Dyes and Pigments 147 (2017) 291–299

Contents lists available at ScienceDirect

Dyes and Pigments

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

Pt(II) diimine complexes bearing difluoro-boron-dipyrromethene acetylide ligands: Synthesis, photophysics, aggregation included emission and optical power limiting properties

Rui Liu [a], [*], Senqiang Zhu [a], Jiapeng Lu [a], Hong Shi [b], Hongjun Zhu [a], [**]

[a] Department of Applied Chemistry, College of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing 211816, China
[b] Jiangsu Vocational College of Information Technology, Wuxi 214153, China

ARTICLE INFO

Article history:
Received 8 July 2017
Received in revised form
14 August 2017
Accepted 15 August 2017
Available online 16 August 2017

Keywords:
Optical power limiting
Aggregation induced emission
Photophysics
Pt(II) diimine complex
Bodipy
Triplet excited state

ABSTRACT

A series of Pt(II) complexes bearing difluoro-boron-dipyrromethene (Bodipy) acetylide ligands and different alkyl/aryl substituted 2,2′-bipyridyl ligands (**Pt-1** – **Pt-3**) were synthesized and characterized. Their photophysics, aggregation included emission (AIE) and optical power limiting properties were systematically investigated *via* UV–Vis absorption, emission, transient absorption, and nonlinear transmission spectroscopy/technique. These complexes exhibit $^1\pi$-π^* transitions/metal-to-ligand charge transfer (^{1}MLCT) absorption bands in UV-Vis spectral region and green fluorescence assigned to $^1\pi$-π^* state mixed with ^{1}MLCT character. All complexes exhibit obvious AIE in CH_3CN-water solution system. When water fraction increased, nanoparticles of Pt(II) complexes were formed owing to the aggregation, and the emission intensity and triplet excited state lifetime both increased. In addition, complexes **Pt-1** – **Pt-3** all exhibit triplet transient absorption (TA) in visible region, where reverse saturable absorption (RSA) could occur. The strength of RSA at 532 nm follows the trend: **Pt-2** > **Pt-3** > **Pt-1**. The significant AIE, TA and OPL properties of these complexes would be useful for rational design of transition-metal complexes with high emission quantum yield, broadband excited-state absorption, long excited-state lifetime, and strong nonlinear absorption for multi-functional applications.

1. Introduction

Pt(II) diimine acetylide complexes have attracted great interest in past decade due to their versatile applications in low-power up-conversion [1–4], organic light-emitting devices (OLEDs) [5,6], luminescent bioimaging [7,8], oxygen sensing [9] and nonlinear optics [10–13]. These applications are essentially on the basis of the square-planar configuration and the multiple intramolecular charge transfer excited states of the Pt(II) complexes, which feature them intermolecular Pt…Pt and/or π–π interactions and rich photophysical properties. The heavy-atom-induced strong spin orbit coupling also gives rise to an efficient intersystem crossing, resulting a long-lived triplet excited state and high triplet quantum yield. In addition, the photophysical properties of Pt(II) diimine acetylide complexes can be readily tuned by structural modifications to meet the different requirements for special application [14–17].

Previous studies on Pt(II) diimine acetylide complexes demonstrated that their photophysical characters, especially the triple state (T_1) lifetime, could be drastically tuned by the substituents and the extended π-conjugation on 2,2′-bipyridyl ligand or acetylide ligands. Sun group [18] revealed that extend the π-conjugation of the ethynylfluorenyl ligand with end-capped electron-donating (diphenylamino) or electron-withdrawing (benzothiazolyl) substituent could improve the T_1 lifetimes of Pt(II) bipyridine complexes. Castellano group [19] discovered that the extension of π-conjugation in bipyridine ligand significantly red-shifts of the absorption and emission of Pt(II) acetylide complexes. In addition, Schanze group [15] changed the substituents on bipyridine ligand in Pt(II) bistolylacetylide complexes, which obviously varied the energy of the Pt→bipyridine metal-to-ligand charge transfer (MLCT) excited state and decreased the triplet lifetimes. Sun group [16] also demonstrated that introducing benzothiazolylfluorenyl substituents on 5,5′-positions of bipyrine ligand dramatically admixed $^3\pi,\pi^*$ excited state into the charge-transfer excited states

---

[*] Corresponding author.
[**] Corresponding author.
E-mail addresses: rui.liu@njtech.edu.cn (R. Liu), zhuhj@njtech.edu.cn (H. Zhu).

http://dx.doi.org/10.1016/j.dyepig.2017.08.024
0143-7208/© 2017 Elsevier Ltd. All rights reserved.

of Pt(II) complexes, which possess long-lived (~50 μs), broadband (visible to the near-IR region) triplet excited-state absorption and strong reverse saturable absorption (RSA).

Aggregation included emission (AIE) phenomenon has been studied widely [20]. Interestingly, by modification of the bipyridyl ligand, Pt(II) complexes also exhibit significant AIE properties. Because of the square planar geometry, Pt(II) complexes are generally influenced by intra- and intermolecular Pt…Pt and π–π interactions, which are sensitive to solvent composition, complex concentration and nucleophiles [21,22]. Kanbara group reported the cationic Pt(II) complex bearing secondary thioamide units, which behaves obviously AIE-active occurred by metal-metal interactions [23]. Therefore, by introducing the specific substituted ligands into the Pt(II) diimine acetylide complexes, we envision maintaining their triplet excited-state absorption, prolonging their triplet excited-state lifetimes, and endowing their AIE features.

As the most popular chromophor, difluoro-boron-dipyrromethene (Bodipy) has been the subject of extensive study by virtue of their strong ground-state absorption, intense luminescence and high chemical stability. Since the triplet state is significant for the application of photodynamic therapy (PDT), triplet–triplet annihilation upconversion (TTA) and optical power limiting (OPL) material, more study is focsed on the investigation of Bodipy's triplet excited state [24]. Proved by Zhao group [25,26], introducing Bodipy acetylide ligands on 2,2′-bipyridyl Pt(II) complexes qualified the complexes long-lived triplet excited states, which is also benefit to achieve the ultimate goal in developing long-lived nonlinear optical materials. In addition, as classical building blocks, carbazole and fluorene have been systematically studied and widely used in the field of photofunctional materials, because of their intense luminescence, structure stability and ease of modification [27–30]. Attaching electron-donating substituents (carbazolyl and fluorenyl) on bipyridyl ligand of Pt(II) complexes would be expected to increase their intramolecular charge transfer and tune their photophysical properties accordingly.

In this work, we report the design and synthesis of three Pt(II) complexes bearing Bodipy acetylide ligands and different alkyl/aryl substituents on bipyridine unit (**Pt-1** – **Pt-3** in Scheme 1). Their photophysical properties were investigated systematically to understand the structure-property correlations and developing novel multi-functional optical materials with long-lived excited-state absorption for AIE and OPL applications.

2. Experimental section

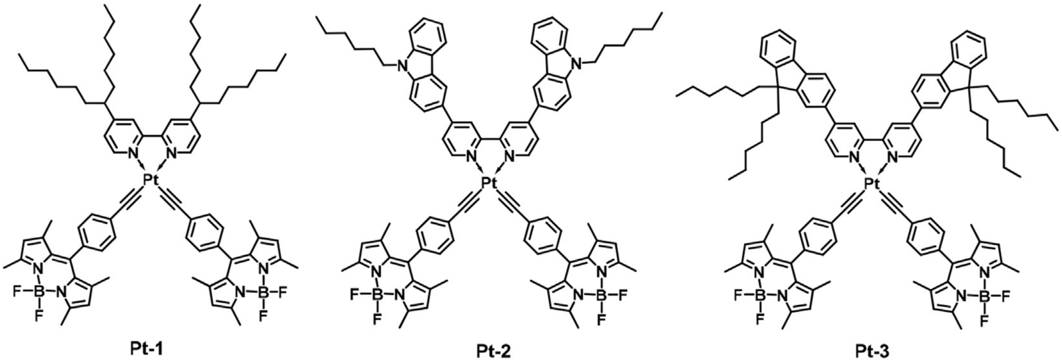
2.1. Synthesis and characterization

All the solvents and other regents were purchased from Aldrich and Sinopharm Chemical Reagent Co. Ltd. and used as received unless otherwise stated. All the HPLC-grade solvents used for spectroscopic study were purchased and were used without any further purification. Toluene, tetrahydrofuran (THF), triethylamine (TEA), diisopropylamine (DIPA) and *N*, *N*-diisopropylethylamine (DIEA) as solvents for chemical synthesis were freshly distilled according to the standard procedures. Lithium diisopropylamide (LDA) was purchased from Aldrich Chemical Reagent Co. Ltd. Ultrapure water was used in the experiments. Silica column chromatography was carried out on silica gel (200–300 mesh). The ligands and complexes were characterized by ^{1}H NMR, ^{19}F NMR and mass spectra. ^{1}H NMR spectra and ^{19}F NMR spectra of the complexes in $CDCl_3$ or DMSO-d_6 solvent were measured on a Bruker Avance instrument, with tetramethylsilane for ^{1}H NMR spectra and $CFCl_3$ for ^{19}F NMR spectra as an internal standard. Mass analyses were performed on a Bruker autoflex III mass spectrometer.

Intermediates **1** was purchased from Energy Chemical Co. Ltd. intermediates **2**, **3**, **4**, **6**, **7** and Bodipy acetylide ligand were synthesized according to literature methods [31–34].

4,4′-bis(9-hexyl-9*H*-carbazol-3-yl)-2,2′-bipyridine (**5**). The mixture of compound 1 (0.8 g, 2.12 mmol), 4,4′-dibromo-2,2′-dipyridine (0.32 g, 1.01 mmol), $Pd(PPh_3)_4$ (0.11 g, 0.1 mmol) and K_2CO_3 (0.56 g, 4.04 mmol) were added into a 100 mL two-neck flask. Then 30 mL toluene and 8 mL H_2O were added. The reaction mixture was stirred and refluxed for 36 h. The reaction mixture was allowed to cool to room temperature. Toluene and water were removed by the rotary evaporation instrument firstly. Then the mixture was washed with water and extracted with ethyl acetate. The combined organic solution dried over anhydrous sodium sulfate and concentrated in vacuo. The residue was purified by column chromatography with petroleum/ethyl acetate (10:1 v/v) to give a white solid in yield of 68%. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.87 (s, 2H), 8.80 (d, J = 5.1Hz, 2H), 8.58 (s, 2H), 8.22 (d, J = 7.7Hz, 2H), 7.95–7.92 (m, 2H), 7.73–7.71 (m, 2H), 7.53–7.50 (m, 4H), 7.45 (d, J = 8.1Hz, 2H), 7.29 (t, J = 7.4Hz, 2H), 4.35 (t, J = 7.2Hz, 4H), 1.95–1.87 (m, 4H), 1.42–1.29 (m, 12H), 0.87 (t, J = 6.9Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 156.82, 150.22, 149.60, 141.02, 140.97, 128.90, 126.11, 124.95, 123.50, 122.95, 121.61, 120.68, 119.31 119.26, 119.10, 109.16, 109.02, 77.41, 77.10, 76.78, 43.27, 31.62, 29.00, 27.02, 22.60, 14.08.

General procedure for the synthesis of **Pt-1**, **Pt-2** and **Pt-3**. The mixture of **4** (**5** or **6**) (0.15 mmol), K_2PtCl_4 (76 mg, 0.18 mmol), water (30 mL), and HCl aqueous solution (10 mL, 2 M) was heated to reflux under argon for 24 h. After the reaction, the reaction mixture was filtered. The collected orange solid was dissolved in CH_2Cl_2 and washed with brine, then dried over $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography on silica gel with CH_2Cl_2 to give a yellow solid **7** (**8** or **9**) [26].



Scheme 1. Structures for Pt(II) complexes **Pt-1** – **Pt-3**.