 5.34, N 4.63.

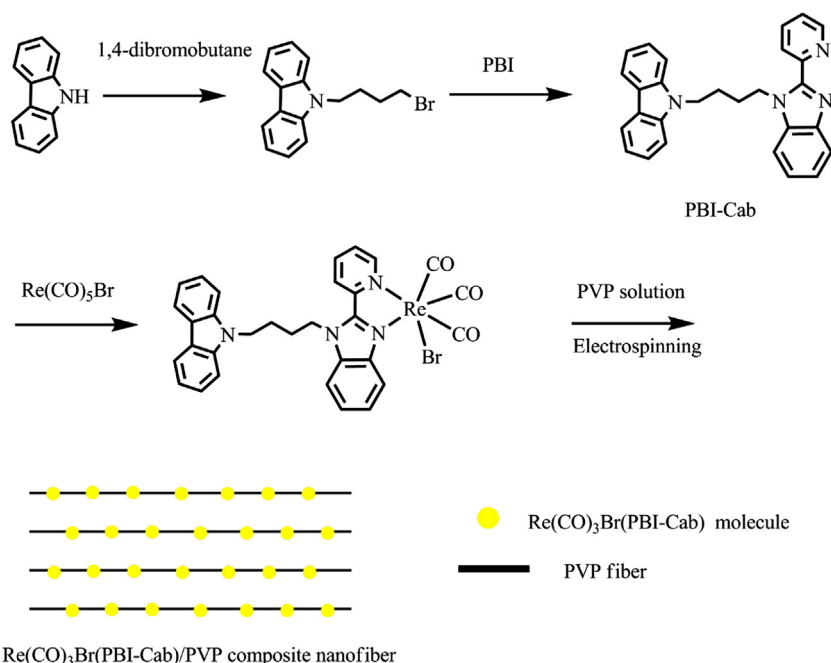
Found: C 63.47, H 5.24, N 4.75. IR (KBr tablet), ν/cm^{-1} : 3050, 2931, 2855, 1583, 1450, 1372.

2.1.2. 9-(4-(2-(Pyridin-2-yl)-1H-benzo[d]imidazol-1-yl)butyl)-9H-carbazole (denoted as PBI-Cab)

PBI-Cab was synthesized according to a literature procedure described as follows [14]. The mixture of 0.37 g of NaH, 1.95 g of PBI, 100 mL of anhydrous DMF and 3.45 g of 9-(4-bromobutyl)-9H-carbazole was stirred at room temperature until the solution was clear. The mixture was stirred for another 24 h at room temperature. Then the solution was poured into 500 mL of cool water. The organic components were extracted with 40 mL of CH_2Cl_2 . After the evaporation of CH_2Cl_2 solvent, the resulting white powder was collected by filter and purified by silica gel column chromatography with petroleum ether and acetic acid ethyl ester (*v/v* = 10:1) to yield 2.1 g of yellow powder. ^1H NMR (CDCl_3 , 500 MHz) δ [ppm]: 2.02 (4H, *m*, *J* = 6.5), 4.34 (2H, *t*, *J* = 6.5), 4.85 (2H, *t*, *J* = 6.5), 7.24–7.34 (8H, *m*), 7.45–7.48 (2H, *m*) 7.83–7.89 (2H, *m*), 8.11 (2H, *d*, *J* = 7.5), 8.41 (1H, *d*, *J* = 8), 8.56 (1H, *d*, *J* = 4). Anal. Calcd for $\text{C}_{28}\text{H}_{24}\text{N}_4$: C 80.74, H 5.81, N 13.45. Found: C 80.87, H 6.03, N 13.17. IR (KBr tablet), ν/cm^{-1} : 3049, 2921, 1582, 1440, 1393.

2.2. Synthesis of $\text{Re}(\text{CO})_3\text{Br}(\text{PBI-Cab})$

The Re(I) complex of $\text{Re}(\text{CO})_3\text{Br}(\text{PBI-Cab})$ was synthesized according to a literature described as follows. The mixture of 0.09 g of PBI-Cab and 0.08 g of $\text{Re}(\text{CO})_5\text{Br}$ in 15 mL of toluene was heated to reflux for 6 h under N_2 protection. After cooling, the solvent was removed by rotary evaporation. The resulting yellow solid was purified on a silica gel column with acetic acid ethyl ester and dichloromethane (*v/v* = 10: 1). Yield: 0.12 g (78%). ^1H NMR (CDCl_3 , 500 MHz) δ [ppm]: 1.98 (2H, *m*), 2.15 (2H, *m*), 4.34 (2H, *t*, *J* = 7.5), 4.41 (2H, *t*, *J* = 7.5), 7.13 (2H, *d*, *J* = 8.5), 7.27 (2H, *d*, *J* = 8), 7.38 (2H, *d*, *J* = 8), 7.46 (4H, *t*, *J* = 8), 7.53 (1H, *t*, *J* = 7), 7.64 (1H, *d*, *J* = 8), 7.73 (1H, *d*, *J* = 8), 8.05 (1H, *d*, *J* = 7.5), 8.12 (2H, *d*, *J* = 7.5). Anal. Calcd for $\text{C}_{31}\text{H}_{24}\text{BrN}_4\text{O}_3\text{Re}$: C 48.57, H 3.16, N 7.31. Found: C 48.33, H 3.27, N 7.23. IR (KBr tablet), ν/cm^{-1} : 2020, 1889. The single crystal of $\text{Re}(\text{CO})_3\text{Br}(\text{PBI-Cab})$ (size = 0.31 mm) was prepared through the solvent evaporation of $\text{Re}(\text{CO})_3\text{Br}(\text{PBI-Cab})$ solution in



Scheme 1. A synthetic procedure for $\text{Re}(\text{CO})_3\text{Br}(\text{PBI-Cab})$ and the corresponding composite fiber of $\text{Re}(\text{CO})_3\text{Br}(\text{PBI-Cab})/\text{PVP}$.

Download English Version:

<https://daneshyari.com/en/article/5400213>

Download Persian Version:

<https://daneshyari.com/article/5400213>

[Daneshyari.com](https://daneshyari.com)