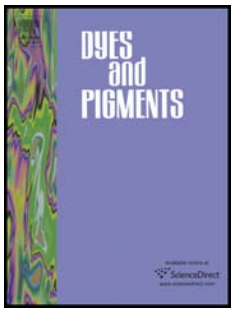

New Iridium Complexes with Two Pre-organized Urea Groups and Thiourea Groups as Phosphorescent Chemosensors for H_2PO_4- and Chiral Carboxylates

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Highlights

- As a versitle platform for phosphorescent chemosensors, bis(benzylic amine) derivative **6** was synthesized.
- A phosphorescent chemosensor **1** displayed a selective phosphorescence enhancement with $H_2PO_4^-$.
- A new iridium complex **2** is reported as a first chiral phosphorescent chemosensor for amino acids.

New Iridium Complexes with Two Pre-organized Urea Groups and Thiourea Groups as Phosphorescent Chemosensors for $H_2PO_4^-$ and Chiral Carboxylates

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Abstract: As a versatile platform for phosphorescent chemosensors, bis(benzylic amine) derivative **6** was synthesized. Two urea groups could be readily introduced for phosphorescent chemosensor **1**. A preorganized binding pocket could induce a selective phosphorescence enhancement with $H_2PO_4^-$. A new iridium complex **2** bearing two thiourea groups as well as glucopyranosyl chiral barriers is reported as a first chiral phosphorescent chemosensor for amino acids.

Keywords: phosphorescence chemosensor, anion recognition, dihydrogen phosphate sensing, chiral recognition, iridium complex

1. Introduction

Numerous efforts have been devoted to the development of methods for the recognition and detection of anions due to their important roles in many chemical and biological processes [1]. Phosphorescent chemosensors have several unique advantages, such as evident Stockes shifts, relatively long lifetimes, etc.. Because of these unique properties, their emission spectra can be utilized to readily discriminate from the background fluorescence normally present in biological and clinical sample [2].

Among the various types of phosphors, cyclometalated iridium (III) complexes have been known to show high phosphorescence efficiency and relatively long lifetimes and, thus, they have been utilized as efficient phosphorescent dopants in organic light emitting diodes (OLEDs) [3]. These highly phosphorescent iridium (III) complexes have also been utilized as phosphorescent chemosensors for anions [4], cysteine/homocystein [5], molecular oxygens [6], cations [7], etc [8].

Even though fluorescent chemosensors for $H_2PO_4^-$ have been extensively studied [9], there has been only one report that evaluated their use as phosphorescent chemosensors.[10]

Similarily, chiral recognitions using fluorescence changes have been actively studied [11], while there has not been an example for chiral phosphorescent

chemosensors. In this paper, we report the first example of $H_2PO_4^-$ selective phosphorescence chemosensor based on the iridium (III) complex. Unlike previous anion selective phosphorescence chemosensors, probe **1** displayed phosphorescence enhancement in the presence of $H_2PO_4^-$. In addition, first example of chiral phosphorescence chemosensor and its chiral recognition towards amino acids are reported.

In this work, we prepared bis(benzylic amine) derivative **6** as a versatile flatform. As a proof of concept, two new phosphorescence chemosensors **1** and **2**, which contained a preorganized binding pocket, were synthesized from **6** and their unique binding properties were studied. We believe this bis(benzylic amine) derivative **6** can be utilized as a valuable platform for the development of new phosphorescent chemosensors in the future.

2. Experimental

2.1 Materials and equipments

General methods unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Flash chromatography was carried out on silica gel (230-400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded using 300 MHz and 75 MHz Chemical shifts were expressed in ppm and coupling constants (*J*) in Hz. UV-vis absorption spectra were measured with an EVOLUTION 201 UV-visible spectrophotometer. Phosphorescence spectra were recorded on Shimadzu RF-5301 pc spectrofluorometer.

2.2 Synthesis

4,4'-Bis (bromomethyl)-2,2`-bipyridine 3

The bipyridine (0.90 g, 4.2 mmol) was dissolved in a mixture of 48% HBr (20 mL) and concentrated sulfuric acid (6.7 mL). The resulting solution was refluxed for 6 h and then allowed to cool to room temperature, and 40 mL of water was added. The pH was adjusted to neutral with NaOH solution and the resulting precipitate filtered, washed with water (pH = 7), and air-dried. The product was dissolved in chloroform (40 mL) and filtered. The solution was dried over magnesium sulfate and evaporated to get a white powder. Yield: 1.2 g (85%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 4.50 (s, 4H), 7.38 (d, 2H), 8.45 (s, 2H), 8.68 (d, 2H).

4,4`-Phthalimidylmethyl-2,2`-bipyridine 4

A mixture of 4,4'-Bis (bromomethyl)-2,2'-bipyridine (0.26 mg, 0.7 mmol) and potassium phthalimide (1.4 g, 7.6 mmol) in DMF (38 mL) was heated at 50 ^{o}C under nitrogen atmosphere. After 5 h, water (60 mL) was added to the mixture, and the organic layer was extracted with $CHCl_3$ (70 mL × 3). The organic layer was dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was washed with methanol, and dried under reduced pressure to give colorless solid. Yield: 180 mg (50 %). ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.61 (d, 2H), 8.37 (s, 2H), 7.87 (m, 2H), 7.74 (m, 2H), 7.28 (d, 2H), 4.93 (s, 4H).

Ir(ppy)2(dphmbpy) 5

A mixture of 4,4'-phthalimidylmethyl-2,2'-bipyridine (0.5 g, 0.47 mmol) and $[(ppy)_2IrCl]_2$ (0.46 g, 0.98 mmol) in a 1:1 (v/v) dichloromethane and methanol

solution was refluxed for 6 h. The solvents were evaporated on rotary evaporation. The residue was dissolved in dichloromethane. The organic solution was washed with brine and then dried over Na_2SO_4.The solvent was removed by rotary evaporator. The light yellow residue was purified by chromatography over silica gel (dichloromethane). Yield: 290 mg (64 %). mp: 231-233 ^oC. ^1H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.89 (s, 2H), 7.87-7.80 (m, 6H), 7.78-7.71 (m, 8H), 7.60 (d, J = 7.69, 2H), 7.48 (d, J = 5.76, 2H), 7.18 (d, J = 5.76, 2H), 7.07 (t, J = 6.59, 2H), 6.97 (t, J =7.41, 2H), 6.85 (t, J = 7.41, 2H), 6.22 (d, J = 7.69, 2H), 5.34 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 167.92, 156.11, 150.35, 148.85, 143.65, 138.39, 134.70, 131.96, 131.83 , 130.94 , 125.97, 125.66, 124.93, 123.92, 123.70, 122.83, 119.83, 40.66; HR FAB-MS m/z [M^+] calcd. For $C_{50}H_{34}IrN_6O_4$ 975.2275 Found: 975.2271; IR (KBr pellet) cm^{-1} 3408.43, 3043.37, 1715.50, 1607.29, 1393.19, 950.71, 725.18.

Ir(ppy)2(dambpy) 6

A mixture of **5** (70 mg, 0.1 mmol) and hydrazine monohydrate (140 μL, 2.9 mmol) in EtOH (5.3 mL) was heated at 100 ^oC for 12 h. Saturated aqueous NaCl solution (18 mL) was added to the mixture. The mixture was adjusted to pH 12 with 50 % NaOH solution. The organic layer was extracted with $CHCl_3$ (50 mL × 3), dried over anhydrous Na_2SO_4, and evaporated to give orange solid. Yield: 180 mg (50 %). mp > 300 ^oC. ^1H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.91 (s, 2H), 7.91-7.88 (d, *J* = 7.96, 2H), 7.76-7.66 (m, 6H), 7.50 (s, 2H), 7.29 (s, 2H), 7.05-6.90 (m, 8H), 6.30 (d, *J* = 7.42, 2H), 4.17 (s, 4H), 2.47 (s, 4H); HR FAB-MS m/z [M^+] calcd. For $C_{34}H_{30}IrN_6$

715.2161 Found: 715.2163; IR (KBr pellet) cm^{-1} 3408.68, 1683.71, 1507.16, 1477.29, 1418.84, 760.26.

Ir(ppy)2(dburebpy) 1

A mixture of **6** (70 mg, 0.08 mmol) and butyl isocyanate (140 μL) in dichloromethane (5.3 mL) was stirring at room temperature for 2 h. The solvents were evaporated on rotary evaporation. The residue was dissolved in dichloromethane. The organic solution was washed with brine and then dried over Na_2SO_4 then removed by rotary evaporator. The light yellow residue was purified by chromatography over silica gel (dichloromethane). Yield: 180 mg (50 %). mp 224 – 225 ^oC. ^1H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.33 (s, 2H), 7.90 (d, *J* = 7.97, 2H), 7.78-7.60 (m, 6H), 7.45 (d, *J* = 6.04, 2H), 7.22 (m, 2H), 7.05-6.97 (m, 6H), 6.93-6.87 (t, *J* = 6.73, 2H), 6.38 (d, 2H), 6.29 (d, *J* = 7.99, 2H), 4.62 (d, *J* = 6.04, 2H), 3.60-3.14 (m, 4H), 1.52-1.47 (m, 4H), 1.38-1.30 (m, 4H), 0.89-0.84 (t, *J* = 7.14, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 168.18, 159.06, 156.73, 155.27, 150.56, 149.29, 148.67, 143.67, 138.12, 131.95, 131.02, 126.35, 124.99, 123.74, 123.39, 122.81, 119.79, 42.67, 40.11, 32.71, 20.35, 14.06; HR FAB-MS m/z [M^+] calcd. For $C_{45}H_{49}IrN_7O_2$ 913.3529. Found: 913.3527; IR (KBr pellet) cm^{-1} 3408.50, 2926.48, 1669.53, 1559.23, 1268.68, 761.07.

GITC appended Iridium (III) complex 2

A solution of GITC (0.22 g, 0.56mmol) was added dropwise to a stirred methylene chloride solution (20 mL) of compound **6** (0.2 g, 0.28 mmol). The mixture was stirred for 2 h under nitrogen gas at room temperature. Purification by flash chromatography (methylene chloride/ methanol = 20:1) offered 0.27 g orange solid compound **2**.

Yield: 65 % mp 226-227 ^{o}C; $[\alpha]_D^{23}$ 15.3 ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.31 (s, 1H), 8.09 (d, J = 8.24, 2H), 7.71-7.85 (m, 8H), 7.50-7.52 (m, 2H), 7.00-7.05 (t, *J* = 7.41, 2H), 6.88-6.94 (t, *J* = 7.41, 2H), 6.82-6.77 (t, *J* = 7.41, 2H), 6.25 (d, *J* = 8.24, 2H), 5.83-5.87 (m, 2H), 4.90-5.26 (m, 7H), 4.10-4.16 (m, 2H), 3.92-3.98 (m, 4H), 3.85 (bs, 2H), 1.86-1.93 (m, 24H), 1.72 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.39, 171.08, 170.51, 170.11, 169.68, 156.63, 152.00, 150.22, 149.66, 148.83, 143.69, 138.29, 131.86, 131.08, 127.37, 125.02, 123.45, 122.91, 119.83, 74.00, 73.37, 70.73, 68.51, 62.25, 47.07, 21.00, 20.84. HR FAB-MS m/z [M+] calcd. For $C_{64}H_{68}IrN_8O_{18}S_2$ 1493.3722 Found:1493.3725; IR (KBr pellet) cm^{-1} 3356, 3408, 1751, 1541, 1226, 1036, 760.

3. Results and discussion

3.1 Synthesis

For the synthesis of probe **1** and **2**, 4,4`-phthalimidyl methyl-2,2`-bipyridine (**4**) was prepared by modifying the reported procedures [12]. Treatment of $[(ppy)_2IrCl]_2$ with 4,4`-phthalimidylmethyl-2,2`-bipyridine (**4**) produced the iridium (III) complex **5** containing bipyridine as the ancillary ligand appended with phthalimidylmethyl groups with a yield of 64 % after column chromatography purification using dichloromethane (Scheme 1). Phthalimidylmethyl iridium (III) complex **5** was then reacted with hydrazine monohydrate to form the versatile intermediate, iridium (III) complex (**6**) bearing dimethylamine groups. Finally, probe **1** and **2** were synthesized by treatment of compound **6** with *n*-butyl isocyanate or

2,3,4,6-*O*-acetyl-β-D-glucopyranosyl isothiocyanate (GITC), respectively, at room temperature in dichloromethane. The detailed synthetic procedures are explained in the Experimental Section and the new compounds were fully characterized by ^{1}H NMR, ^{13}C NMR and high resolution mass spectroscopy.

Insert Scheme 1

3.2 Spectral studies of iridium (III) complex 1

The assay methods for UV-vis spectra and phosphorescence spectra: Firstly, Ir(II) complexes were dissolved in distilled CH_2Cl_2 to make 1.0×10^{-3}M solution. Then the solution was diluted to quartz cell filled with 3 mL acetonitrile using microsyringe to 1.0×10^{-5}M test solution. And because of the emission sensitivity to oxygen, all samples in phosphorescence experiments were deaerated with argon for ca. 8 min before measurement and the gas flow is kept during the measurement.

The UV-vis spectra and phosphorescence spectra of iridium (III) complex **1** in acetonitrile are shown in Fig. S1. In the UV-vis spectra, due to the ligand-centered LC (π-π*) and spin-allowed metal-to ligand charge transfer (^{1}MLCT) transitions, an intense absorption bands at around 250-280 nm and relatively weak absorption at 290-450 nm were observed. The addition of $H_2PO_4^-$ anions (100 equiv.) did not induce any significant change in its UV-vis absorption as shown in Fig. S1. Fig. 1 shows the photoluminescence properties of iridium (III) complex **1**. The iridium (III) complex **1** exhibited phosphorescence with a maximum wavelength of 560 nm in acetonitrile

upon excitation at 372 nm. To explore the anion selectivity of the iridium (III) complex **1**, binding experiments were performed using tetrabutylammonium salts of F^-, Cl^-, Br^-, I^-, CH_3COO^-, and $H_2PO_4^-$ (Fig. 1a). The addition of $H_2PO_4^-$ (100 equiv.) resulted in an enhancement of the phosphorescence of iridium (III) complex **1** with a 14 nm blue shift (Fig. 1b), which could also be observed by the naked eye (Fig. 2). From the phosphorescence titration experiments of iridium (III) complex **1** (10 μM) with $H_2PO_4^-$, the association constant were calculated to be 1.06×10^5 M^{-1}.

Insert Figure 1

Insert Figure 2

If the receptor was connected to the ligand through a spacer, the interaction of the receptor with the analyte may perturb the energy levels of the excited states [3a]. Thus the phosphorescence enhancement of iridium (III) complex **1** with $H_2PO_4^-$ can be attributed to the moderate increase in the energy level of the triplet excited state which was demonstrated by the 14 nm blue shift of phosphorescence. This increases the intersystem crossing efficiency and enhances the triplet quantum yield, thus inducing a "switch on" of the emission.

We also investigated the phosphorescence lifetime variation with $H_2PO_4^-$. The system for nanosecond phosphorescence lifetime spectroscopy is illustrated in Fig. S2. As shown in Fig. 2b, the phosphorescence lifetime of complex **1** increased markedly upon the addition $H_2PO_4^-$. The phosphorescence lifetime of complex **1** changed from 0.34 μs to 0.6 μs as the $H_2PO_4^-$ concentration increased from 0.0 to 200.0 μM.

3.2. Chiral recognition of iridium (III) complex 2

Then, Iridium (III) complex **2** was examined for chiral recognition with tetrabutyl ammonium salts of *t*-Boc-amino acids and 3,5-dinitrobenzoyl (DNB)-amino acids, such as alanine (Ala), valine (Val), threonine (Thr), leucine (Leu), phenylglycine (Phg) and phenylalanine (Phe). Phosphorescence titrations of iridium (III) complex **2** (10 μM) with D- and L-*t*-Boc-amino acid derivatives in acetonitrile are illustrated in the supporting informations. Iridium (III) complex **2** showed phosphorescence enhancement with *t*-Boc-amino acid derivatives. Based on phosphorescence titrations data of iridium (III) complex **2** with *t*-Boc-amino acid derivatives, the association constants (*K*) were calculated according to the linear Benesi-Hildebrand expression (Table 1).[17] In general, iridium (III) complex **2** showed larger K_a values for D-*t*-Boc amino acid derivatives than those for L-isomers. For example, the association constant of **2** with D- and L-*t*-Boc-leucine were calculated as 1.10×10^5 and 3.48×10^4 M^{-1}, respectively, with the K_D/K_L of 3.16.

Insert Table 1

Compared to the *t*-Boc series, iridium (III) complex **2** displayed phosphorescence quenching effects with DNB derivatives. The phosphorescence titrations of iridium (III) complex **2** (10 μM) with D-DNB-threonine and L-DNB-threonine in acetonitrile are also illustrated in the supporting informations. L-DNB-threonine induced larger

phosphorescence quenching effect than D-isomer. The phosphorescence quenching effects of Iridium complex **2** can be attributed to the -NO_2 group of DNB [11d]. The association constants with DNB-amino acid derivatives were summarized in Table 2. As shown in Table 2, iridium (III) **2** showed larger K_a values for L-DNB-amino acid derivatives. The Job`s plot experiment indicated a 1:1 formation between amino acids and hosts (Fig. S3).

Insert Table 2

4. Conclusion

In conclusion, here, we report the first example of phosphorescence chemosensor for $H_2PO_4^-$. Iridium (III) complex **1** contained two preorganized urea groups for the recognition of $H_2PO_4^-$. Methylene linkers between bipyridine and urea moieties in probe **1** not only provided a nice binding pocket for the selective recognition of $H_2PO_4^-$ but also resulted in a higher phosphorescence enhancement with $H_2PO_4^-$, which can be compared to the phosphorescence quenching effects of reported iridium (III) complexes bearing the urea group directly on the benzene. A new chiral phosphorescent iridium (III) complex **2** bearing two preorganized thiourea groups as binding sites and two GITC groups as chiral barriers was studied for the recognition of the α-amino acid derivatives. In addition, bis(benzylic amine) derivative **6** holds great promise for use as a valuable platform for the development of new phosphorescence chemosensors through the introduction of various binding sites.

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References

[1] (a) M. Wenzel, J. Hiscock, P. Gale, Anion receptor chemistry: highlights from 2010, Chem. Soc. Rev. 41 (2012) 480-520. (b) S. Kim, J. Sessler, Ion pair receptors, Chem. Soc. Rev. 39 (2010) 3784-3809. (c) A. Li, J. Wang, F. Wang, Y. Jiang, Anion complexation and sensing using modified urea and thiourea-based receptors, Chem. Soc. Rev. 39 (2010) 3729-3745. (d) R. Martínez-Máñez, F. Sancanón, Fluorogenic and Chromogenic Chemosensors and Reagents for Anions, Chem. Rev. 103 (2003) 4419-4476. (e) E. Galbraith, T. James, Boron based anion receptors as sensors, Chem. Soc. Rev. 39 (2010) 3831-3842. (f) M. Jun, B. Roy, K. Ahn, "Turn-on" fluorescent sensing with "reactive" probes, Chem. Commun. 47 (2011) 7583-7601. (g) E. J. Jun, H. Liu, J. Choi, J. Y. Lee, J. Yoon, New fluorescent receptor composed of two imidazoliums, two pyrenes and a boronic acid for the recognition of DOPAC, Sensor & Actuator B: Chemical. 176 (2013), 611-617. (h) S. K. Kim, H. N. Kim, Z. Xiaoru, H. N. Lee, H. N. Lee, J. H. Soh, K. M. K. Swamy, J. Yoon, Recent Development of Anion Selective Fluorescent Chemosensors, Supramolecular Chem. 19 (2007), 221-227. (i) Y. Zhou, Z. Xu and Juyoung Yoon, Fluorescent and Colorimetric Chemosensors for Detection of Nucleotides, FAD and NADH: Highlighted Research

During 2004-2010, Chem. Soc. Rev. 40 (2011) 2222-2235. (j) N. R. Song, J. H. Moon, E. J. Jun, J. Choi, Y. Kim, S.-J. Kim, J. Y. Lee, J. Yoon, Cyclic Benzobisimidazolium Derivative for the Selective Fluorescent Recognition of HSO_4^- in Aqueous Solution via C-H Hydrogen Bondings, Chem. Sci. 4 (2013) 1765-1771. (k) Z. Guo, N. R. Song, J. H. Moon, M. Kim, E. J. Jun, J. Choi, J. Y. Lee, C. W. Bielawski, J. L. Sessler, J. Yoon, A Benzobisimidazolium Based Fluorescent and Colorimetric Chemosensor for CO_2, J. Am. Chem. Soc. 134 (2012), 17846-17849.

[2] (a) C. M. G. dos Santos, A. Harte, S. Quinn, T. Gunnlaugsson, Recent developments in the field of supramolecular lanthanide luminescent sensors and self-assemblies, Coord. Chem. Rev. 252 (2008) 2512-2527. (b) V. Yam, E. Cheng, Highlights on the recent advances in gold chemistry-a photophysical perspective, Chem. Soc. Rev. 37 (2008) 1806-1813. (c) Q. Zhao, F. Li, C. Huang, Phosphorescent chemosensors based on heavy-metal complexes, Chem. Soc. Rev. 39 (2010) 3007-3030. (e) V. Guerchais, J. Fillaut, Sensory luminescent iridium(III) complexes for cation recognition, Coord. Chem. Rev. 255 (2011) 2448-2457. (f) J. Sun, W. Wu, J. Zhao, Long-Lived Room-Temperature Deep- Red-Emissive Intraligand Triplet Excited State of Naphthalimide in Cyclometalated Ir^{III} Complexes and its Application in Triplet-Triplet Annihilation-Based Upconversion, Chem. Eur. J. 18 (2012) 8100-8112.

[3] S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razaq, H. Lee, C. Adachi, P. Burrows, S. Forrest, M. Thompson, Highly Phosphorescent Bis-Cyclometalated

Iridium Complexes: Synthesis, Photophysical Characterization, and Use in Oganic Light Emitting Diodes, J. Am. Chem. Soc. 123 (2001) 4304-4312.

[4] (a) P. Anzenbacher, Jr., D. Tyson, K. Jursíková, F. Castellano, Luminescence Lifetime-Based Sensor for Cyanide and Related Anions, J. Am. Chem. Soc. 124 (2002) 6232-6233. (b) Q. Zhao, F. Li, S. Liu, M. Yu, Z. Liu, T. Yi, C. Huang, Highly Selective Phosphorescent Chemosensor for Fluoride Based on an Iridium(III) Complex Contating Arylborane Units, Inorg. Chem. 47 (2008) 9256-9264. (c) D. Jose, P. Kar, D. Koley, B. Ganguly, W. Thiel, H. Ghosh, A. Das, Phenol-and Catechol-Based Ruthenium(II) Polypyridyl Complexes as Colorimetric Sensors for Fluoride Ions, Inorg. Chem. 46 (2007) 5576-5584. (d) Y. You, S. Park, A Phosphorescent Ir(III) Complex for Selective Fluoride Ion Sensing with a High Signal-to-Noise Ratio, Adv. Mater. 20 (2008) 3820-3826. (e) Y. Sun, S. Wang, Extending π-Conjugation of Triarylborons with a 2,2-Bpy Core: Impact of Donor-Acceptor Geometry on Luminescence, Anion Sensing, and Metal Ion Binding, Inorg. Chem. 49 (2010) 4394-4404. (f) T. Kwon, H. Kim, J. Hong, Phosphorescent Thymidine Triphosphate Sensor Based on a Donor-Acceptor Ensemble System using Intermolecular Energy Transfer, Chem. Eur. J. 14 (2008) 9613-9619.

[5] (a) Y. Tang, H. Yang, H. Sun, S. Liu, J. Wang, Q. Zhao, X. Liu, W. Xu, S. Li, W. Huang, Rational Design of an “OFF-ON” Phosphorescent Chemodosimeter Based on an Iridium(III) Complex and Its Application for Time-Resolved Luminescent Detection and Bioimaging of Cysteine and Homocysteine, Chem. Eur. J. 19 (2013) 1311-1319. (b) H. Chen, Q. Zhao, Y. Wu, F. Li, H. Yang, T. Yi, C. Huang, Selective

Phosphorescence Chemosensor for Homocysteine Based on an Iridium(III) Complex, Inorg. Chem. 46 (2007) 11075-11081.

[6] (a) Y. Liu, H. Guo, J. Zhao, Ratiometric luminescent molecular oxygen sensors based on unit-luminophores of C^N Pt(II)(acac) complexes that show intense visible-light absorption and balanced fluorescence/phosphorescence dual emission, Chem. Commun. 47 (2011) 11471-11473. (b) L. Huynh, Z. Wang, J. Yang, V. Stoeva, A. Lough, I. Manners, D. Winnik, Evaluation of Phosphorescent Rhenium and Iridium Complexes in Polythionylphosphazene Films for Oxygen Sensor Application, Chem. Mater. 17 (2005) 4765-4773. (c) K. McGee, Veltkamp, B. Marquardt, K. Mann, Porous Crystalline Ruthenium Complexes Are Oxygen Sensors, J. Am. Chem. Soc. 129 (2007) 15092-15093.

[7] (a) M. Schmittel, H. Lin, Luminescent Iridium Phenanthroline Crown Ether Complex for the Detection of Silver(I) Ions in Aqueous Media, Inorg. Chem. 46 (2007) 9139-9145. (b) W. Tang, X, Lu, K. Wong, V. Yam, Synthesis, photophysics and binding studies of Pt(II) alkynyl terpyridine complexes with crown ether pendant. Potential luminescent sensors for metal ions, J. Mater. Chem. 15 (2005) 2714-2720. (c) Y. You, Y. Han, Y. Lee, S. Park, W. Nam, S. Lippard, Phosphorescent Sensor for Robust Quantification of Copper(II) Ion, J. Am. Chem. Soc. 133 (2011) 11488-11491.

[8] S. Ji, W. Wu, W. Wu, H. Guo, J. Zhao, Ruthenium(II) Polyimine Complexes with a Long-Lived 3IL Excited State or a 3MLCT/3IL Equilibrium: Efficient Triplet Sensitizers for Low-Power Upconversion, Angew. Chem. Int. Ed. 50, (2011) 1626-1629.

[9] (a) A. Coskun, B. Baytekin, E. Akkaya, Novel fluorescent chemosensor for anions via modulation of oxidative PET: a remarkable 25-fold enhancement of emission, Tetrahedron Lett. 44 (2003) 5649-5651. (b) S. K. Kim, D. Seo, S. J. Han, G. Son, I.-J. Lee, C. Lee, K. D. Lee, J. Yoon, A New Imidazolium Acridine Derivative as Fluorescent Chemosensor for Pyrophosphate and Dihydrogen Phosphate, Tetrahedron 64 (2008), 6402-6405. (c) R. Hanshaw, S. Hilkert, H. Jiang, B. Smith, An indicator displacement system for fluorescent detection of phosphate oxyanions under physiological conditions, Tetrahedron Lett. 45 (2004) 8721-8724. (d) M. Boiocchi, L. Fabbrizzi, M. Garolfi, M. Licchelli, L. Mosca, C. Zanini, Templated Synthesis of Copper(II) Azacyclam Complexes Using Urea as a Locking Fragment and Their Metal-Enhanced Binding Tendencies towards Anions, Chem. Eur. J. 15 (2009) 11288-11297. (e) D. Kim, H. Hwang, J. Sessler, C. Lee, A dicationic calyx[4]pyrrole derivative and its use for the selective recognition and displacement-based sensing of pyrophosphate, Chem. Sci. 3 (2012) 1819-1824. (f) S. K. Kim, N. J. Singh, J. Kwon, I.-C. Hwang, S. J. Park, K. S. Kim, J. Yoon, Fluorescent Imidazolium Receptors for the Recognition of Pyrophosphate, Tetrahedron 62 (2006), 6065-6072.

[10] T. Lazarides, T. Miller, J. Jeffery, T. Ronson, H. Adams, M. Ward, Luminescent complexes of Re(I) and Ru(II) with appended macrocycle groups derived from 5,6-dihydroxyphenanthroline: cation and anion binding, Dalton Trans. 2005, 528-536.

[11] (a) L. Pu, Enantioselective Fluorescent Sensor: A Tale of BINOL, Acc. Chem. Res. 45 (2012) 150-163. (b) A. Accetta, R. Corradini, R. Marchelli, Enantioselective Sensing by Luminescence, Top. Curr. Chem. 300 (2011)175-216. (c) Y. Zhou, J.

Yoon, Recent progress in fluorescent and colorimetric chemosensors for detection of amino acids, Chem. Soc. Rev. 41 (2012) 52-67. (d) Y. Kim, H. Lee, N. Singh, H. Choi, J. Xue, K. Kim, J. Yoon, M. Hyun, Anthracene Derivatives Bearing Thiourea and Glucopyranosyl Groups for the Highly Selective Chiral Recognition of Amino Acids: Opposite Chiral Selectivities from Similar Binding Units, J. Org. Chem. 73 (2008) 301-304. (e) M. K. Choi, H. N. Kim, H. J. Choi, J. Yoon, M. H. Hyun, Chiral Anion Recognition by Color Change Utilizing Thiourea, Azophenol and Glucopyranosyl Groups, Tetrahedron Lett. 49 (2008), 4522-4525.

[12] S. Fukuda, A. Satake, Y. Kobuke, Synthesis of hexazincporphyrin and hexamine substituted Ru(bipy)3 complexes for alternate self-assembly by tritopic coordination, Thin Solid Films. 499 (2006) 263-268.

Scheme Title and Captions of Figures

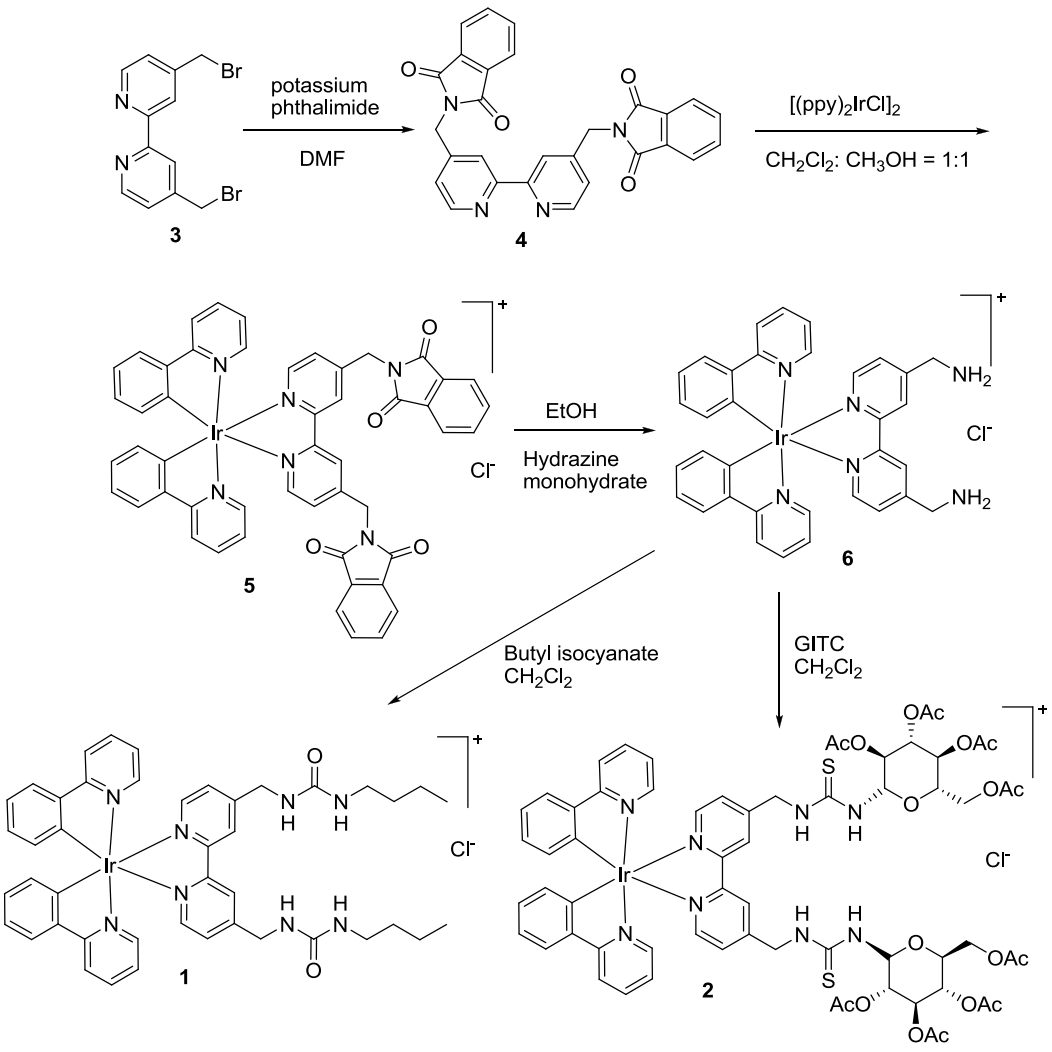
Scheme 1. Synthesis of iridium (III) complex **1** and **2**.

Figure 1. (a) The phosphorescence spectra of iridium (III) complex **1** (10 μM) upon addition of different anions (10 eq) in CH_3CN. (b) The phosphorescence titration spectra of iridium (III) complex **1** (10 μM) upon addition of tetrabutyl ammonium dihydrogenphosphate in CH_3CN. Excitation wavelength: 372 nm.

Figure 2. (a) Phosphorescence changes iridium (III) complex **1** by naked-eye upon the addition of tetrabutyl ammonium dihydrogenphosphate in CH_3CN. Excitation wavelength: 365 nm. (b) The phosphorescence lifetime of iridium (III) complex **1** (20 μM) and **1** with $H_2PO_4^-$ (10 eq.) in CH_3CN.

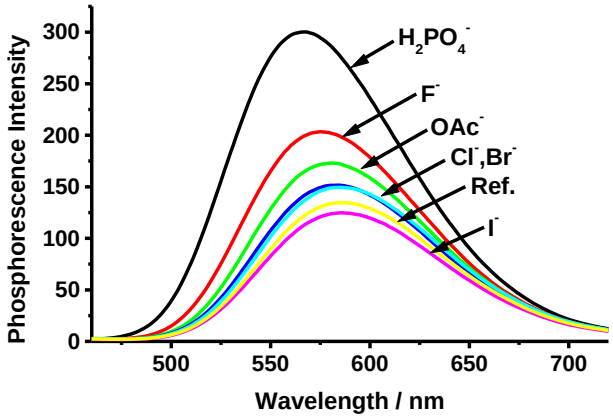
Table 1. The association constants (M^{-1}) of iridium (III) complex **2** with *t*-Boc-amino acid derivatives in acetonitrile.

Table 2. The association constants (M^{-1}) of iridium (III) complex **2** with DNB-amino acid derivatives in acetonitrile.



Scheme 1. Synthesis of iridium (III) complex **1** and **2**.

(a)



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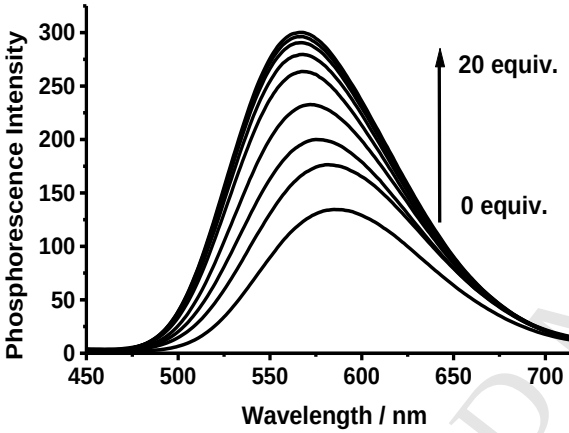
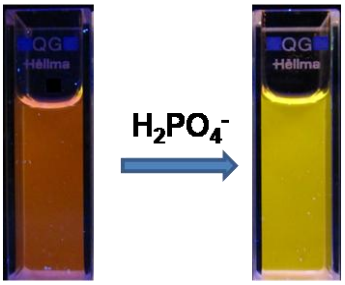


Figure 1. (a) The phosphorescence spectra of iridium (III) complex **1** (10 μM) upon addition of different anions (10 eq) in CH_3CN. (b) The phosphorescence titration spectra of iridium (III) complex **1** (10 μM) upon addition of tetrabutyl ammonium dihydrogenphosphate in CH_3CN. Excitation wavelength: 372 nm.

(a)



(b)

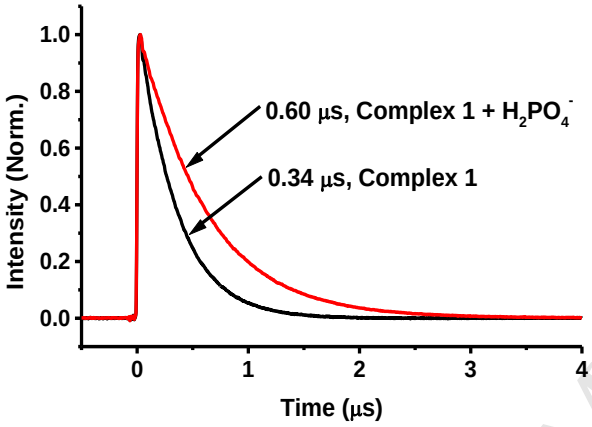


Figure 2. (a) Phosphorescence changes iridium (III) complex **1** by naked-eye upon the addition of tetrabutyl ammonium dihydrogenphosphate in CH_3CN. Excitation wavelength: 365 nm. (b) The phosphorescence lifetime of iridium (III) complex **1** (20 μM) and **1** with $H_2PO_4^-$ (10 eq.) in CH_3CN.

Table 1. The association constants (M^{-1}) of iridium (III) complex **2** with *t*-Boc-amino acid derivatives in acetonitrile.

Guest	$K_D(M^{-1})$	K_D/K_L	$K_L(M^{-1})$
Phenylglycine	9.00×10^4	1.91	4.71×10^4
Leucine	1.10×10^5	3.16	3.48×10^4
Valine	4.83×10^4	1.72	2.81×10^4
Threonine	-	-	5.00×10^3
Alanine	4.62×10^4	1.32	3.50×10^4
Phenylalanine	3.52×10^4	2.05	1.72×10^4

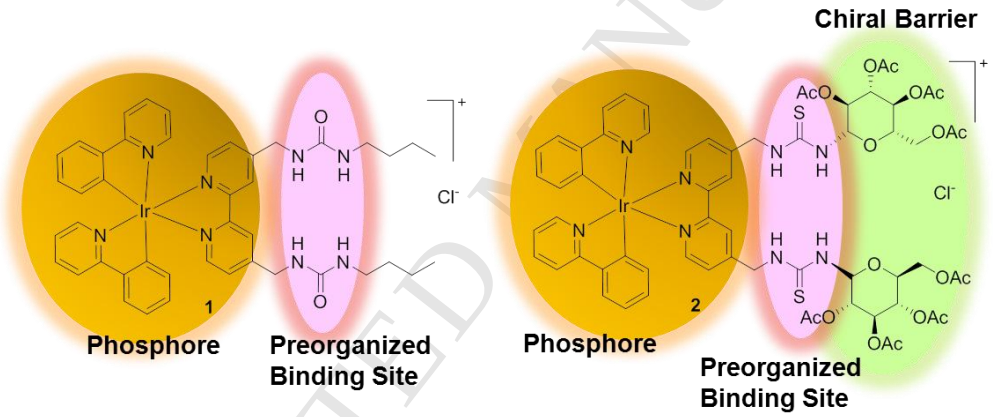
Table 2. The association constants (M^{-1}) of iridium (III) complex **2** with DNB-amino acid derivatives in acetonitrile.

Guest	$K_D(M^{-1})$	K_L/K_D	$K_L(M^{-1})$
Phenylglycine	1.74×10^4	0.88	1.53×10^4
Leucine	2.95×10^4	1.73	5.11×10^4
Valine	4.67×10^3	1.25	5.82×10^4
Threonine	5.07×10^3	3.04	1.54×10^4
Alanine	3.09×10^4	1.19	3.68×10^4
Phenylalanine	2.60×10^4	2.25	5.85×10^4

Graphical Abstract

New Iridium Complexes with Two Pre-organized Urea Groups and Thiourea Groups as Phosphorescent Chemosensors for $H_2PO_4^-$ and Chiral Carboxylates

Yinan Li, Liu Yifan, Dayoung Nam, Sungnam Park, Juyoung Yoon* and Myung Ho Hyun*



Highlights

- As a versitle platform for phosphorescent chemosensors, bis(benzylic amine) derivative **6** was synthesized.
- A phosphorescent chemosensor **1** displayed a selective phosphorescence enhancement with $H_2PO_4^-$.
- A new iridium complex **2** is reported as a first chiral phosphorescent chemosensor for amino acids.

Supporting Informations for

New Iridium Complexes with Two Pre-organized Urea Groups and Thiourea Groups as Phosphorescent Chemosensors for $H_2PO_4^-$ and Chiral Carboxylates

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† equally contributed to this work

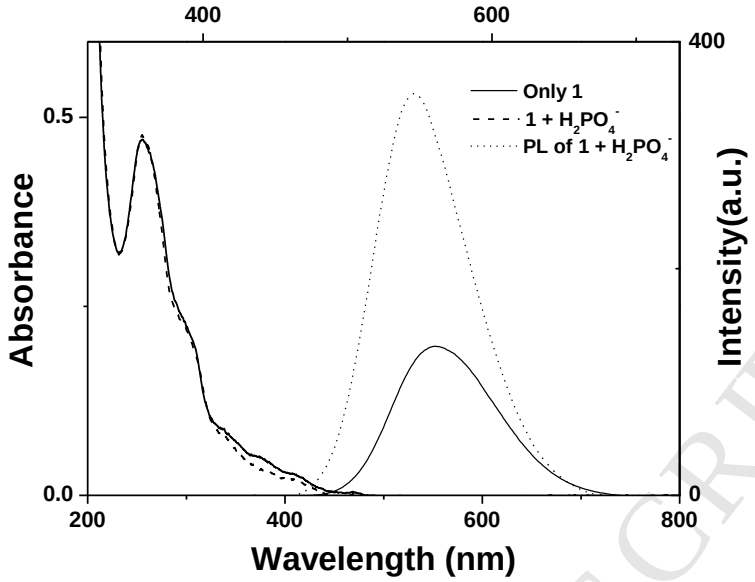


Figure S1. UV-vis spectra and phosphorescence spectra of iridium (III) complex **1** (10 μM) in acetonitrile.

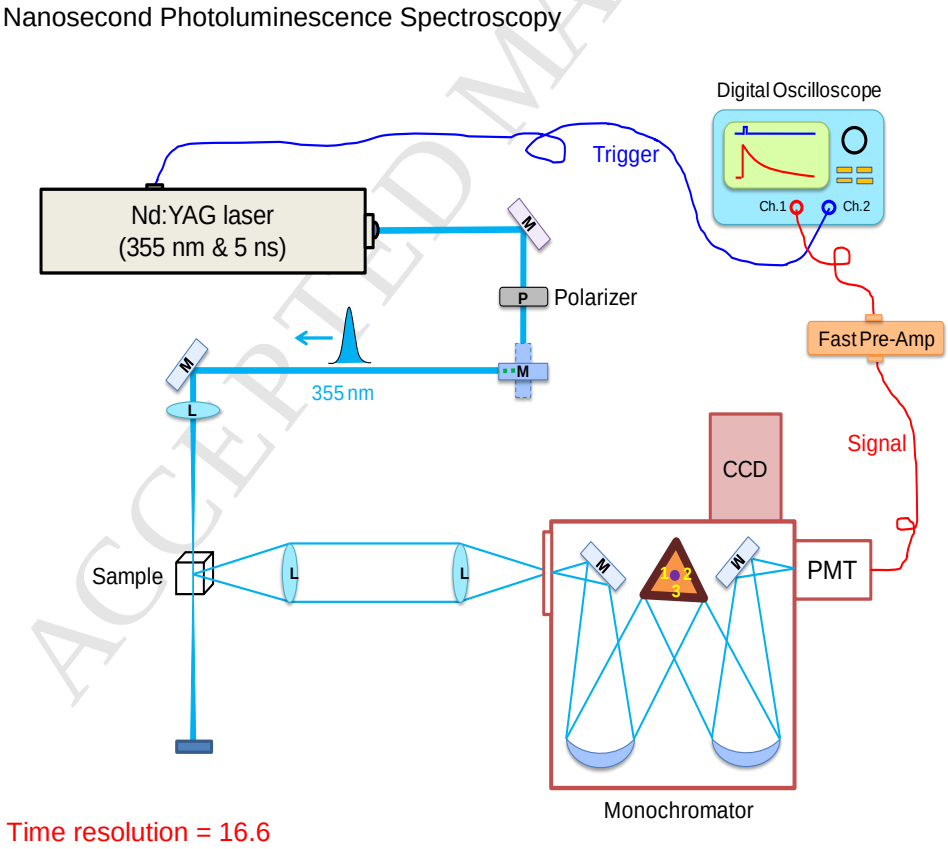


Figure S2. System for phosphorescence life time measurements.

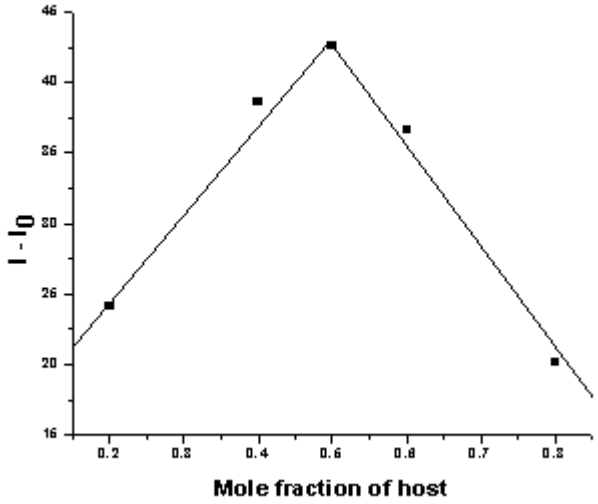
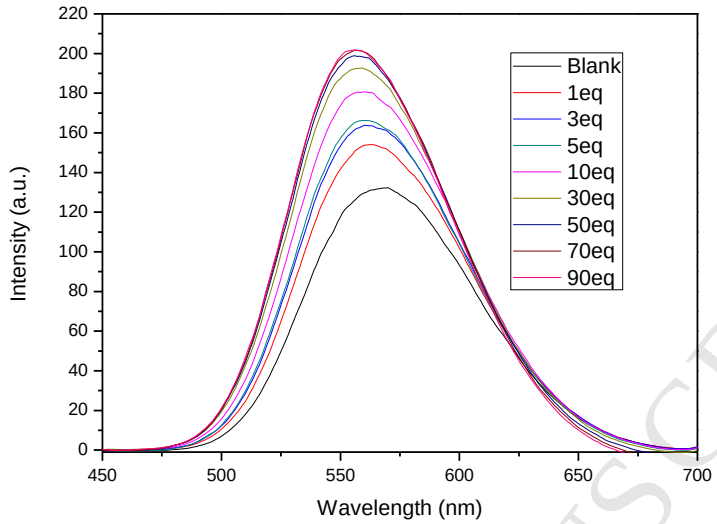


Figure S3. Job`s plot of complex 2 and D-*t*-Boc-Leucine amino acid in acetonitrile.

a)



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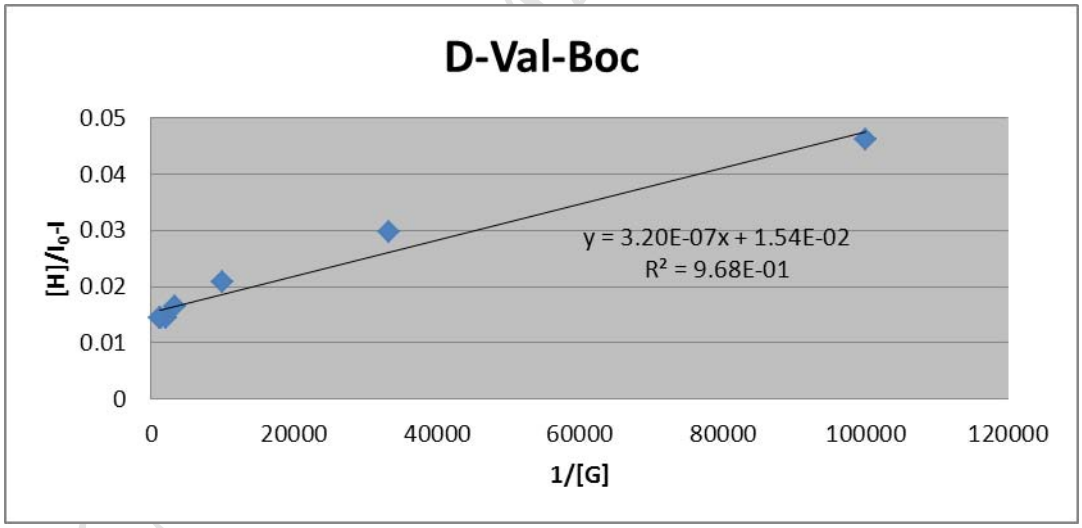
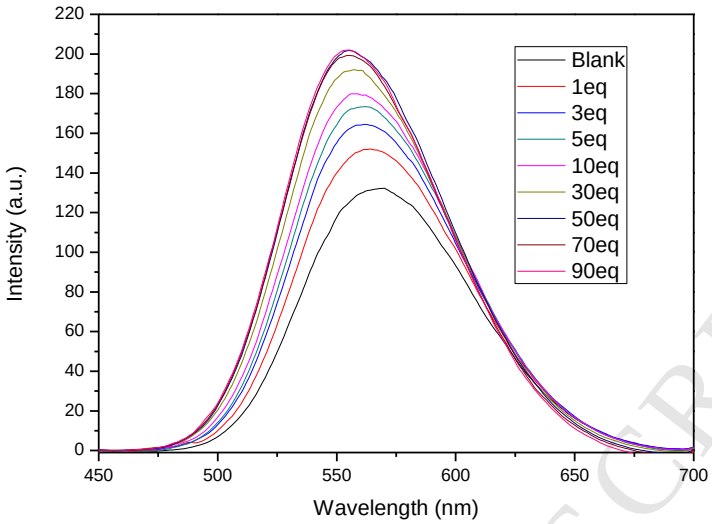


Figure S4. (a) The phosphorescence titration spectra of GITC appended iridium (III) complex **2** (10 μM) upon addition of *t*-Boc-D-valine in 100 % CH_3CN. (b) Benesi-Hildebrand plot of PL spectra of complex **2**.

a)



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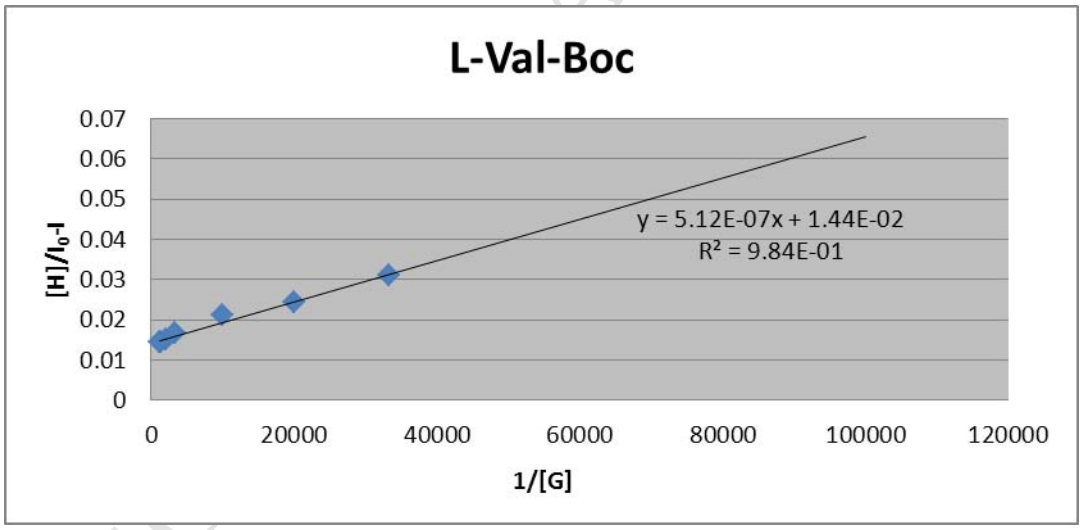
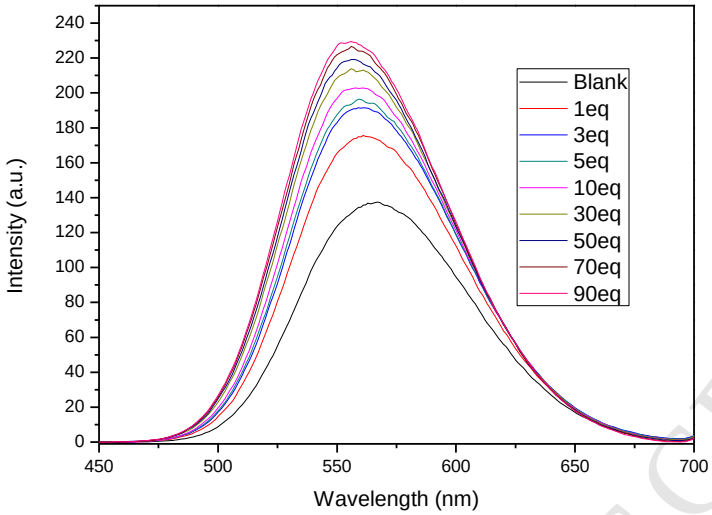


Figure S5. (a) The phosphorescence titration spectra of GITC appended iridium (III) complex **2** (10 μM) upon addition of *t*-Boc-L-valine in 100 % CH_3CN. (b) Benesi-Hildebrand plot of PL spectra of complex **2**.

a)



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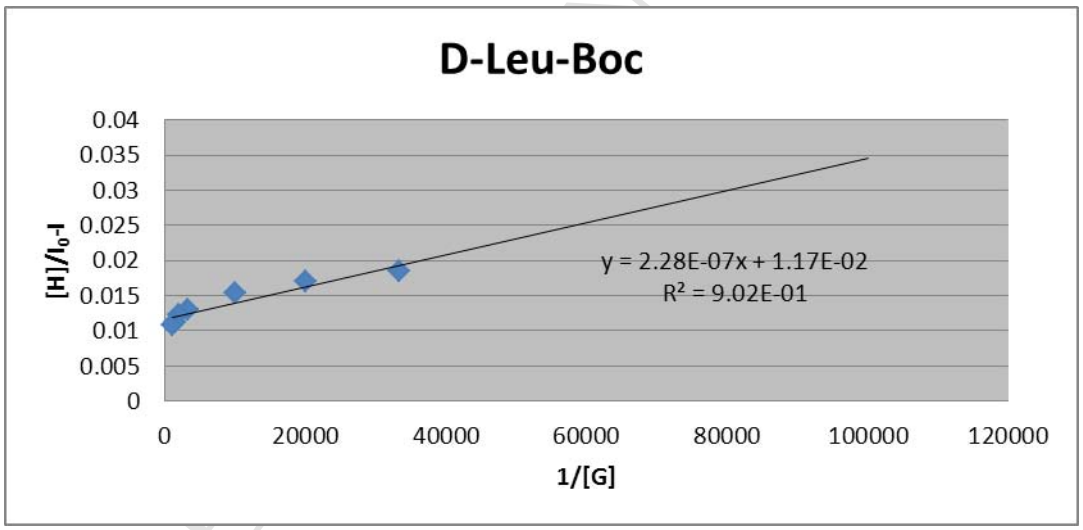
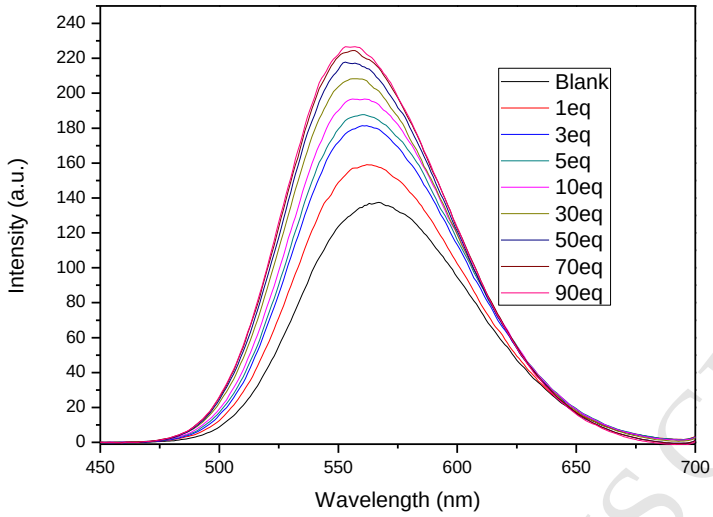


Figure S6. (a) The phosphorescence titration spectra of GITC appended iridium (III) complex **2** (10 μM) upon addition of t-Boc-D-leucine in 100 % CH_3CN. (b) Benesi-Hildebrand plot of PL spectra of complex **2**.

a)



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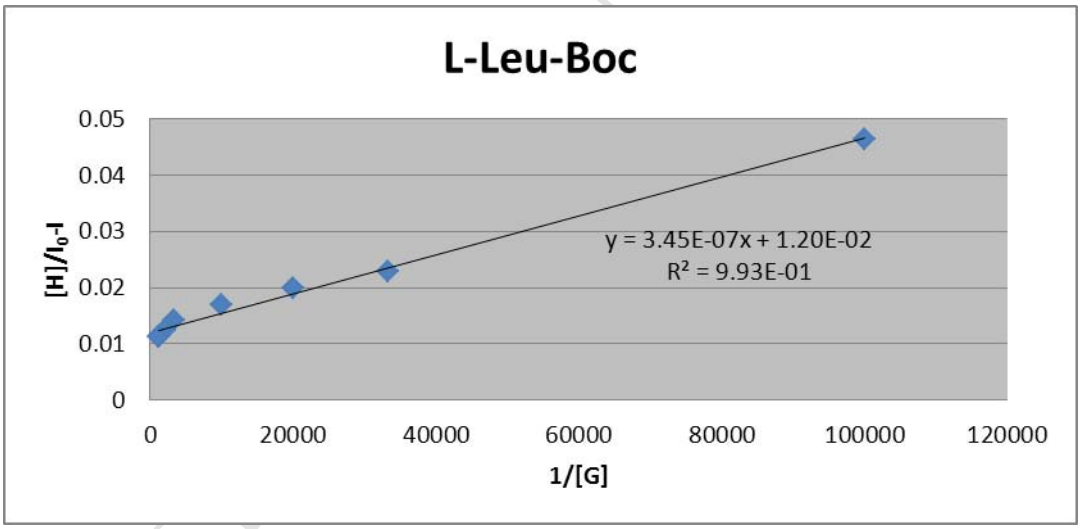
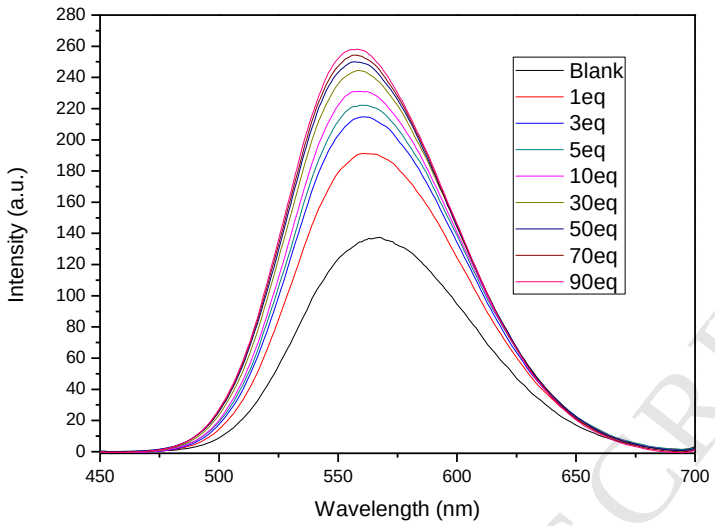


Figure S7. (a) The phosphorescence titration spectra of GITC appended iridium (III) complex **2** (10 μM) upon addition of *t*-Boc-L-leucine in 100 % CH_3CN. (b) Benesi-Hildebrand plot of PL spectra of complex **2**.

a)



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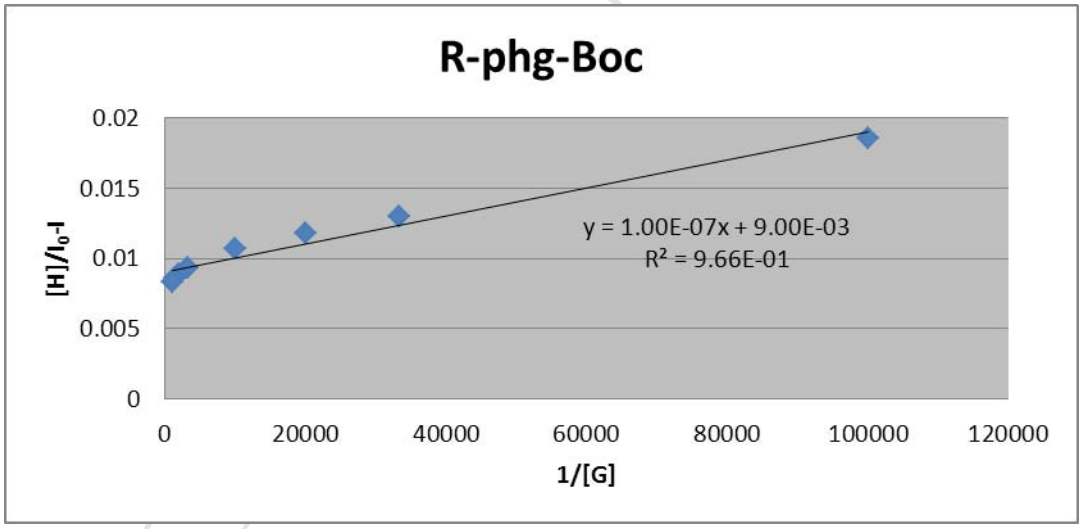
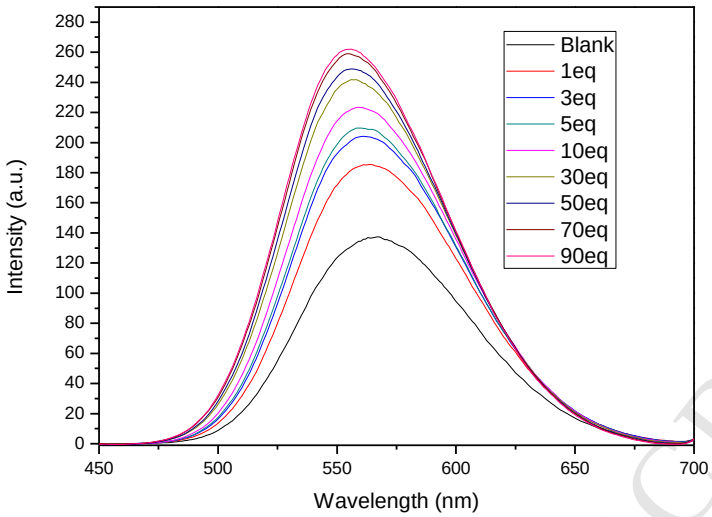


Figure S8. (a) The phosphorescence titration spectra of GITC appended iridium (III) complex **2** (10 μM) upon addition of t-Boc-R-phenylglycine in 100 % CH_3CN. (b) Benesi-Hildebrand plot of PL spectra of complex **2**.

a)



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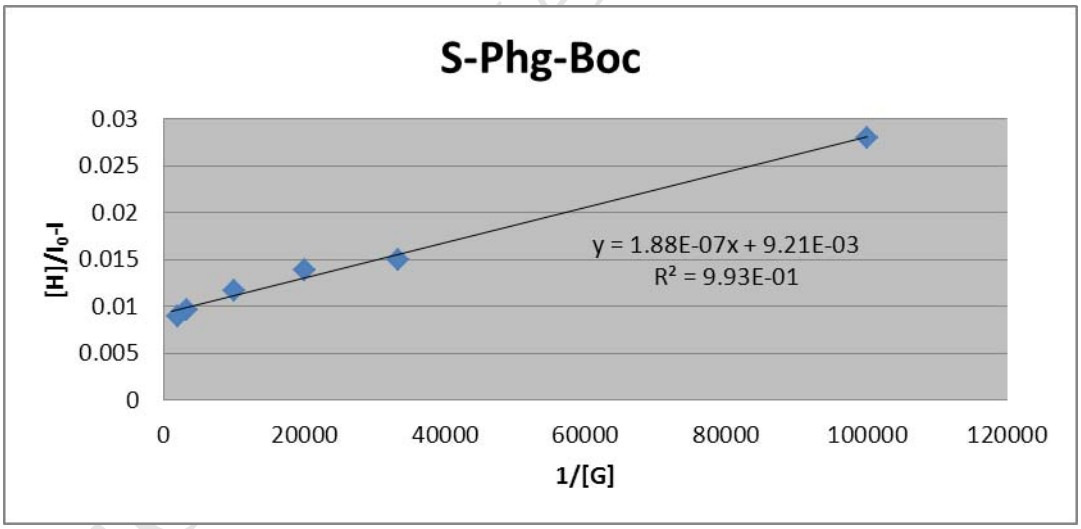
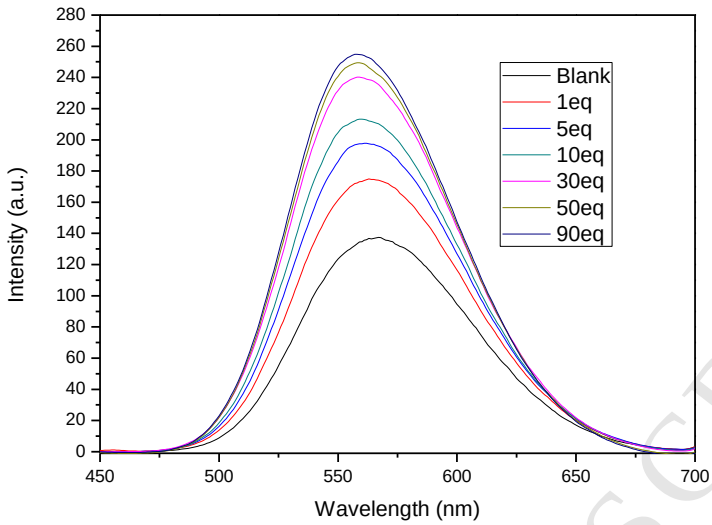


Figure S9. (a) The phosphorescence titration spectra of GITC appended iridium (III) complex **2** (10 μM) upon addition of *t*-Boc-S-phenylglycine in 100 % CH_3CN. (b) Benesi-Hildebrand plot of PL spectra of complex **2**.

a)



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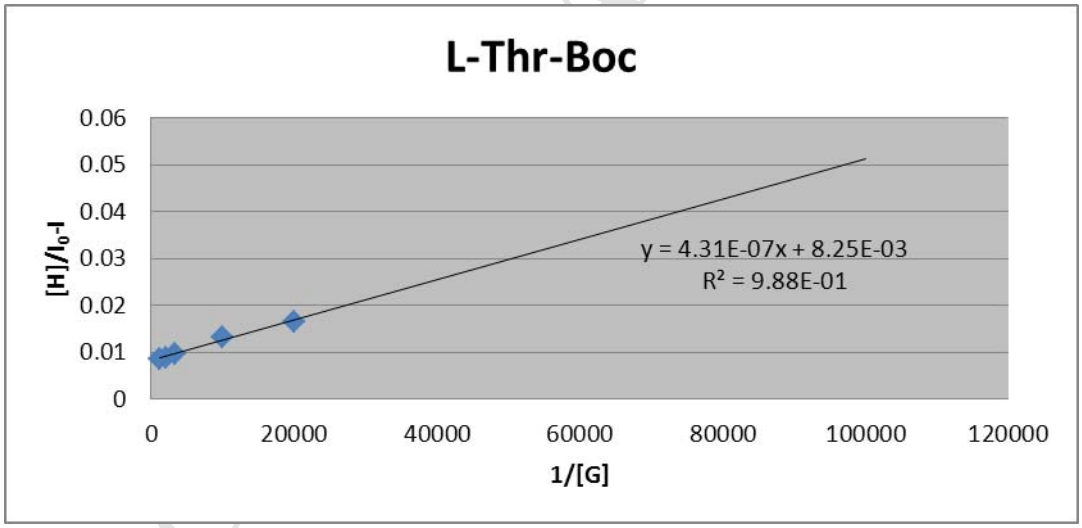
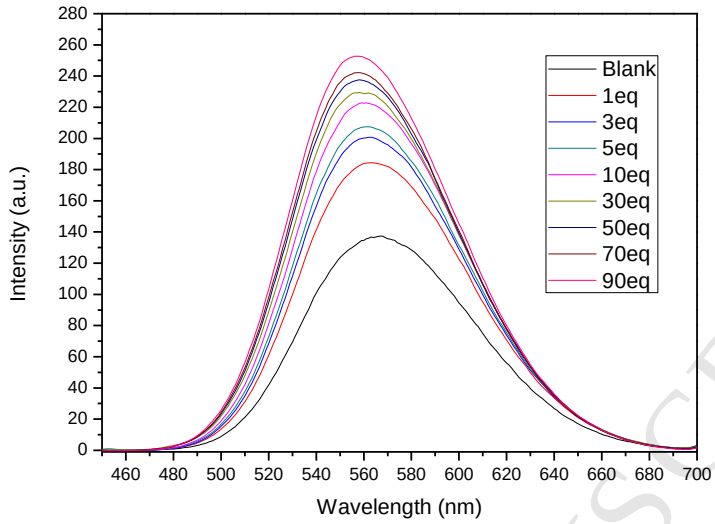


Figure S10. (a) The phosphorescence titration spectra of GITC appended iridium (III) complex **2** (10 μM) upon addition of *t*-Boc-L-threonine in 100 % CH_3CN. (b) Benesi-Hildebrand plot of PL spectra of complex **2**.

a)



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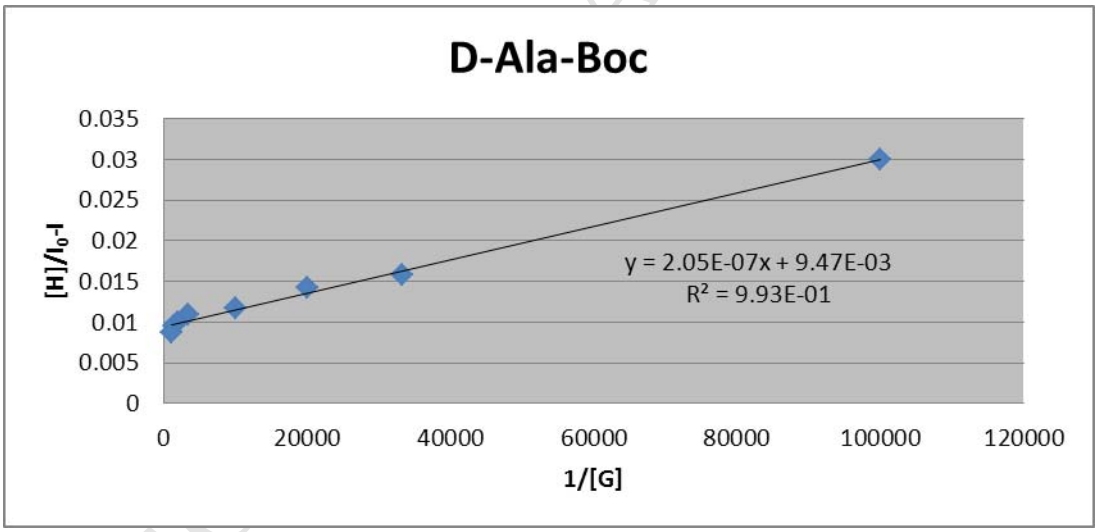
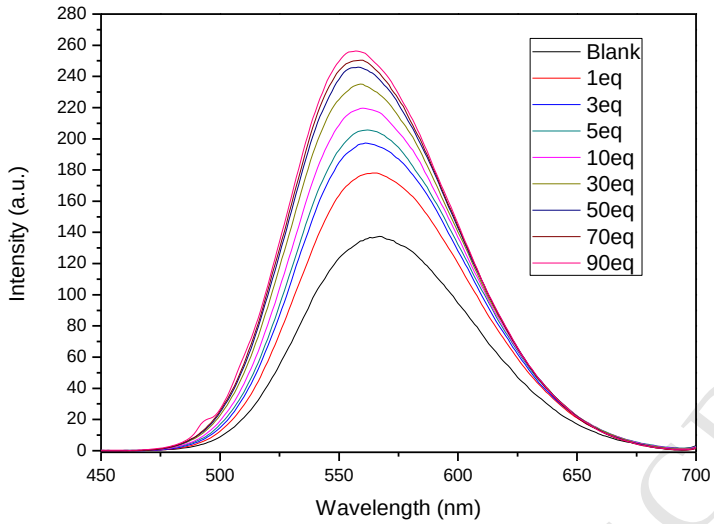


Figure S11. (a) The phosphorescence titration spectra of GITC appended iridium (III) complex **2** (10 μM) upon addition of *t*-Boc-D-alanine in 100 % CH_3CN. (b) Benesi-Hildebrand plot of PL spectra of complex **2**.

a)



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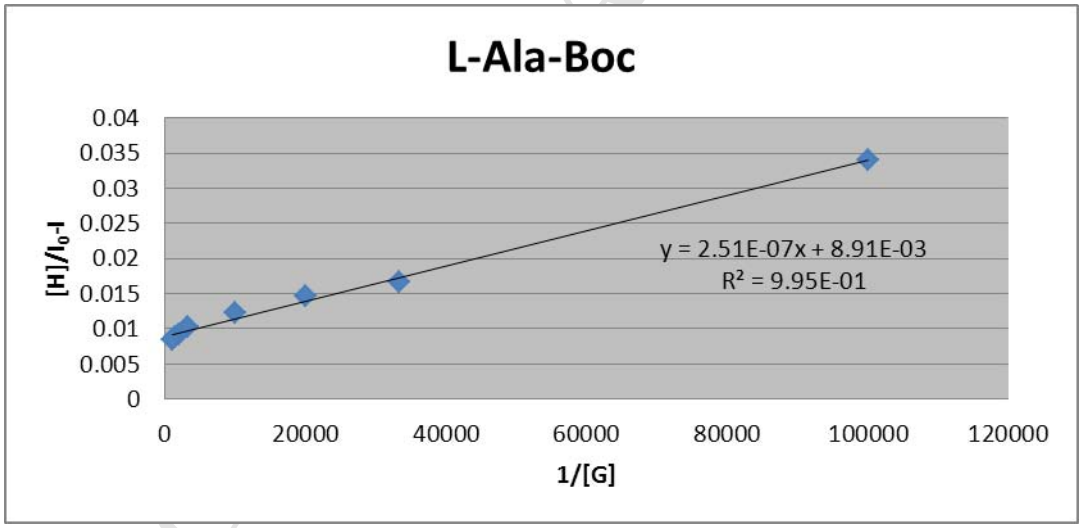
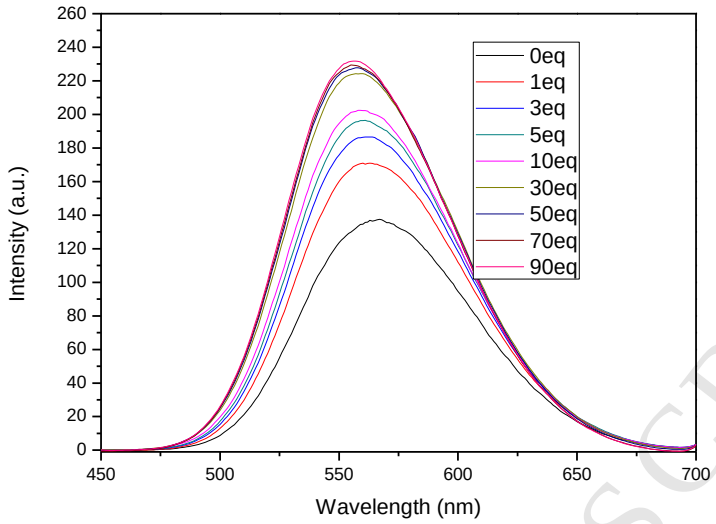


Figure S12. (a) The phosphorescence titration spectra of GITC appended iridium (III) complex **2** (10 μM) upon addition of *t*-Boc-L-alanine in 100 % CH_3CN. (b) Benesi-Hildebrand plot of PL spectra of complex **2**.

a)



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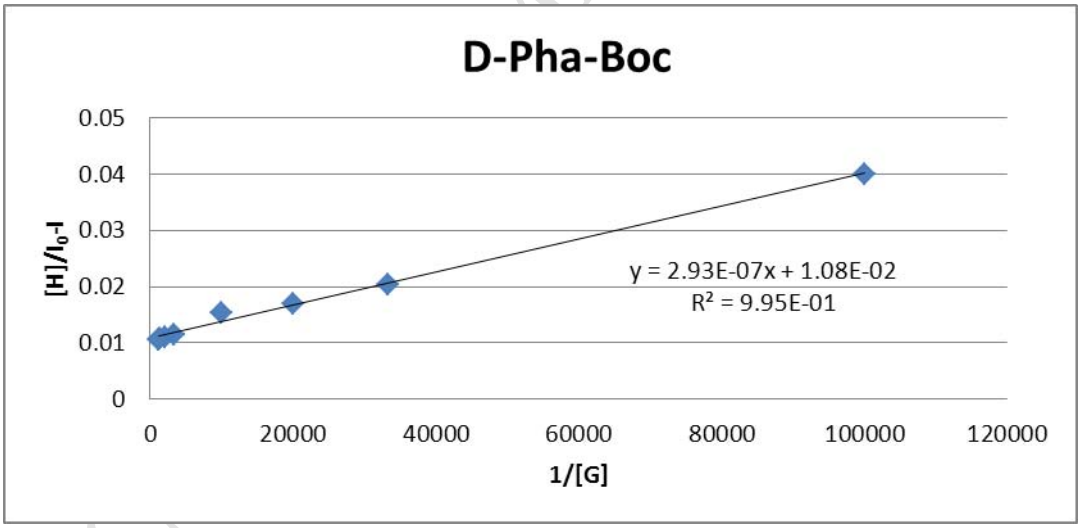
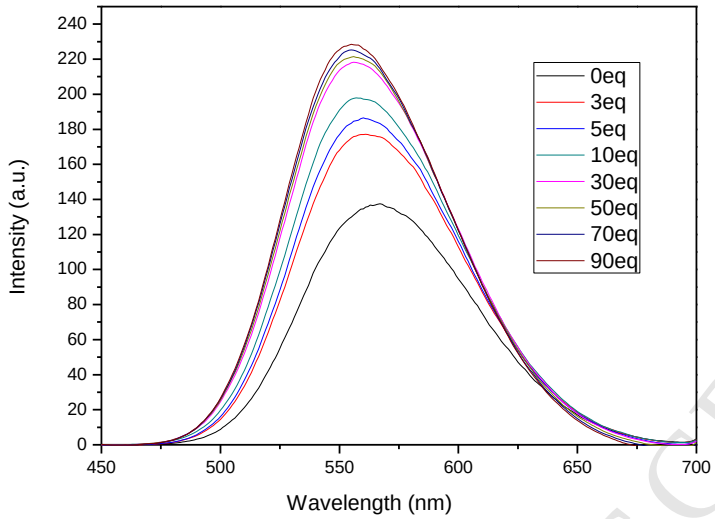


Figure S13. (a) The phosphorescence titration spectra of GITC appended iridium (III) complex **2** (10 μM) upon addition of *t*-Boc-D-phenylalanine in 100 % CH_3CN. (b) Benesi-Hildebrand plot of PL spectra of complex **2**.

a)



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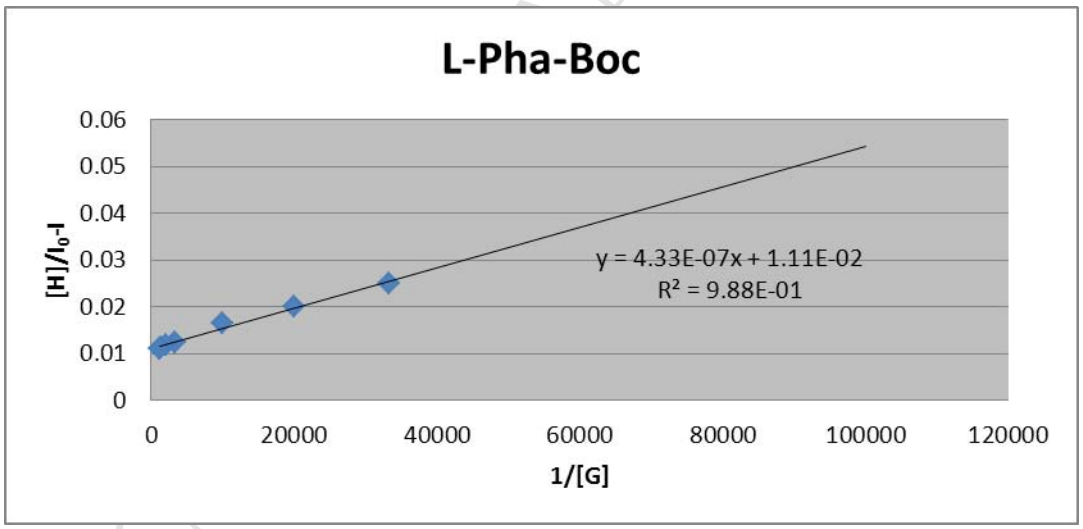
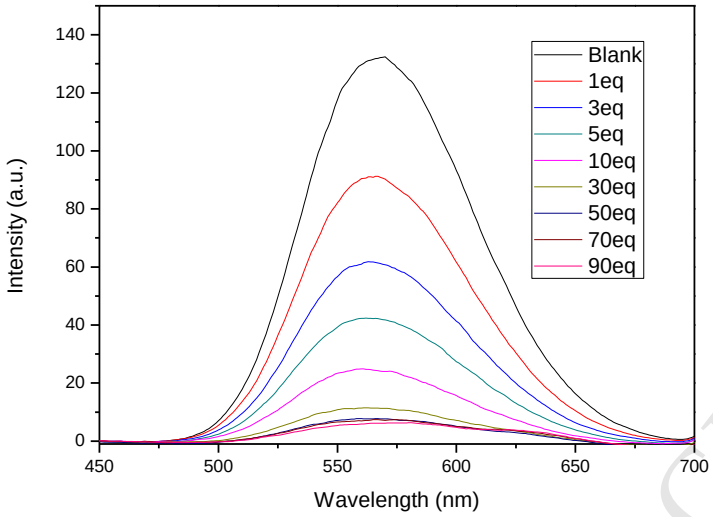


Figure S14. (a) The phosphorescence titration spectra of GITC appended iridium (III) complex **2** (10 μM) upon addition of t-Boc-L- phenylalanine in 100 % CH_3CN. (b) Benesi-Hildebrand plot of PL spectra of complex **2**.

a)



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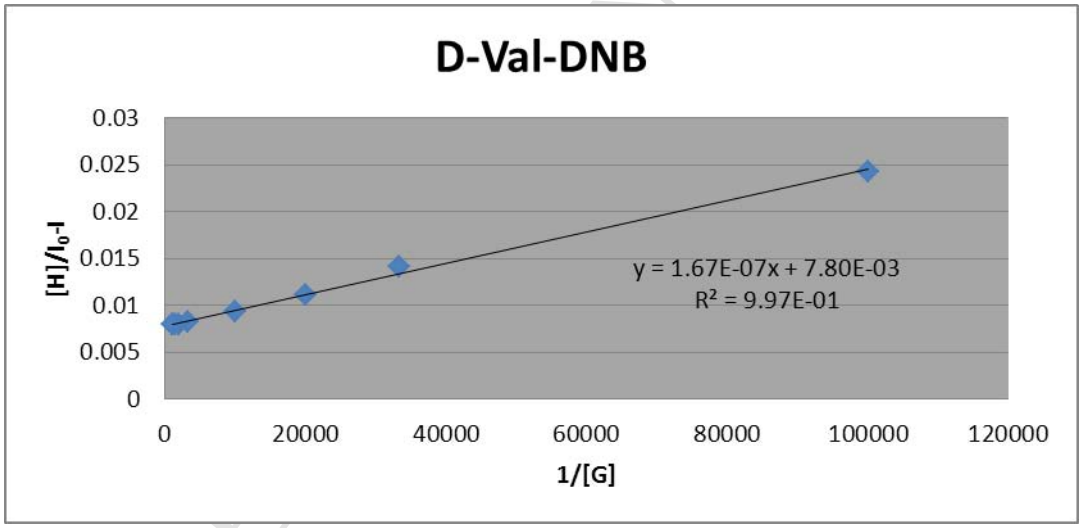
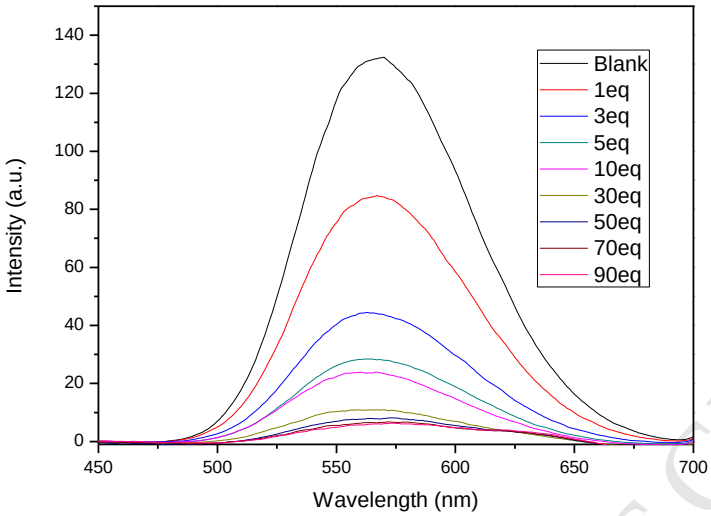


Figure S15. (a) The phosphorescence titration spectra of GITC appended iridium (III) complex **2** (10 μM) upon addition of DNB-D-valine in 100 % CH_3CN. (b) Benesi-Hildebrand plot of PL spectra of complex **2**.

a)



b)

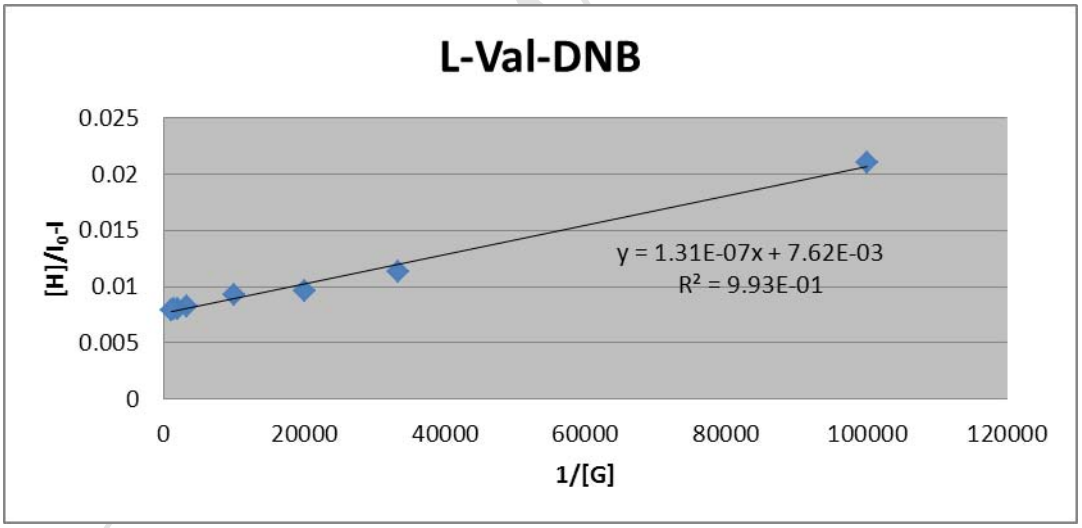
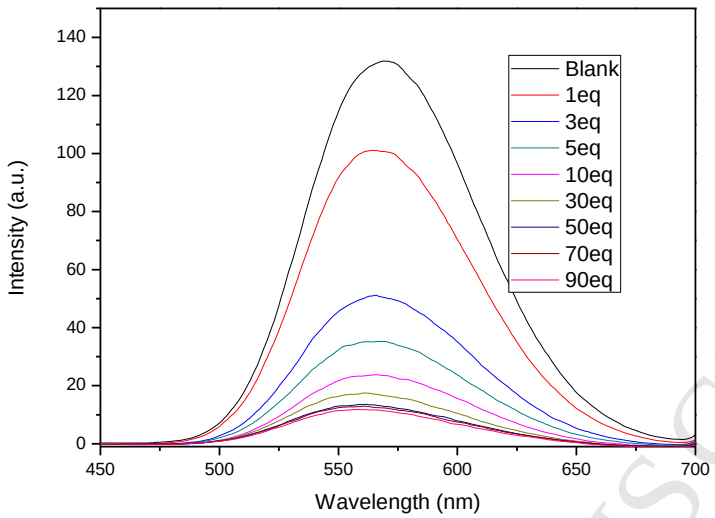


Figure S16. (a) The phosphorescence titration spectra of GITC appended iridium (III) complex **2** (10 µM) upon addition of DNB-L-valine in 100 % CH_3CN. (b) Benesi-Hildebrand plot of PL spectra of complex **2**.

a)



b)

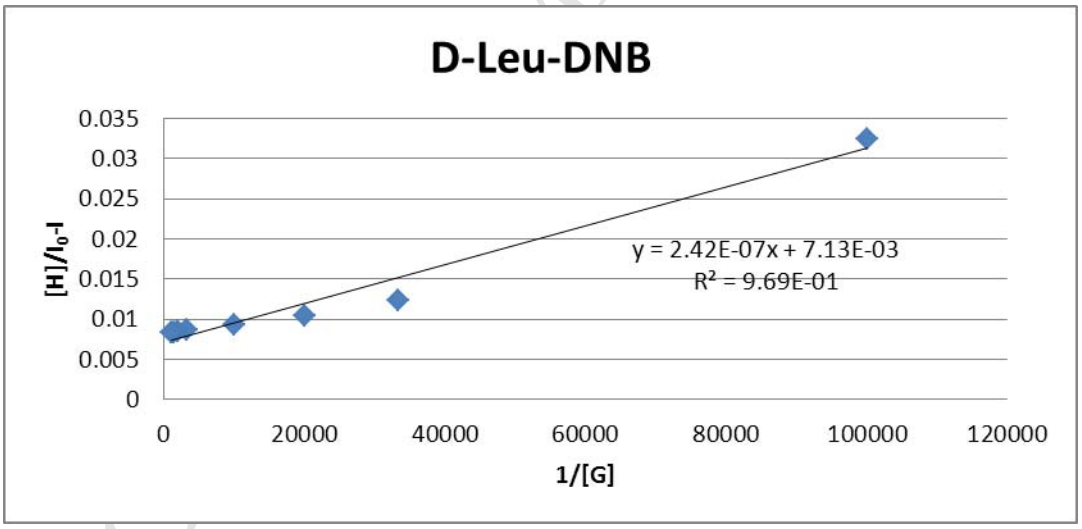
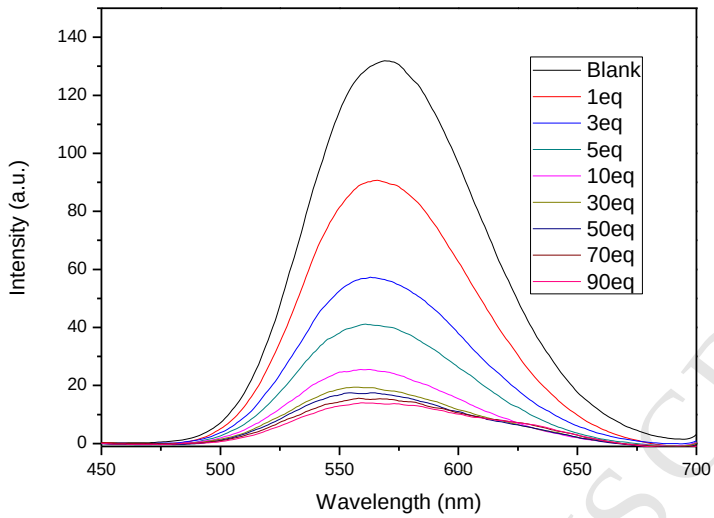


Figure S17. (a) The phosphorescence titration spectra of GITC appended iridium (III) complex **2** (10 μM) upon addition of DNB-D-leucine in 100 % CH_3CN. (b) Benesi-Hildebrand plot of PL spectra of complex **2**.

a)



b)

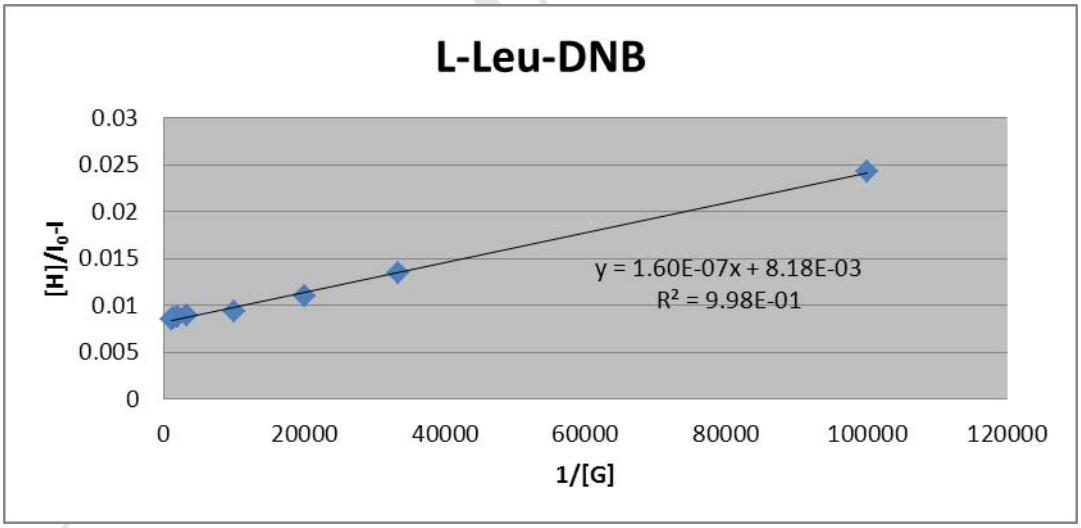
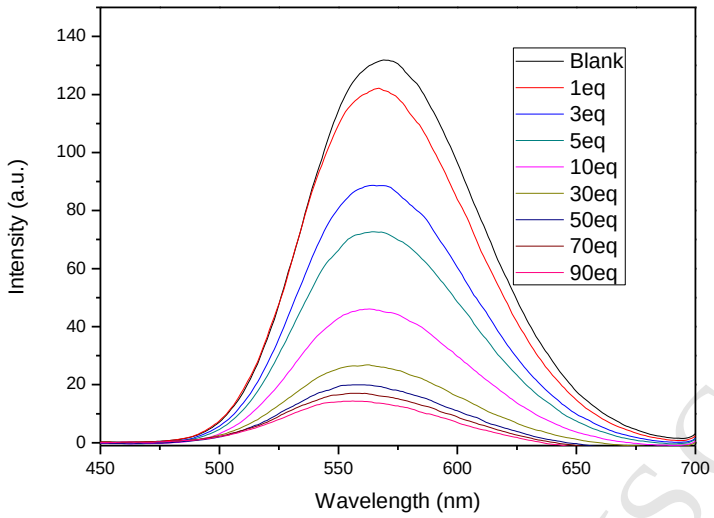


Figure S18. (a) The phosphorescence titration spectra of GITC appended iridium (III) complex **2** (10 μM) upon addition of DNB-L-leucine in 100 % CH_3CN. (b) Benesi-Hildebrand plot of PL spectra of complex **2**.

a)



b)

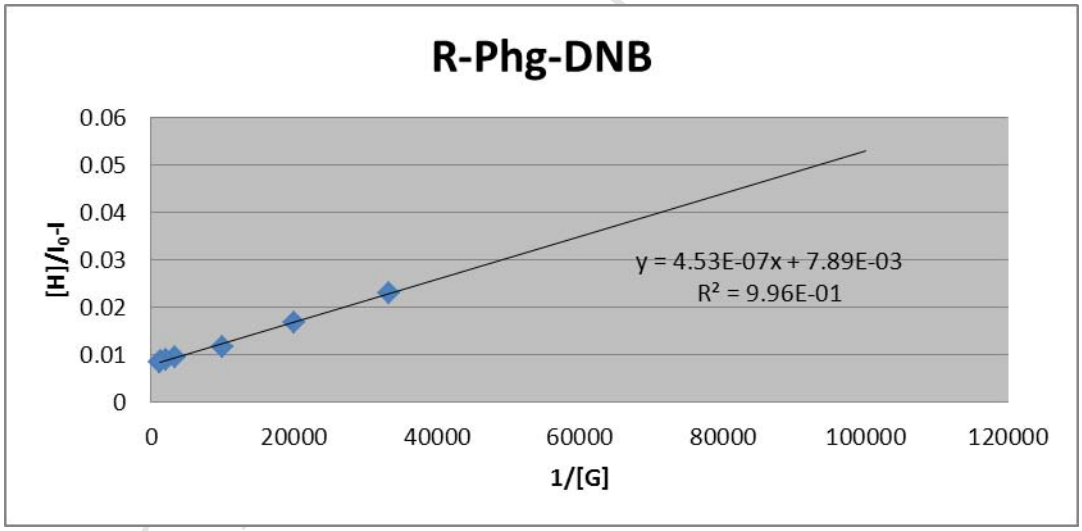
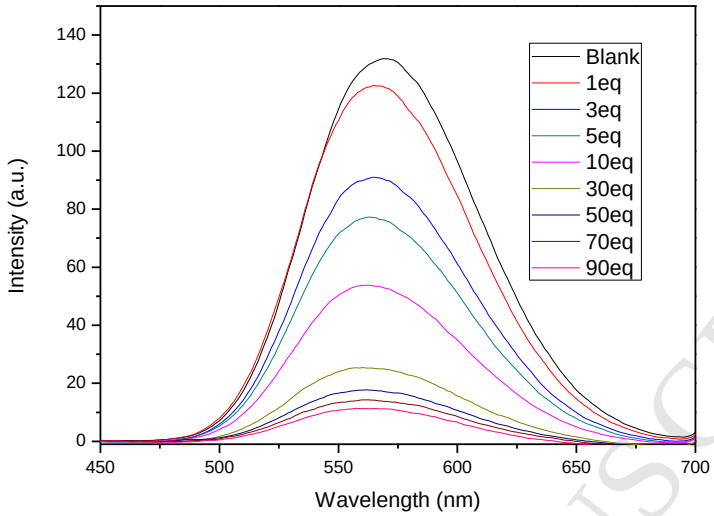
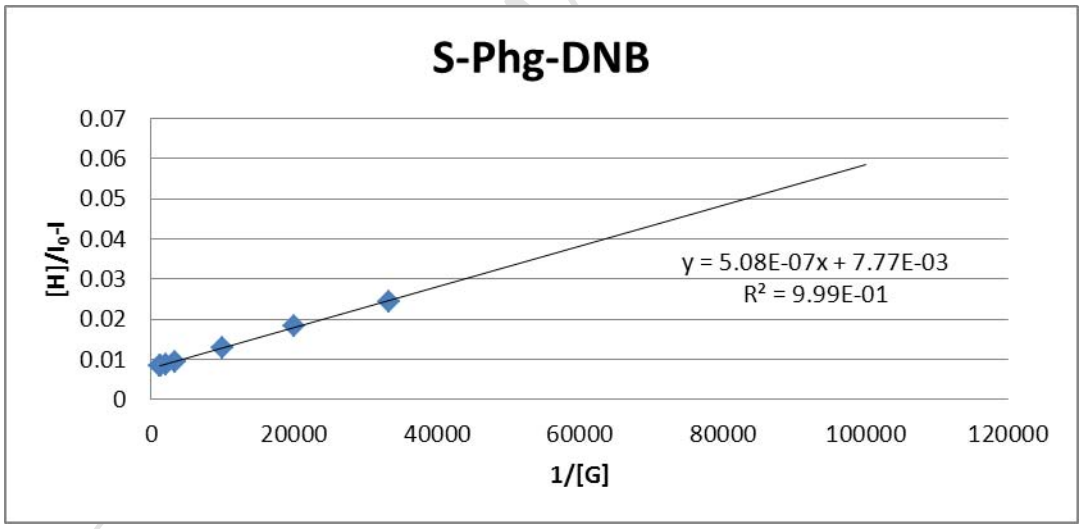


Figure S19. (a) The phosphorescence titration spectra of GITC appended iridium (III) complex **2** (10 μM) upon addition of DNB-R-phenylglycine in 100 % CH_3CN. (b) Benesi-Hildebrand plot of PL spectra of complex **2**.

a)



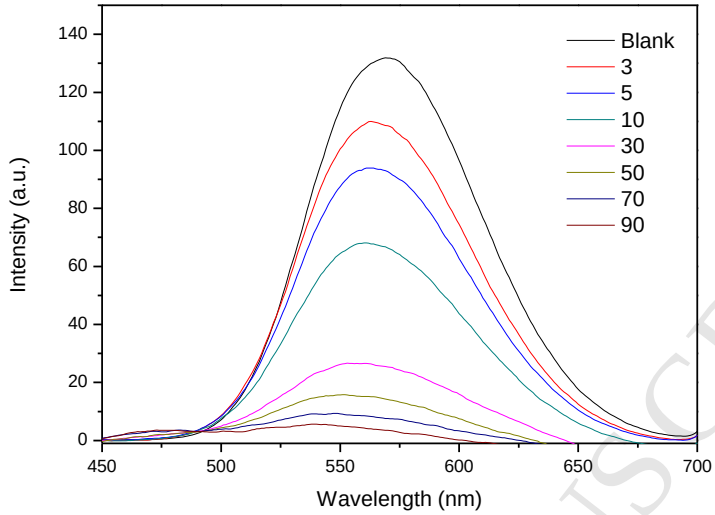
b)



FigureS 20. (a) The phosphorescence titration spectra of GITC appended iridium (III) complex **2** (10 μM) upon addition of DNB-S-phenylglycine in 100 % CH_3CN. (b) Benesi-Hildebrand plot of PL spectra of complex **2**.

.

a)



b)

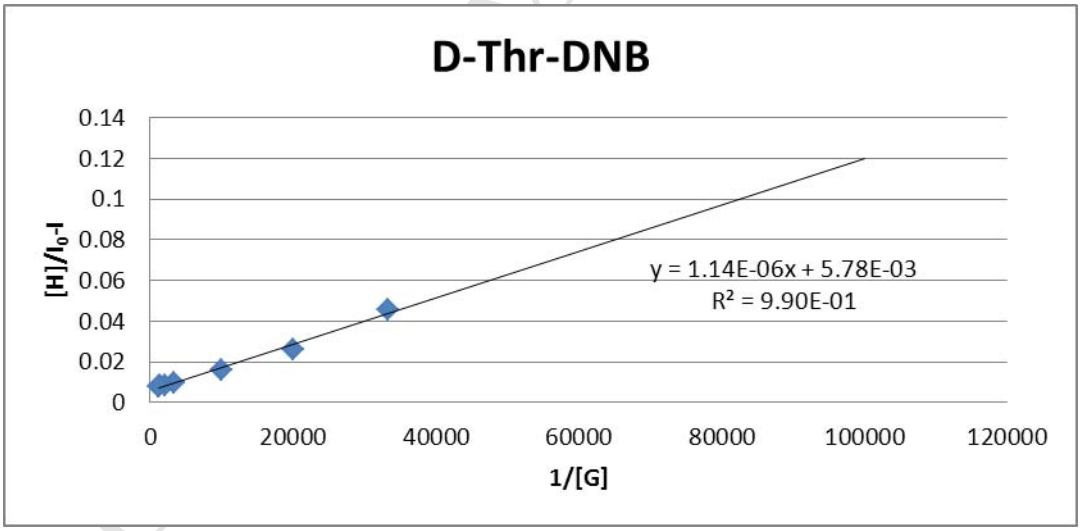
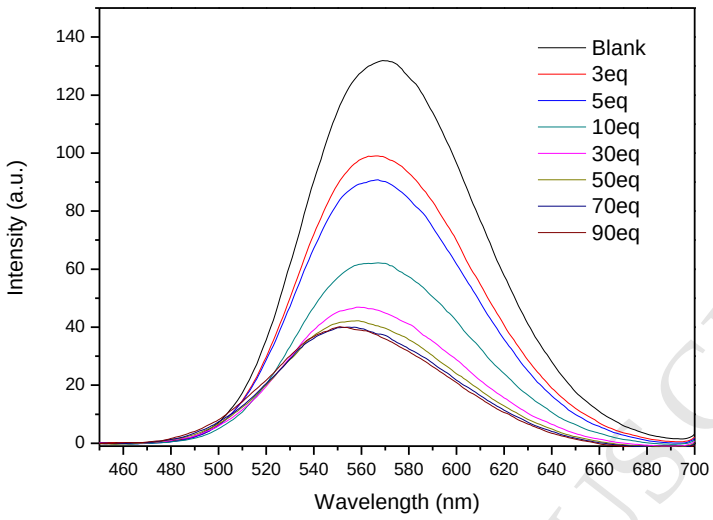


Figure S21. (a) The phosphorescence titration spectra of GITC appended iridium (III) complex **2** (10 μM) upon addition of DNB-D-threonine in 100 % CH_3CN. (b) Benesi-Hildebrand plot of PL spectra of complex **2**.

a)



b)

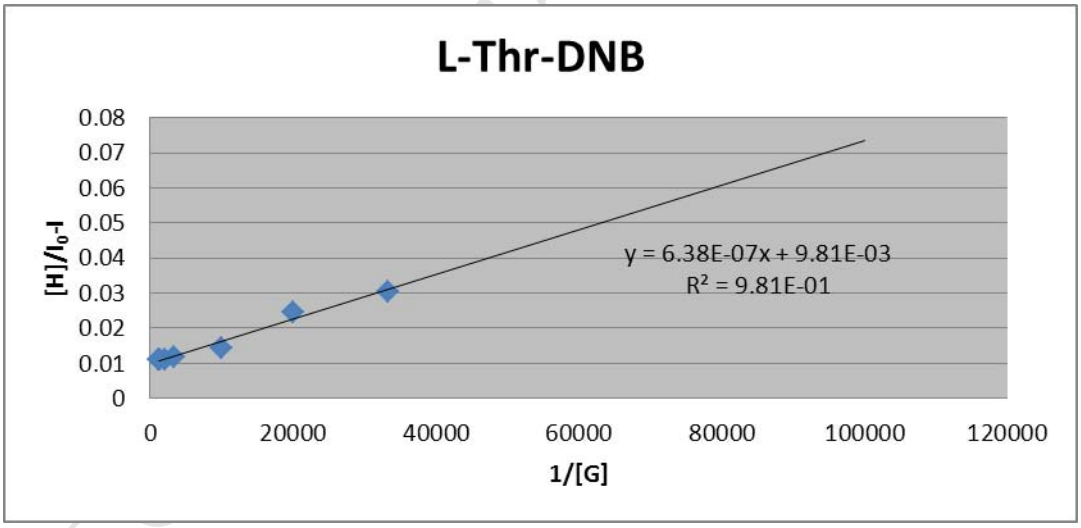
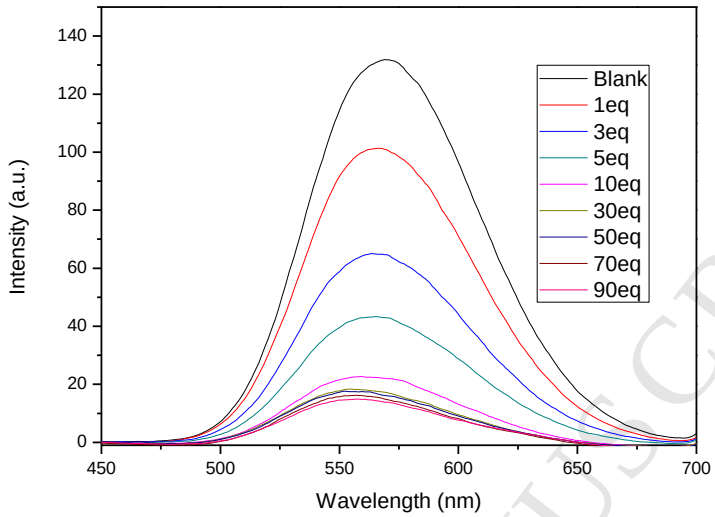


Figure S22. (a) The phosphorescence titration spectra of GITC appended iridium (III) complex **2** (10 μM) upon addition of DNB- L -threonine in 100 % CH_3CN. (b) Benesi-Hildebrand plot of PL spectra of complex **2**.

a)



b)

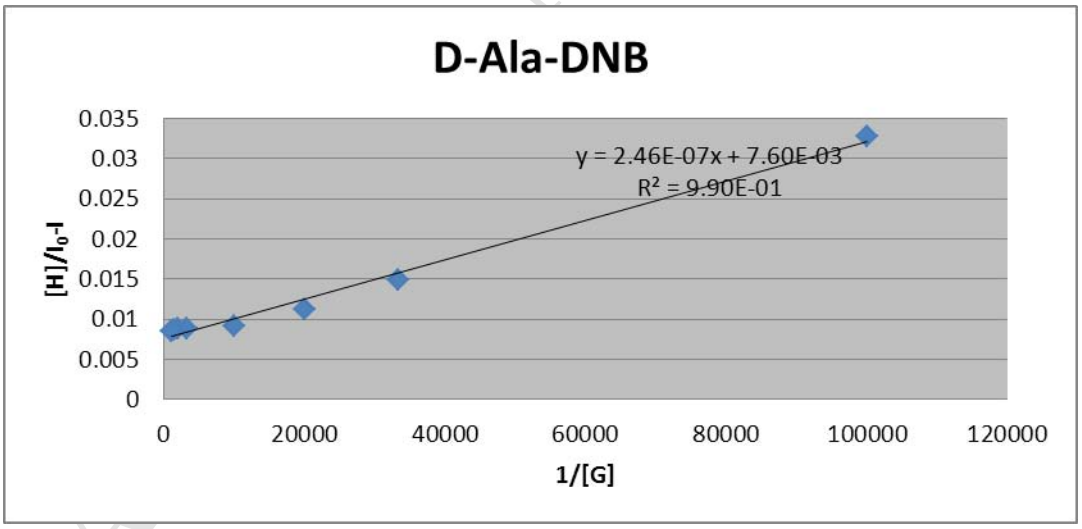
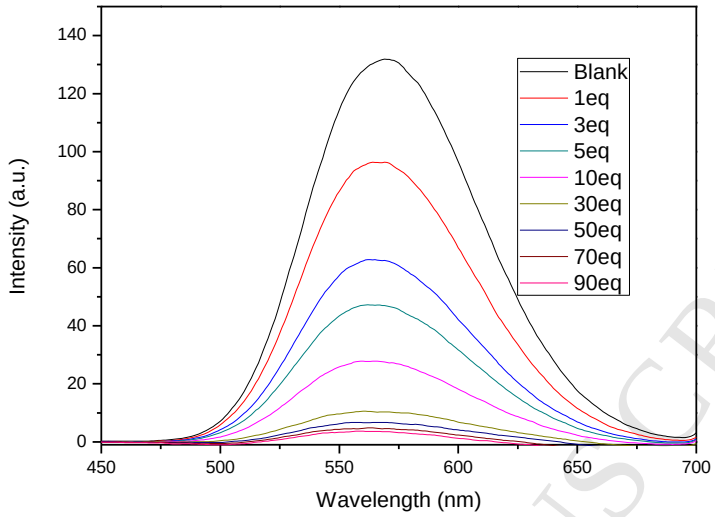


Figure S23. (a) The phosphorescence titration spectra of GITC appended iridium (III) complex **2** (10 μM) upon addition of DNB-D-alanine in 100 % CH_3CN. (b) Benesi-Hildebrand plot of PL spectra of complex **2**.

a)



b)

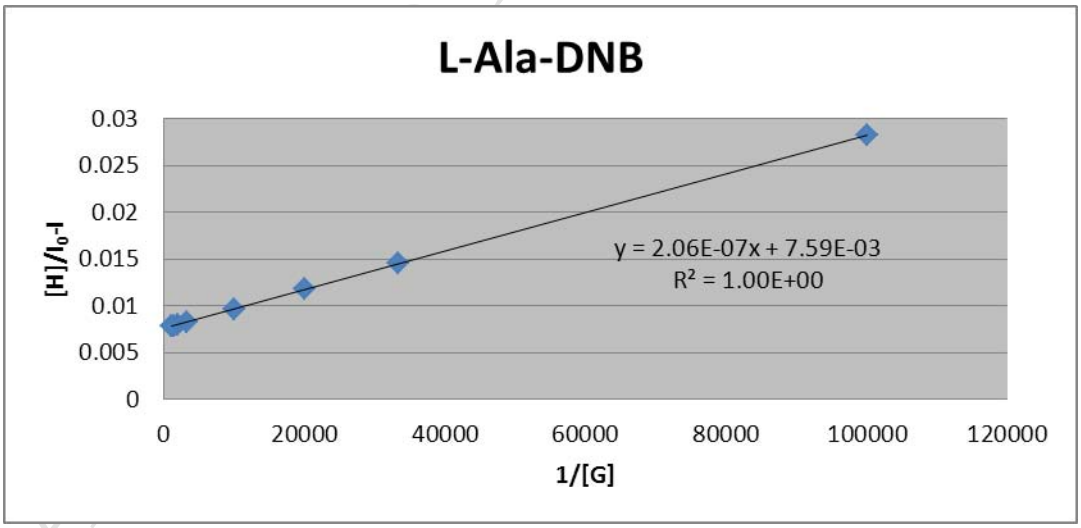
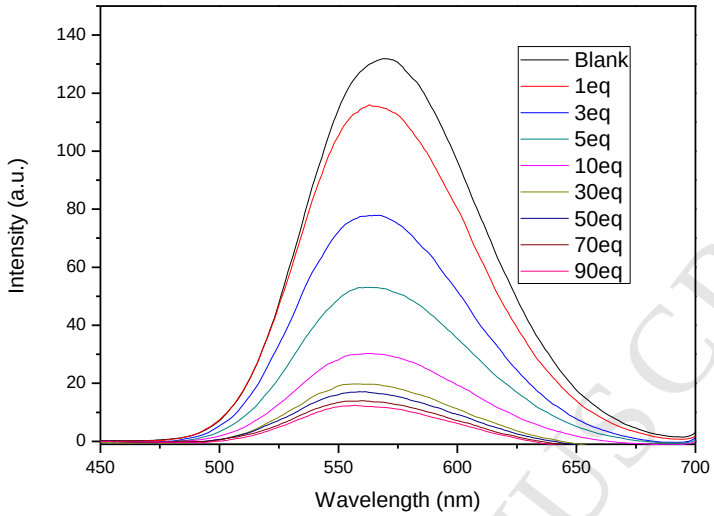


Figure S24. (a) The phosphorescence titration spectra of GITC appended iridium (III) complex **2** (10 μM) upon addition of DNB-L-alanine in 100 % CH_3CN. (b) Benesi-Hildebrand plot of PL spectra of complex **2**.

a)



b)

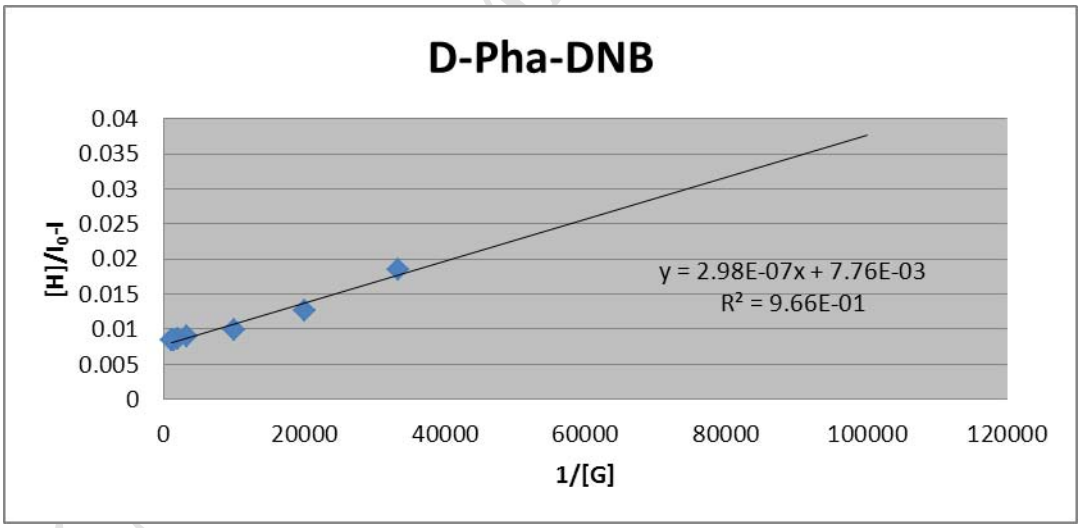
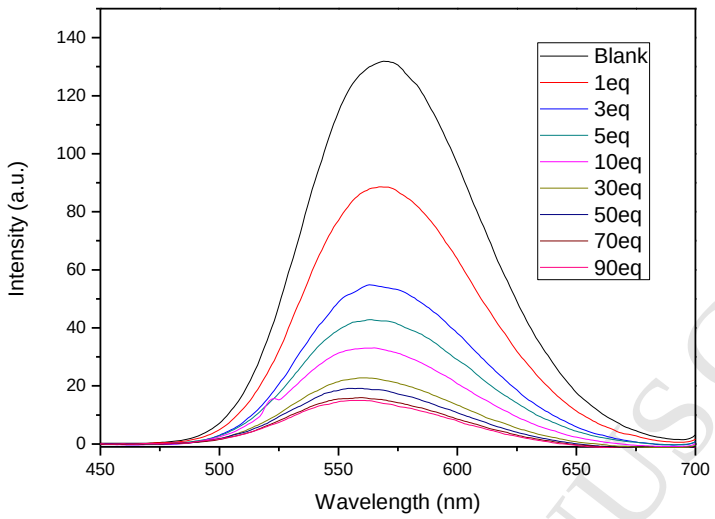


Figure S25. (a) The phosphorescence titration spectra of GITC appended iridium (III) complex **2** (10 μM) upon addition of DNB-D-phenylalanine in 100 % CH_3CN. (b) Benesi-Hildebrand plot of PL spectra of complex **2**.

a)



b)

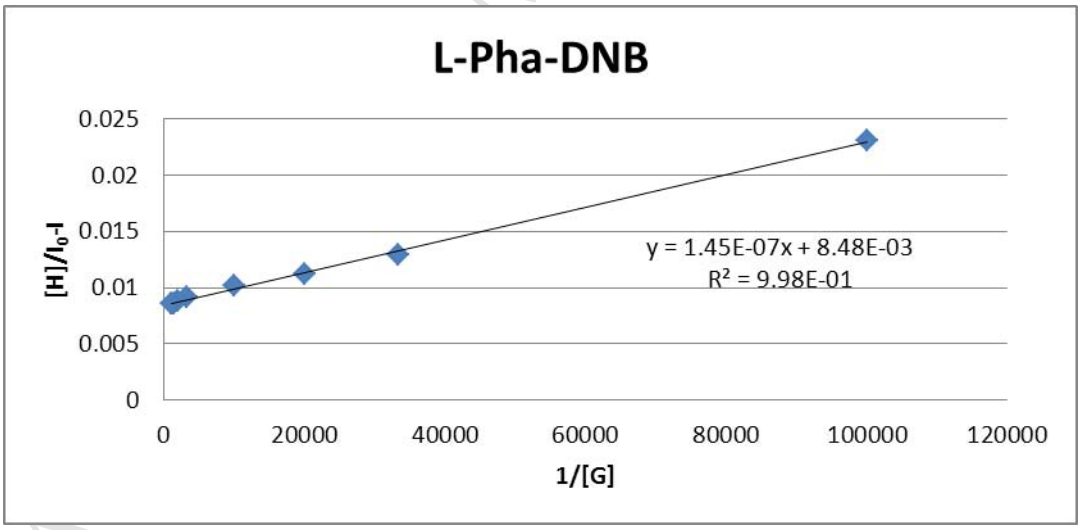


Figure S26. (a) The phosphorescence titration spectra of GITC appended iridium (III) complex **2** (10 μM) upon addition of DNB-L-phenylalanine in 100 % CH_3CN. (b) Benesi-Hildebrand plot of PL spectra of complex **2**.