Sensors and Actuators B 241 (2017) 224–229

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

# Iridium complex bearing urea groups as a phosphorescent chemosensor for chiral anion recognition

Ying Hu[a,1], Yinan Li[b,1], Joonyoung F. Joung[c,1], Jun Yin[d], Sungnam Park[c], Juyoung Yoon[a,*], Myung Ho Hyun[b,*]

[a] Department of Chemistry and Nano Science, Ewha Womans University, Seoul 120-750, South Korea
[b] Department of Chemistry and Chemistry Institute for Functional Materials, Pusan National University, Busan 690-735, South Korea
[c] Department of Chemistry, Korea University, Seoul 136-701, South Korea
[d] Key Laboratory of Pesticide and Chemical Biology of the Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, PR China

ARTICLE INFO

*Article history:*
Received 10 September 2016
Received in revised form 11 October 2016
Accepted 17 October 2016
Available online 18 October 2016

*Keywords:*
Phosphorescent chemosensor
Iridium complex
Anion recognition
Chiral recognition
Chemosensor

ABSTRACT

Luminescent chemosensors for chiral molecules have drawn significant attention. In this study, a new iridium complex **1** bearing two urea groups and ethyl naphthalene groups was synthesized as a phosphorescent chemosensor for chiral anion recognition. Addition of *t*-Boc amino acids induced phosphorescence enhancement with the maximum emission at 560 nm. As large as $K_D/K_L$ value of 5.0 was observed for iridium complex **1** with phenylglycine. Two urea groups provide a preorganized binding site for the carboxylates, whereas two ethyl naphthalenes act as chiral barriers.



## 1. Introduction

In recent years, luminescence recognition of biologically important anions, especially chiral anions, has been extensively studied [1]. Chirality is very important in biology and chemistry because most of the biologically important molecules including amino acids, peptide and proteins are chiral, and biologically important processes involve chiral interactions. Moreover, the importance of enantiomerically pure drugs in bioscience and clinical medicine also played a key role in the development of luminescent chemosensors for chiral detection. In the past decade, luminescent chemosensors, sensing chiral guests, have been actively developed, and the mechanisms for chiral recognition and different optical outputs have been extensively studied [2–7]. Recognition and different optical outputs have been extensively studied [2–7].

Phosphorescent chemosensors can show large Stokes shifts and long lifetimes, which are advantageous over fluorescent chemosensors [8]. Even though fluorescent sensing of chiral anions has been actively reported [2–7], phosphorescence chiral recognition has been rarely studied.

In this study, we report a new phosphorescent chemosensor based on the iridium (III) complex **1** for the chiral recognition of amino acids. To detect chiral anions, two urea-binding group and chiral barrier were introduced into the ancillary ligand. The urea group with two acidic NH hydrogens functioned as a binding pocket for anions, whereas two ethyl naphthalenes act as chiral barriers. Iridium (III) complexes **1** showed phosphorescence enhancement with the maximum emission of 560 nm upon adding *t*-Boc amino acids. As large as $K_D/K_L$ value of 5.0 was observed for iridium complex **1** with phenylglycine (Scheme 1).

## 2. Experimental

### 2.1. Synthesis

#### 2.1.1. Materials and methods

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Thin layer chromatography (TLC) was carried out using Merck 60 $F_{254}$ plates with thickness of 0.25 mm. Preparative TLC was performed using Merck 60 $F_{254}$ plates with the thickness of 1 mm.

Melting points were measured using a Büchi 530 melting point apparatus. $^1$H NMR and $^{13}$C NMR spectra were recorded using

* Corresponding author.
*E-mail addresses:* jyoon@ewha.ac.kr (J. Yoon), mhhyun@pusan.ac.kr (M.H. Hyun).
[1] Equally contributed to this work.

http://dx.doi.org/10.1016/j.snb.2016.10.076
0925-4005/

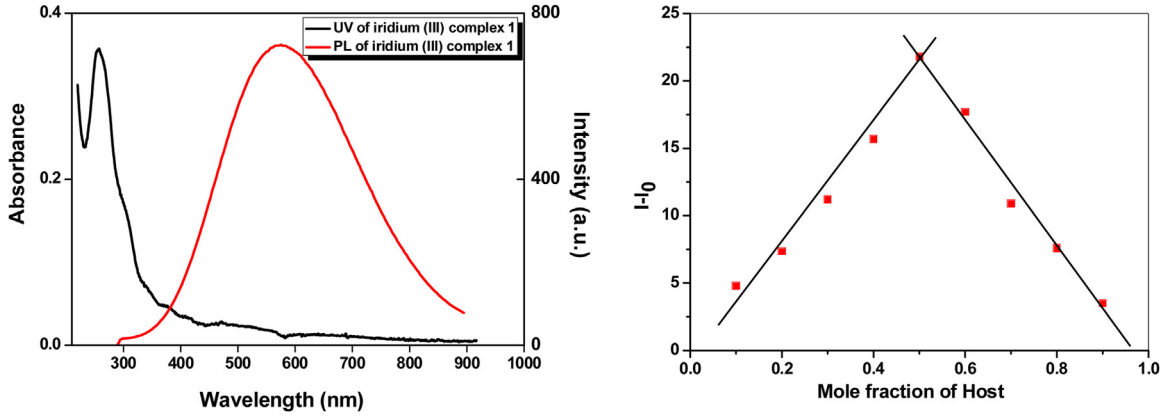
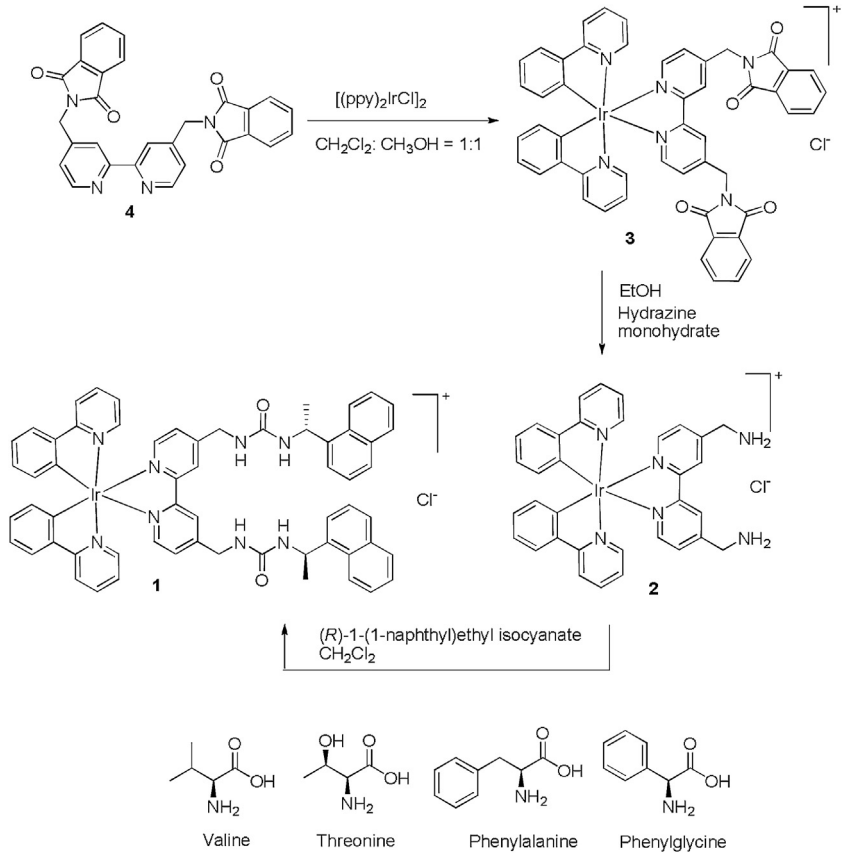



**Fig. 1.** The UV–vis spectra and phosphorescence spectra of iridium (III) complex **1** in acetonitrile (Left) and Job's plot of iridium (III) complex **1** and D-*t*-Boc-phenylglycine in acetonitrile (Right). Total concentration of the two components (the iridium (III) complex **1** and the D-*t*-Boc-phenylglycine) was kept at 1 μM, while the molar ratio of the iridium (III) complex **1** (X) was varied.




**Scheme 1.** Synthesis of iridium (III) complex **1** and structures of the amino acids examined in this study.

300 MHz and 75 MHz Chemical shifts were expressed in ppm and coupling constants (*J*) in Hz. Chemical shifts were given in ppm and coupling constants (*J*) in Hz. UV–vis absorption spectra were measured with an EVOLUTION 201 UV–vis spectrophotometer. Phosphorescence spectra were recorded on Shimadzu RF–5301 pc spectrofluorometer.

### 2.1.2. Synthesis of *1*

A solution of (*R*)-1-(1-naphthyl)ethyl isocyanate (0.20 g, 0.99 mmol) was added dropwise to a stirred methylene chloride solution (20 mL) of compound **3** (0.5 g, 0.45 mmol). The mixture was stirred for 2 h under nitrogen gas at room temperature. After purification by flash chromatography (methylene chloride/methanol = 20:1), compound **1** was obtained as orange solid in 50% yield (0.37 g). Yield: 50% mp 210–212 °C; $[\alpha]_D^{15}$ 32.4. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 9.38 (s, 2H), 8.13 (d, $J$ = 8.52 Hz, 2H), 7.87–7.89 (m, 2H), 7.65–7.78 (m, 10H), 7.53–7.59 (m, 2H), 7.43–7.46 (m, 4H), 7.37–7.41 (m, 4H), 7.30–7.35 (m, 2H), 7.21–7.25 (m, 2H), 6.88–7.05 (m, 6H), 6.28 (t, $J$ = 6.32 Hz, 2H), 5.64–5.80 (m, 4H), 4.57–4.67 (m, 4H), 1.47–1.51 (m, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 168.11, 158.20, 156.68, 154.87, 154.77, 150.52, 149.39, 148.64, 143.67, 141.61, 141.54, 138.22, 138.15, 133.99, 131.93, 131.02, 130.86, 128.78, 127.28, 126.44, 125.86, 125.35, 124.99, 123.53, 122.82, 122.64, 119.77,46.05, 42.87, 23.22.HR FAB-MS $m/z$ [$M^+$]