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Room temperature phosphorescence of a palladium(II) complex sensitized by unsymmetric perylene bisimide

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Abstract

A novel palladium(II) complex (Phpy)Pd(Pery-q) based on cyclopalladated 2-phenylpyridine coordinated to 5-unsymmetric perylene bisimide-8-hydroxyquinoline was synthesized and characterized by ^{1}H NMR, MS-ESI, elemental analysis and IR spectra. The complex displayed room temperature phosphorescence (RTP) in CH_2Cl_2 solution with a lifetime of *ca.* 14.2 μs, arising from the sensitized intraligand charge transfer (^{3}ILCT) of the appended 8-hydroxyquinoline and was dependent on the ligand orbital perturbed by the metal. Its long-lived emission is affected by aggregation in poly(*N*-vinylcarbazole) (PVK) film and solid state. The incorporation of an unsymmetric perylene bisimide unit into the 5-substituted-8-hydroxyquinoline ligand prevented thermally activated processes involving non-emissive metal-centered (MC) levels and sensitized (Phpy)Pd in terms of access to the ^{3}ILCT state. The singlet state of perylene bisimide assisted by heavy metal results in the existence of intersystem crossing to ^{3}ILCT of the 8-hydroxyquinoline ligand, thus radiatively decaying to the ground state of (Phpy)Pd(Pery-q).

Keywords: Room temperature phosphorescence (RTP); Sensitization; Palladium(II) complex; Intraligand charge transfer (ILCT)

1. Introduction

There has been considerable interest in the phosphorescence of transition metal complexes at room temperature for their potential applications in lifetime-based chemical sensing, biophysics, clinical chemistry and organic light-emitting diodes (OLEDs) [1–3]. A common requisite for such luminophores is that they possess a relatively long lifetime in fluid solution at ambient temperature. Room temperature phosphorescence (RTP) has many advantages over other luminescence methods namely, large Stokes shift, high signal-to-noise ratio, good selectivity and easily measurable luminescence lifetimes. The triplet state of some metal complexes displays significantly long lifetimes with typical phosphorescence measurable on the microsecond scale. It is known that many platinum(II) complexes are phosphorescent [4] and are successfully used as emitters for tuning photo- and electro-phosphorescence [5,6]. In contrast with the same group element Pt(II), much less is known about the phosphorescence of palladium(II) complexes, especially at room temperature [7–11] which may be attributed to the presence of thermally accessible metal-centered (MC) excited states, leading to the rapid deactivation of excited luminescent state [10]. Typically, phosphorescence can be observed in the cold rigid matrix, wherein the thermally activated process can be prevented. However, such rigorous measurement conditions restrict their practical application. Hence, developing a system with phosphorescent emission at room temperature is of great significance [1,2]. Perylene bisimides are well known chromophores with high fluorescence quantum yield and have been extensively studied as components of organic-based photovoltaic devices [12–16], artificial light-harvesting complexes [17–19], lasers [20,21], and other photonic devices [22,23]. However, to the best of our knowledge, discussion of perylene bisimide derivatives as phosphorescent sensitizers is very rare. In this paper, we report a novel palladium(II) complex based on cyclopalladated 2-phenylpyridine via the incorporation of an unsymmetric perylene bisimide

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unit into the 5-substituted-8-hydroxyquinoline ligand as shown in Fig. 1. The synthesized complex shows a long-decay, red luminescence with a lifetime in the microsecond range at room temperature, typical of phosphorescence, which originates from the ^{3}ILCT state of the corresponding 8-hydroxyquinoline ligand. Such ILCT transition involves charge transfer from the phenolic to the pyridyl side of the two-ring fused quinoline system, which is dependent on the lone pair on the iminic nitrogen atom and the ligand orbital perturbed by the metal [24]. In agreement with Castellano's suggestion [5], substantial lifetime lengthening can be accomplished by introducing specific selected organic chromophore(s) to the ligand structure such that the ligand-localized (intraligand, IL) excited states are strategically positioned below the metal ligand charge transfer (MLCT) manifold. The unusual room temperature phosphorescence is discussed and attributed to the high-efficient sensitization of the unsymmetric perylene bisimide and concomitant heavy metal-assisted intersystem crossing.

2. Experimental

All commercially available reagents and solvents were used without further purification. Palladium(II) acetate (99%) and 2-phenylpyridine (97%) were purchased from Lancaster. [(PhPy)Pd(μ-Oac)]$_2$ was synthesized according to the literature [25]. ^{1}H NMR spectra were recorded on a Brucker AM-500 spectrometer using TMS as internal standard at room temperature; mass spectra were obtained at 70 eV on a VG12-250 (VG Mass lab). Elemental analysis data were determined by a Perkin Elmer 240c instrument. Infrared spectra were determined by a Nicolet FT-IR20SX instrument.

The synthetic route for the complex is shown in Fig. 1.

2.1. (Phpy)Pd(Pery-q)

To an aqueous solution of sodium hydroxide (11 mg, 0.260 mmol), Pery-q (140 mg, 0.136 mmol) and CH_2Cl_2 (10 mL) was added a suspension of [(PhPy)Pd(μ-Oac)]$_2$ (44 mg, 0.068 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred at room temperature for 10 h and the solvent was removed under reduced pressure. The pure product was obtained by column chromatography on silica gel (CH_2Cl_2:CCl_4 = 5:1) to give target complex (42 mg), yield 24%, m.p. > 300 °C. ^{1}H NMR ($CDCl_3$, ppm): $\delta = 0.92$ (t, 3H, $J = 7.3$ Hz, $-CH_3$), 1.38 (m, 2H, $-CH_2-$), 1.63 (m, 2H, $-CH_2-$), 2.33 (s, 12H, phenyl-CH_3), 4.09 (t, 2H, $J = 7.4$ Hz, $-NCH_2-$), 5.62 (s, 2H, $-NCH_2-$), 6.82 (d, 8H, $J = 8.2$ Hz, phenyl-H), 6.95 (d, 1H, $J = 7.0$ Hz, phpy-H), 7.09 (d, 8H, $J = 8.2$ Hz, phenyl-H), 7.1 (m, 1H, quinoline-H), 7.18 (m, 2H, phpy-H), 7.47 (d, 1H, $J = 7.6$ Hz, quinoline-H), 7.51 (t, 1H, $J = 5.3$ Hz, quinoline-H), 7.68 (d, 1H, $J = 7.9$ Hz, phpy-H), 7.75 (d, 1H, $J = 8.3$ Hz, phpy-H), 7.83 (t, 1H, $J = 7.5$ Hz, phpy-H), 8.10 (s, 2H, perylene-H), 8.17 (s, 2H, perylene-H), 8.80 (d, 1H, $J = 5.0$ Hz, quinoline-H), 8.87 (d, 1H, $J = 4.8$ Hz, quinoline-H), 9.0 (d, 1H, $J = 8.5$ Hz, phpy-H), 9.1 (d, 1H, $J = 4.9$ Hz, phpy-H). IR (KBr): 3437, 2937, 1700, 1655, 1580, 1500, 1410, 1340, 1280, 1200, 1112, 933, 800, 750 cm^{-1}. MS: *m/z* [$M^+ + K$] 1327. Elemental analysis: calc. for $C_{77}H_{58}N_4O_9Pd$: C 71.71%, H 4.53%, N 4.34%; found: C 71.82%, H 4.45%, N 4.30%.

2.2. Photophysical measurements

UV–vis spectra were recorded on a Varian Cary 100 Spectrometer. Fluorescence spectra were recorded on a Varian Cary Eclipse fluorescent spectrometer and transient luminescence spectra were obtained with a single photon counting spectrofluorimeter from Edinburgh Analytical Instruments (FLS920). This instrument was also utilized for time-correlated single photon counting (TCSPC) experiments. TCSPC data were analyzed by iterative convolution of the luminescence decay profile with the instrument response function using the software provided by Edinburgh Instruments. Low temperature emission was detected by inserting a 5 mm (internal diameter) NMR tube containing appropriate compounds in CH_2Cl_2 into a quartz-tipped finger dewar of the ice salt-bath. The concentration of ligand and its corresponding complex in CH_2Cl_2 is 2.12×10^{-6} M in all our measurements. All photophysical experiments were performed at ambient conditions except the degassed measurements mentioned for control experiment.

3. Results and discussion

3.1. Synthesis and structural characterization

In terms of molecular design, an asymmetric perylene bisimide unit was introduced into the 5-substituted-8-hydroxyquinoline

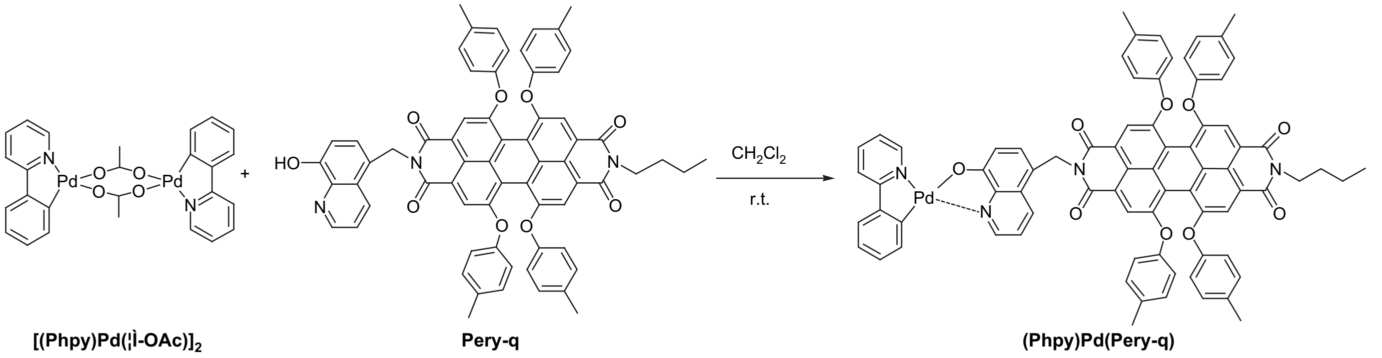

Fig. 1. Synthetic route of complex (Phpy)Pd(Pery-q).

ligand, which then coordinated with cyclopalladated 2-phenylpyridine (Fig. 1). The ligand Pery-q was prepared according to our previous work [26] and $[(PhPy)Pd(\mu\text{-}Oac)]_2$ was prepared as described in the literature [25]. However, the solubility of parent perylene bisimides is always poor and they cannot be dissolved in most common solvents, for example, in chloroform, benzene, acetone or even in high polarity solvents, such as DMSO and DMF; this poses problems for both synthesis and purification. One approach to improve such poor solubility has been used to suppress cofacial aggregation of the parent perylene bisimide by incorporating bulky groups at the perylene backbone, such as 4-methylphenoxy, 4-*tert*-butylphenoxy groups [27–29] or long chain *sec*-alkyl groups ("swallow tail" substituents [30,31]) at the *N*-aryl unit. For the intermediate of Pery-q, substitution of 4-methylphenoxy group can increase its solubility significantly.

In spite of the high coordinative capacity of 8-hydroxyquinoline unit with the metal cation, we found that the yield of the target complex was not good. The Pd(II) complex (Phpy)Pd(Pery-q) was finally isolated by column chromatography on silica gel (CH_2Cl_2:$CCl_4 = 5{:}1$) but in low yield (24%). It is believed that the introduction of a large perylene bisimide unit effected ligand coordination to some extent although the large group was attached to the rear side of the ligand.

The chemical structure of the (Phpy)Pd(Pery-q) complex was fully characterized by ^{1}H NMR, ESI-MS, elemental analysis and IR spectra. Generally, when the Pery-q ligand was coordinated with Pd^{2+}, it should have had a larger effect on the chemical shift of protons neighboring the N and O atoms than that of other protons in the quinoline ring, as demonstrated in our previous work on the ^{1}H NMR spectra of $(Pery\text{-}q)_3Al$ [26]. For the (Phpy)Pd(Pery-q) complex, there also exists a similar phenomenon. Mass spectra showed an *m*/*z* peak at 1327, corresponding to $[M^+ + K]$; comparison of the infrared spectra of Pery-q and (Phpy)Pd(Pery-q) provides evidence of a coordination effect. For the (Phpy)Pd(Pery-q) complex the vibration peak at about 3400 cm^{-1} was very weak, indicative of the disappearance of hydroxyl group due to coordination. In addition, there was a new characteristic vibration band at about 1112 cm^{-1} assigned to the C–O stretching vibration for C–O–Pd bond, which is consistent with a previous study of 8-hydroxyquinoline chelates [32].

3.2. Absorption and fluorescence

Due to the substitution of a 4-methylphenoxy group on the perylenediimide unit, the target complex (PhPy)Pd(Pery-q) is readily soluble in CH_2Cl_2, $CHCl_3$, THF and sparingly soluble in toluene, CH_3CN, DMF and alcoholic solvents. The UV–vis absorption spectra of (PhPy)Pd(Pery-q) and the ligand Pery-q in CH_2Cl_2 solution are shown in Fig. 2. For (PhPy)Pd(Pery-q), there exists three main peaks at 452, 546 and 591 nm arising from the typical transition absorption of perylene bisimide. There were some 10 nm red shifts in the maximal absorption of (Phpy)Pd(Pery-q) relative to that of Pery-q (Fig. 2); also it should be pointed out that the transition peak at about 434 nm for the parent bis-chelate palladium(II) complex unit [7], arising from an electron transfer from phenolic to pyridyl side, cannot be clearly discernible. This can be attributed to the large difference in molar extinction coefficient at 434 nm ($\varepsilon_{(PhPy)Pd(Q)} = 2440\ M^{-1}\,cm^{-1}$, $\varepsilon_{(Phpy)Pd(Pery\text{-}q)} = 18\,000\ M^{-1}\,cm^{-1}$), resulting in the characteristic peak at 434 nm overlapping with the absorption background of (Phpy)Pd(Pery-q). The fluorescence emission of the complex and its ligand Pery-q are close to the peaks at 617 and 613 nm, respectively (Fig. 3). In addition, the complex shows a small, red shift on the UV–vis absorption and PL emission when increasing the solvent polarity from CH_2Cl_2 to THF.

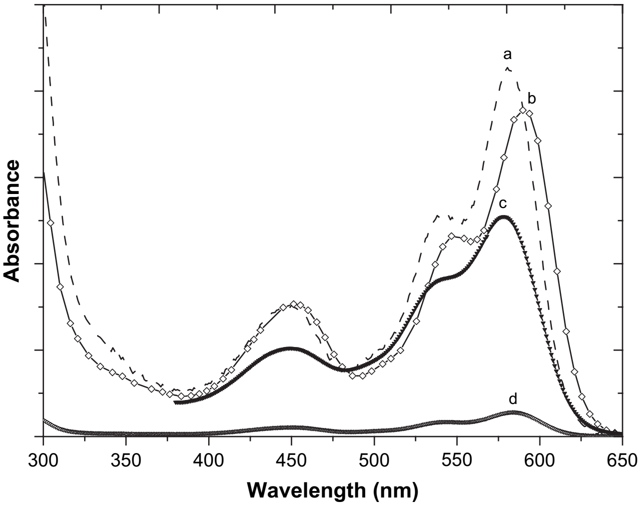

Fig. 2. Absorption spectra of complex (Phpy)Pd(Pery-q) and ligand Pery-q at room temperature: (a) ligand in CH_2Cl_2; (b) complex in CH_2Cl_2; (c) complex in PVK (2 wt%); (d) complex in solid powder.

3.3. Room temperature phosphorescence

At present, most reports focused on the porphyrin system in terms of phosphorescent Pd(II) complexes [8,33–36]. The

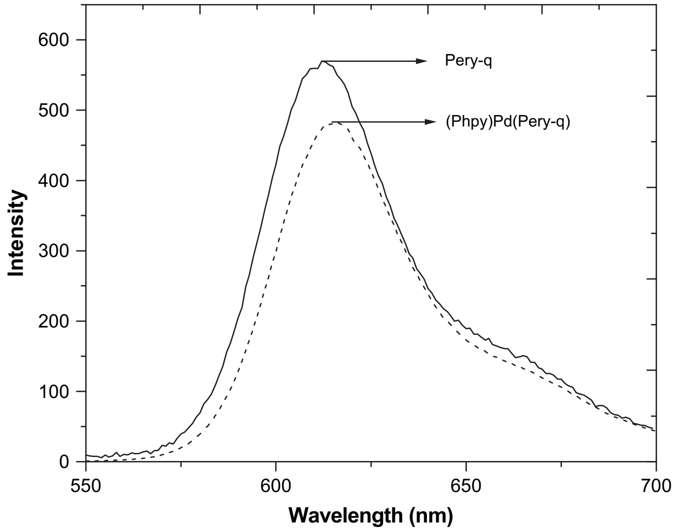

Fig. 3. Fluorescence spectra of complex (Phpy)Pd(Pery-q) and ligand Pery-q at room temperature in CH_2Cl_2 upon excitation at 540 nm.

absence of photoluminescence for Pd(II) complexes at room temperature is probably due to the significant structural distortions of the emissive excited states from the ground states, leading to a facile non-radiative pathway [10]. Consistent with the above mentioned steady-state fluorescence in the case of (PhPy)Pd(Pery-q), time-resolved luminescence was observed at 617 nm (Fig. 4a) with a lifetime of 7.09 ns, typical of fluorescent emission with a single-exponential decay, which originated from the perylene bisimide. However, delayed phosphorescence could be separated from the tail of the fluorescent band at room temperature in time-resolved experiments. We simply used a nanosecond time gate in the intensified charge-coupled device (CCD), triggering the detector immediately after the laser pulse rather than introducing a delay after the pulse, to separate the long-lived emission from the prompt ones. As shown in Fig. 4b upon selective excitation of perylene bisimide unit (540 nm) where (Phpy)Pd(Q) unit has no absorption, the time-delayed phosphorescence emission of the complex was located at 635 nm with a lifetime of *ca.* 14.2 μs. The intensity decreased dramatically when the delay time changed from 5 to 100 μs. Such large lifetime difference between (Phpy)Pd(Pery-q) and Pery-q definitely rules out the possibility that the observed phosphorescence is from the singlet excited state of perylene bisimide chromophore. For the ligand Pery-q under the same measurements mentioned above, we could not separate its corresponding delayed emission and only obtained a lifetime of 7.09 ns, indicative of a typical fluorescent emission.

The triplet state resulting in the delayed phosphorescence is reached by intersystem crossing from the lowest singlet state, which is ascribed to an observed lifetime of τ_f. The efficiency of triplet formation is $\tau_f \kappa_{isc}$, where κ_{isc} is the rate coefficient of intersystem crossing. In the absence of recrossing to the singlet state, the emissive triplet can undergo either spontaneous emission or internal conversion to the ground electronic state, energy transfer or chemistry including electron transfer. If the emitting states of ^{3}IL and MC lie too close in energy, they can thermally equilibrate, thereby quenching the emission through fast non-radiative decay through MC states. The energy gap between MC and lowest energy emitting excited state has been considered to be one of the limiting factors for emission efficiency, i.e., a small energy gap between emitting and MC states leads to poor emission efficiency [37]. In the case of (Phpy)Pd(Pery-q), the unexpected delayed phosphorescence might be attributed to the introduced perylene bisimide, which might prevent thermally activated process involving non-emissive MC levels via strategically positioning the ^{3}IL excited states below the ^{3}MLCT manifold. A proof is 10 nm red shift in absorption spectra, indicating that there exists the interaction between 8-hydroxyquinolinate and the incorporated perylene bisimide units.

We excluded the delayed phosphorescence arising from the ^{3}MLCT state of Pd in that the excited state usually involves non-radiative decay at room temperature and aerated conditions [38]. Notably, considering that there was only an 18 nm shift between the fluorescence and phosphorescence peaks of the complex, the possibility of the emission originating from the triplet state of ^{3}Pery (1.2 eV) was ruled out. Indeed, the usually detected phosphorescent emission of perylene bisimide is about 1033 nm [37,39,40], which is markedly different from that of our results (635 nm). Finally, we assigned the emission to the ^{3}ILCT in 8-hydroxyquinol ligand, which can be characterized by charge transfer from the lone pair p-orbital at the oxygen with the lowest π*-orbital possessing greater electron density on the pyridyl moiety [41,42]. The strong spin–orbit coupling of the heavy metal atom allows for efficient intersystem crossing between the singlet and triplet states [43]. We also measured the delayed phosphorescent emission spectra of the complex selectively excited at the perylene bisimide (590 nm); almost identical phosphorescent emission spectra were obtained, indicating that the phosphorescence originated from sensitization of the perylene bisimide

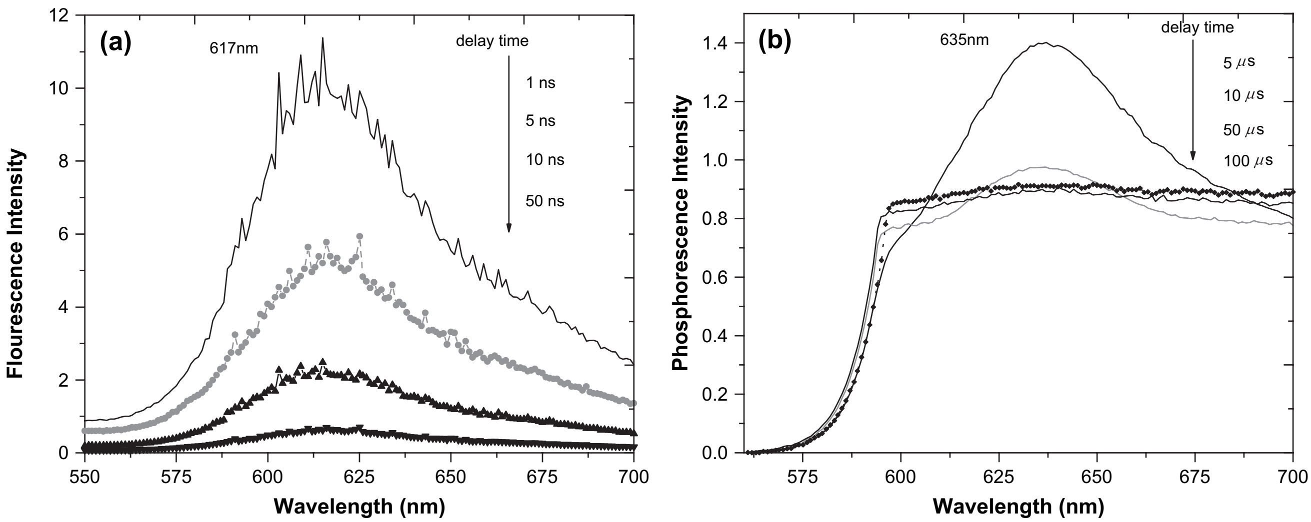

Fig. 4. Room temperature laser-induced luminescence spectra of complex (Phpy)Pd(Pery-q) in CH_2Cl_2 solvents ($\lambda_{ex} = 540$ nm, 288 K): (a) time-resolved fluorescence emission spectra; (b) time-resolved phosphorescence emission spectra.

unit. The singlet state of perylene bisimide will decay via two paths:

(i) radiative decay to its ground state resulting in the characteristic perylene bisimide fluorescence (617 nm);
(ii) intersystem crossing to the ^{3}ILCT state of the 8-hydroxyquinoline ligand with heavy metal assistance, resulting in the observed phosphorescence (635 nm).

The assignment of 8-hydroxyquinoline rather than 2-phenylpyridine as ligand in ^{3}ILCT is based on the triplet emission data for complex $Pd(qol)_2$ (620 nm) and $[Pd(ppy)Cl]_2$ (460 nm) [41,44]. Generally, the emission from ^{3}ILCT in the free 8-hydroxyquinoline ligand can only be obtained at very low temperature and in degassed solution. For the room temperature phosphorescence resulting from (Phpy)Pd(Pery-q), we consider that sensitization of the unsymmetric perylene bisimide-8-hydroxyquinoline ligand occurs.

In general, RTP can be quenched by molecular oxygen during measurement since oxygen is one of the most effective dynamic quenchers in liquid room temperature phosphorimetry [35,45,46]. As normally observed for emission from triplet states, RTP in (PhPy)Pd(Pery-q) is always quenched by oxygen. For our results, the emission intensity obtained in degassed solution was almost three times higher than that measured under aerated conditions (Fig. 5), indicating that the molecular oxygen also bears the responsibility for the emission quenching in our synthesized complex. In addition, phosphorimetry is usually carried out using a rigid matrix cooled at liquid nitrogen temperature (77 K) in order to prevent radiation deactivation of the triplet state due to intermolecular collision. The phosphorescence emission of (PhPy)Pd(Pery-q) was markedly dependent on temperature (Fig. 6). When the temperature was lowered from 15 to −30 °C, the phosphorescence intensity strengthened gradually. In the case of measurement of the complex in poly(vinylcarbazole) (PVK) in the solid state, increasing the concentration of (PhPy)Pd(Pery-q) doped in the PVK film by spin coating decreased the phosphorescence emission intensity dramatically and in solid state the intensity is too weak to be detected (Fig. 7). It is suggested that the phosphorescence of (PhPy)Pd(Pery-q) is affected by aggregation resulting in the possibility of radiation energy loss of the excited molecules.

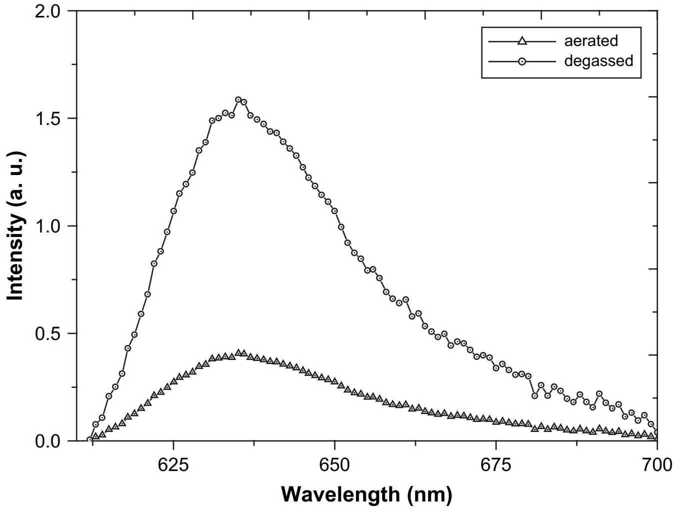

Fig. 5. Phosphorescent emission of complex (Phpy)Pd(Pery-q) in CH_2Cl_2 solution under aerated and degassed conditions selectively excited at the wavelength of 540 nm.

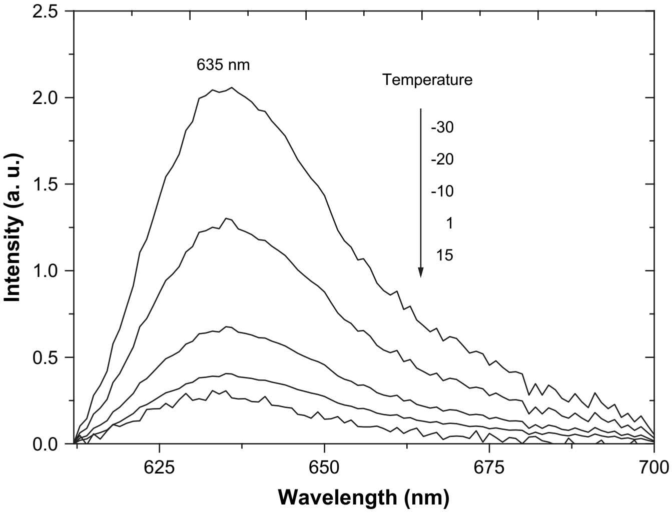

Fig. 6. Long-lived phosphorescence emission spectra of complex (Phpy)Pd(Pery-q) selectively excited at the wavelength of 540 nm in CH_2Cl_2 measured at temperature ranging from 15 to −30 °C.

4. Conclusions

The room temperature phosphorescence of palladium(II) complex (Phpy)Pd(Pery-q) sensitized by unsymmetric perylene bisimide is described. The complex displayed phosphorescence with a lifetime in the microsecond range, arising from the ^{3}ILCT state of the 8-hydroxyquinoline ligand and was dependent on the ligand orbital perturbed by the metal palladium. The fluorescence and phosphorescence of the

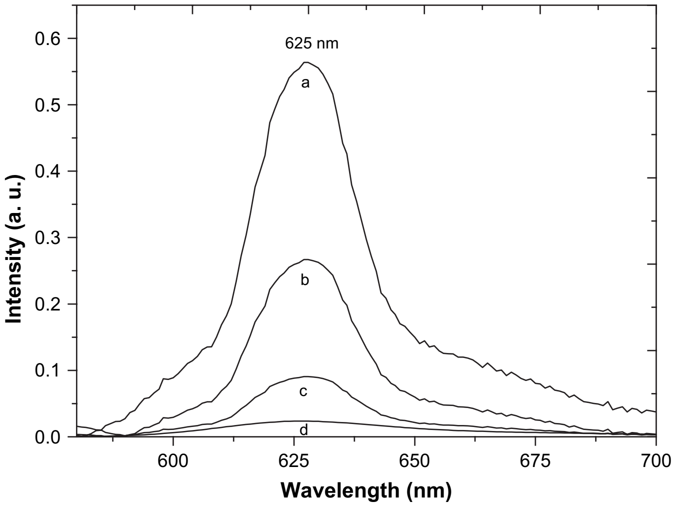

Fig. 7. Long-lived phosphorescence emission spectra of complex (Phpy)Pd(Pery-q) excited at the wavelength of 540 nm in PVK film and in solid state measured at room temperature with complex content (wt%): curve (a) 2%, curve (b) 20%, curve (c) 40%, and curve (d) solid powder.

complex were separated by laser pulse and time-delayed technology. In contrast, the long-lived emission from the Pery-q ligand could not be obtained under the same measurement conditions. The excited singlet state of the appended perylene bisimide can decay along two paths: (i) radiative decay to its ground state resulting in the characteristic perylene bisimide fluorescence (617 nm); (ii) intersystem crossing to the ^{3}ILCT state of the 8-hydroxyquinoline ligand with heavy metal assistance, resulting in the observed phosphorescence (635 nm). In PVK film or the solid state, the complex also exhibited long-lived emission but with decreased intensity due to aggregation. (Phpy)Pd(Pery-q) represents an alternative molecular design that imparts long lifetime red photoluminescence to a synthetically facile, metal–organic system. Such molecules have important potential applications in emerging luminescence-based technologies and excited state chemistry schemes, serving to further enhance our knowledge regarding manipulation of molecular excited states.

Acknowledgements

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