Comment on 'aggregation-induced phosphorescent emission (AIPE) of iridium(III) complexes': origin of the enhanced phosphorescence†

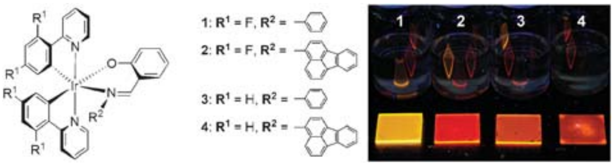
Youngmin You,[a] Hyun Sue Huh,[b] Kil Suk Kim,[c] Soon W. Lee,[b] Dongho Kim[c] and Soo Young Park*[a]

Received (in Cambridge, UK) 17th April 2008, Accepted 27th May 2008
First published as an Advance Article on the web 24th July 2008
DOI: 10.1039/b806541a

An investigation of the photophysics of Ir(III) complexes with controlled ligand structures and our quantum chemical calculations attest that the most probable explanation for the reported 'aggregation-induced phosphorescent emission', which was originally claimed to be related to an intermolecular excimer, is restricted intramolecular motion.

Phosphorescent cyclometalated Ir(III) complexes are of increasing interest due to their promising electroluminescence applications. In a recent communication in this journal, Zhao *et al.* reported the enhanced phosphorescence phenomena in the solid state, so-called 'aggregation-induced phosphorescent emission', of heteroleptic Ir(III) complexes.[1] The complexes, $Ir(ppy)_2(DBM)$ and $Ir(ppy)_2(SB)$ (See Scheme 1), exhibit high contrast on (solid state)/off (solution state) phosphorescence behavior. Since such responsive optical modulation could be very useful in active sensors,[2] it is particularly important to understand the underlying mechanism of this phenomenon. Based on their crystal structure analysis, triplet state determination for the ancillary ligands in Gd(III) complexes, and density functional theory (DFT) calculations, Zhao *et al.* concluded that the mechanism of enhanced phosphorescence in the solid state is related to excimeric interactions between the cyclometalating ligands (ppy) of adjacent complexes.

In our series of studies of phosphorescent Ir(III) complexes with chromophoric ancillary ligands,[3] we have independently developed heteroleptic Ir(III) complexes that exhibit very similar phosphorescence behavior. However, our observations indicate that the enhanced phosphorescence in the solid state (EPSS) originates from restricted intramolecular relaxation rather than from intermolecular excimer states as proposed by Zhao *et al.* In this communication, we demonstrate phosphorescence modulation for four different Ir(III) complexes for various media and temperatures. The systematic variation of the structures of the complexes enabled us to investigate the origin of their EPSS behavior. Based on our time-dependent (TD)-DFT and unrestricted single-excitation configuration interaction (UCIS) calculations as well as photophysical data, we conclude that the restricted rotational motion of the *N*-aryl moiety is responsible for the EPSS, which is very similar to that found in the aggregation-induced emission (AIE) of siloles.[4]



Scheme 1 Structures of the Ir(III) complexes and their phosphorescence in solution (CH_2Cl_2, Ar-saturated) and neat film states. $Ir(ppy)_2(DBM)$: R^1 = H, DBM = 1,3-diphenyl-1,3-propanedione; $Ir(ppy)_2(SB)$: R^1 = H, R^2 = 1-naphthyl.[1]

The chemical structures of the complexes investigated in this report are shown in Scheme 1. Note the following variations in the ligands used in this series: cyclometalating ligands, 2-(2,4-difluorophenyl)pyridine (dfppy, **1** and **2**) and 2-phenylpyridine (ppy, **3** and **4**); and imine-based ancillary ligands, 2-(phenyliminomethyl)-phenol (pip, **1** and **3**) and 2-((fluoranthen-3-ylimino)methyl)-phenol (fip, **2** and **4**). The ligand structures are nearly identical to the complex synthesized by Zhao *et al.* (see the caption to Scheme 1). All the complexes exhibit very high contrast EPSS ($\Phi_{solid}/\Phi_{solution} > 10^2$). If the cyclometalating ligand's excimeric states of **1** and **2** (or **3** and **4**) are responsible for their EPSS, the phosphorescence λ_{max} of **1** and **2** (or **3** and **4**) should be identical. However, our observation is that **2** and **4** exhibit solid state phosphorescence that is bathochromically shifted with respect to that of **1** and **3** respectively, as summarized in Table 1. Since the oxidation potentials of **1** and **2** (or **3** and **4**) are nearly identical, we deduce that the observed EPSS color change is directly related to the chemical structure of the ancillary ligand. In other words, because the ordering of the electrochemical bandgaps (and the optical bandgaps, see the ESI for the absorption spectra†) of the

Table 1 Photophysical and electrochemical data of the Ir(III) complexes

	PL λ_{max}/nm	Φ_{solid}[a]	$\Phi_{solution}$[b]	E_{ox}/V[c]	E_{red}/V[c]
1	563	0.53	0.0020	1.06	—[d]
2	596	0.24	0.0013	1.07	−1.53
3	581	0.20	0.0011	0.90	—[d]
4	604	0.18	0.0019	0.88	−1.56

[a] Absolute PLQY. [b] Quinine sulfate reference. [c] Relative to Ag/Ag^+. [d] Not observable up to −1.6 V.

---

[a] *Department of Materials Science & Engineering, Seoul National University, San 56-1, Shillim-Dong, Kwanak-Gu, Seoul, 151-744, Korea. E-mail: parksy@snu.ac.kr; Fax: +82-2-886-8331; Tel: +82-2-880-8327*
[b] *Department of Chemistry (BK21), Sungkyunkwan University, Natural Science Campus, Suwon, 440-746, Korea*
[c] *Department of Chemistry, Yonsei University, Seoul, 120-749, Korea*

† Electronic supplementary information (ESI) available: Photophysical data, calculation results and synthetic details. CCDC reference numbers 684918 and 684919. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b806541a

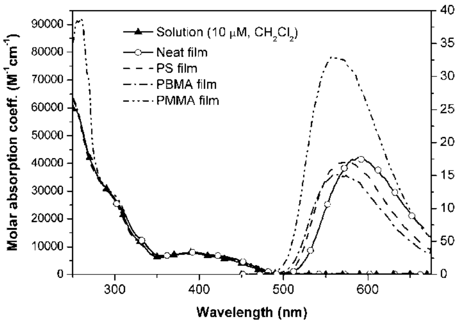


Fig. 1 Absorption and phosphorescence spectra of **1** in solution (Ar-saturated), neat film (spin-coated), and doped polymer film states (2 wt%, spin-coated). The absorption spectra of the films were vertically adjusted to show the similarity of their spectral shapes.

complexes is the same as that of their phosphorescence peak energies (**2** < **1**, **4** < **3**, Table 1), we suggest that the phosphorescent state involved in the EPSS in each case is constructed from the ancillary ligand's LUMO but not from the cyclometalating ligand's excimeric (LL) orbital.

It has been reported that luminescence efficiency greatly increases in the solid state due to special molecular arrangements such as *J*-[5] or cross-stacking.[6] In order to determine whether the observed EPSS behavior stems from such ground state interactions in the solid state, we compared the absorption and phosphorescence spectra obtained for the solution and neat film states. The spectra of **1** are displayed in Fig. 1 (see SI 1 in ESI† for the spectra of **2–4**). The absorption spectrum of the neat film contains an apparent ancillary ligand-related transition (~400 nm) as well as a cyclometalating ligand-centered transition (<280 nm), and so is virtually identical to that of the solution, with highly enhanced phosphorescence recorded for the neat and doped films. We conclude that ground state interactions such as *J*- or cross-aggregation are not responsible for the observed EPSS behavior.

We also investigated the properties of polymer films with various complex doping ratios (Fig. 2). We found that the shapes of the absorption spectra of the doped PMMA films do not vary despite the large variation in doping conditions (up to 80 wt%). Similarly, there are no significant changes in the phosphorescence spectra,‡ which were weighted according to the absorbance of the excitation wavelength (345 nm). Most importantly, the observation that a 1 wt% PMMA film exhibits EPSS indicates that its origin is not an excimeric or aggregated state.

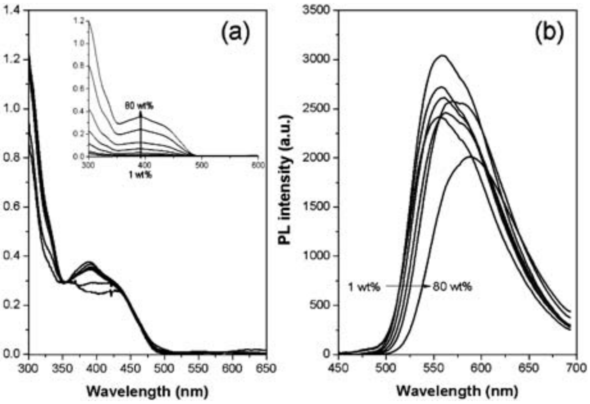


Fig. 2 Absorption (a, normalized at 355 nm) and phosphorescence (b) spectra of PMMA films doped with 1–80 wt% of **1**. The fluctuations in the two absorption spectra near 400 nm are due to the instrumental detection limits. The raw absorption spectra are shown in the inset of (a).

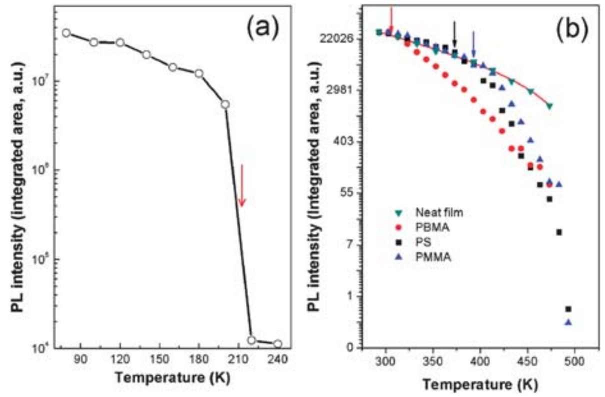


Fig. 3 Plots of the phosphorescence intensity of **1** in solution (a, $CHCl_3$ solution, 10 μM) and film states (b, neat or polymer films (2 wt%)) as a function of temperature. The arrows indicate the melting point of the solvent or T_g of the polymers. Refer to the ESI for the spectra and photos.†

More convincing evidence for the origin of the EPSS is presented in Fig. 3. When we froze an initially non-phosphorescent fluid $CHCl_3$ solution (10 μM) containing **1**, bright yellow phosphorescence was observed. The variation of the phosphorescence intensity of the frozen solution with temperatures (80–240 K) is shown in Fig. 3(a): there is a very abrupt decrease in phosphorescence intensity near the melting point of the $CHCl_3$ solvent. This behavior is reversible and is also reproduced in other solvents (*t*-BuOH, DMF, THF, and CH_2Cl_2).

Moreover, a similar temperature dependence is observed for polymer films (poly(methyl methacrylate) (PMMA, Mn ~ 120 000), poly(butyl methacrylate) (PBMA, $M_w \approx 337\,000$) and poly(styrene) (PS, $M_w \approx 230\,000$)) doped with **1** (2 wt%). As shown in Fig. 3(b), the phosphorescence intensities of the doped polymer films decrease as the temperature increases. An important finding is that the slopes of plots of phosphorescence intensity *vs.* temperature for the polymer films change at certain critical temperatures, but below the critical temperatures, the slopes are virtually identical to that of the neat film of **1** *i.e.*, the control sample (solid line).§ Initially, the phosphorescence intensities decrease along the solid line shown. However, the curves start to deviate from this line and their slopes become steeper than that of the solid line. It should be noted that the critical temperature in each case is very close to T_g of the polymer (PBMA = 15 °C, PS = 94 °C, PMMA = 114 °C). We also found a similar two-state change in the phosphorescence lifetime of **1** (PMMA film, 2 wt%, SI 6†), with a critical temperature that again is similar to T_g of the polymer. It should be noted that, in these temperature variation experiments, a dilute concentration was used that precludes any ground state or excited state interchromophoric interactions. The above results show that the EPSS phenomenon is associated with restricted freedom of intramolecular motions, which is known to produce enhanced fluorescence of organic compounds[7] or thermally induced phosphorescence deactivation of porphyrins[8] and Rh(III) complexes.[9]

As many other Ir(III) complexes containing dfppy and ppy cyclometalating ligands do not exhibit high contrast EPSS, it is evident that the imine-based ancillary ligands (SB[1], pip and fip)

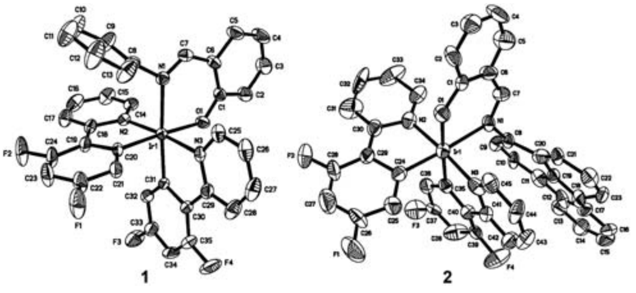


Fig. 4 Perspective views of **1** and **2** crystals with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. The dihedral angles (C7–N1–C8–C9) are 67.9° (**1**) and 66.6° (**2**).

are responsible. Particularly, we consider that a rotation around the N–aryl ring bond of the ancillary ligands could be a rational origin.[4] In the crystal structure of **1** (Fig. 4¶), the dihedral angle (C7–N1–C8–C9) is 68°. In contrast, the optimized triplet state geometry (UCIS/lanl2dz) of **1** has a dihedral angle of 44°, which indicates that the initially twisted conformation is susceptible to rotation toward planarization. In addition, the potential energy surface for dihedral angle change (Fig. 5, 0–180°) obtained with TD-DFT (b3lyp/6-31g**:lanl2dz) calculations provides convincing evidence that (1) there is a state-crossing near 65°, which is very close to the dihedral angle of the crystal, and (2) bond rotation around the N–aryl ring only has a small energy barrier ($\sim$0.72 kcal mol^{-1}) for the state-crossing. Since the bond rotation strongly affects the orbital distribution of the LUMO (SI 8†), we propose that the thermally activated bond rotation (C7–N1–C8–C9) perturbs the nature of the phosphorescent state, which subsequently results in non-phosphorescent decay. In other words, the restricted intramolecular motion in the ancillary ligand suppresses a non-radiative channel in the solid state and results in EPSS. A similar explanation has been reported for a homoleptic Ir(III) complex with pyridyl azolate cyclometalating ligands that exhibits temperature-dependent dual phosphorescence.[10] In that report, the dual phosphorescence was discussed in the light of a thermally induced switch from a phosphorescent state to a relatively weakly phosphorescent state. In addition, very rich photophysics is known for imine compounds such as our ancillary ligands, some of which have been reported to exhibit saliently enhanced fluorescence in the solid state.[11]

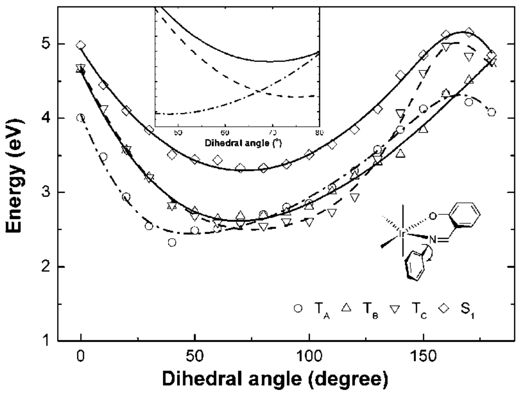


Fig. 5 The potential energy surface for **1** for N–phenyl ring bond (see inset structure) rotation (TD-DFT, b3lyp/6-31g**:lanl2dz). The inset curve provides a magnified view for 45–80°. Refer to SI 7 for the involved MOs of the triplet states.†

In summary, the enhanced phosphorescence in the solid state (EPSS) of heteroleptic Ir(III) complexes (**1–4**) with imine-based ancillary ligands has been investigated. Our TD-DFT and UCIS calculations as well as photophysical data indicate that the EPSS phenomena stem from restricted intramolecular motion.

We acknowledge the financial support of the Korea Science and Engineering Foundation (KOSEF) through the National Research Laboratory. The program was funded by the Ministry of Education, Science and Technology (No. 2006-03246). The work of Mr Won-Ik Jung in carrying out transient PL measurements is greatly appreciated.

Notes and references

‡ The observed red shift in the 80 wt% film can be attributed to excimeric interactions.

§ The neat film can be regarded as a system self-doped in a higher T_g material. The T_g of **1–4** are higher than 250 °C.

¶ Crystal data for **1·CHCl₃**: $C_{36}H_{23}Cl_3F_4IrN_3O$, M = 888.12, monoclinic, space group $P2_1/c$, a = 12.6771(5), b = 28.1017(11), c = 9.8656(4) Å, β = 105.082(2)°, V = 3393.5(2) Å^3, Z = 4, D_c = 1.738 g cm^{-3}, μ = 4.227 mm^{-1} (MoKα, λ = 0.71073 Å), T = 296 K, no. of reflns measured = 55 116, no. of reflns unique = 8413 (R_{int} = 0.0284), no. of reflns with $I > 2\sigma(I)$ = 7095, no. of params refined = 413, max., in $\Delta\rho$ = 2.930 e Å^{-3}, min., in $\Delta\rho$ = −0.948 e Å^{-3}, GOF on F^2 = 1.060, R_1 = 0.0415, wR_2 = 0.1123. CCDC 684918. Crystal data for **2**: $C_{45}H_{26}F_4IrN_3O$, M = 892.89, orthorhombic, space group $Pna2_1$, a = 13.5267(6), b = 24.8476(11), c = 23.8083(10) Å, V = 8002.1(6) Å^3, Z = 8, D_c = 1.482 g cm^{-3}; μ = 3.392 mm^{-1}, no. of reflns measured = 76 093, no. of reflns unique = 18 234 (R_{int} = 0.0821), no. of reflns with $I > 2\sigma(I)$ = 9221, no. of params refined = 974, max., in $\Delta\rho$ = 1.152 e Å^{-3}, min., in $\Delta\rho$ = −0.714 e Å^{-3}, GOF on F^2 = 0.970, R_1 = 0.0518, wR_2 = 0.0827. CCDC 684919. For crystallographic data in CIF and other electronic formats see DOI: 10.1039/b806541a

1 Q. Zhao, L. Li, F. Li, M. Yu, Z. Liu, T. Yi and C. Huang, *Chem. Commun.*, 2008, 685.
2 H. Mastuzaki, H. Kishida, H. Okamoto, K. Takizawa, S. Matsunaga, S. Takaishi, H. Miyasaka, K. Sugiura and M. Yamashita, *Angew. Chem., Int. Ed.*, 2005, **44**, 3240 and references therein.
3 Y. You and S. Y. Park, *J. Am. Chem. Soc.*, 2005, **127**, 12438; Y. You, K. S. Kim, T. K. Ahn, D. Kim and S. Y. Park, *J. Phys. Chem. C*, 2007, **111**, 4052; Y. You, J. Seo, S. H. Kim, K. S. Kim, T. K. Ahn, D. Kim and S. Y. Park, *Inorg. Chem.*, 2008, **47**, 1476.
4 J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu and B. Z. Thang, *Chem. Commun.*, 2001, 1740; H. Tong, Y. Dong, M. Häußler, J. W. Y. Lam, H. H.-Y. Sung, I. D. Williams, J. Sung and B. Z. Tang, *Chem. Commun.*, 2006, 1133; J. Chen, B. Xu, X. Ouyang, B. Z. Tang and Y. Cao, *J. Phys. Chem. A*, 2004, **108**, 7522; Q. Zang, Z. Li, Y. Dong, C. Di, A. Qin, Y. Hong, L. Ji, Z. Zhu, C. K. W. Jim, G. Yu, Q. Li, Z. Li, Y. Liu, J. Qin and B. Z. Tang, *Chem. Commun.*, 2007, 70.
5 B.-K. An, S.-K. Kwon, S.-D. Jung and S. Y. Park, *J. Am. Chem. Soc.*, 2002, **124**, 14410; H. Yoshika and K. Nakatsu, *Chem. Phys. Lett.*, 1971, **11**, 255; B.-K. An, D.-S. Lee, J.-S. Lee, Y.-S. Park, H.-S. Song and S. Y. Park, *J. Am. Chem. Soc.*, 2004, **126**, 10232.
6 Z. Xie, B. Yang, F. Li, G. Cheng, L. Liu, G. Yang, H. Xu, L. Ye, M. Hanif, S. Liu, D. Ma and Y. Ma, *J. Am. Chem. Soc.*, 2005, **127**, 14152.
7 R. O. Loutfy and B. A. Arnold, *J. Phys. Chem.*, 1982, **86**, 4205; S. Kim and S. Y. Park, *J. Photochem. Photobiol. A: Chem.*, 2007, **191**, 19; C. E. Kung and J. K. Reed, *Biochemistry*, 1986, **25**, 6114; C. E. Kung and J. K. Reed, *Biochemistry*, 1989, **28**, 6678.
8 J. Andéasson, H. Zetterqvist, J. Kajanus, J. Mårtensson and B. Albinsson, *J. Phys. Chem. A*, 2000, **104**, 9307.
9 J. A. Brozik and G. A. Crosby, *J. Phys. Chem. A*, 1998, **102**, 45.
10 Y.-S. Yeh, Y.-M. Cheng, P.-T. Chou, G.-H. Lee, C.-H. Yang, Y. Chi, C.-F. Shu and C.-H. Wang, *ChemPhysChem*, 2006, **7**, 2294.
11 J. Harada, T. Fujiwara and K. Ogawa, *J. Am. Chem. Soc.*, 2007, **129**, 16216; A. Dreuw, J. Plötner, L. Lorenz, J. Wachtveitl, J. E. Djanhan, J. Brüning, T. Metz, M. Bolte and M. U. Schumidt, *Angew. Chem., Int. Ed.*, 2005, **44**, 7783.