

COMMUNICATION

Highly luminescent imidoamidinato platinum(II) complexes formed by the coupling of 1*H*-pyrazole-1-carboxamide with nitriles used as reaction solvents†

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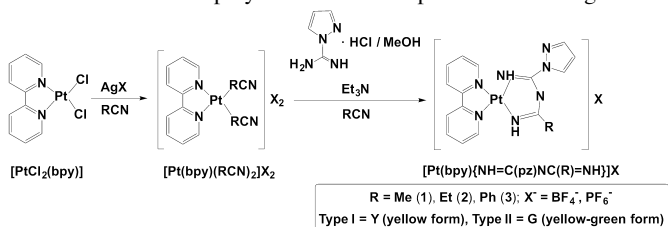
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A series of imidoamidinato Pt(II) complexes have been prepared by the reaction of [Pt(bpy)(RCN)₂]²⁺ (R = Me, Et, Ph) generated in nitrile solution with 1*H*-pyrazole-1-carboxamide. These complexes exhibit bright yellow or yellow-green luminescence in the solid state and mechanochromic behavior.

Platinum(II) complexes containing aromatic amines such as α-diimines and terpyridines are known to exhibit luminescence from various excited states depending on the nature of aromatic amines and the extent of metal-metal interactions with neighboring Pt(II) ions intermolecularly or intramolecularly.¹⁻⁵ The metallophilic interactions have attracted much attention, because the emissive state of Pt(II) complexes are very sensitive to the slight structural changes, which lead to the interesting phenomena such as vapochromism, mechanochromism and thermochromism.⁶⁻⁸ We have reported that the emissive state dramatically changes according to the change of bulkiness of substituent group (*i.e.* Pt•••Pt separations) in the non-substituted pyrazolate- and 3,5-dimethylpyrazolate-bridged dinuclear Pt(II) complexes of 2,2'-bipyrimidine.^{9,10} We have also shown that the careful tuning of the basicity of pyrazolate ligands enables us to control the structure of mononuclear Pt(II) complexes formed by the reaction of [PtCl₂(C₂H₅CN)₂] with pyrazolate ligands, leading to the selective formation of heteropolynuclear Pt complexes.¹¹ During further

investigation of the reactions of Pt(II) ion with various pyrazole derivatives, we unexpectedly obtained brightly luminescent imidoamidinato Pt(II) complexes formed by the coupling of the coordinated nitriles with pyrazolecarboxamide. The bis(imidoamidinato) Pt(II) and Pt(IV) complexes have already been prepared by the reaction of an amidine PhC(=NH)NHPH with [PtCl₂(RCN)₂] (R = Et, CH₂Ph, Ph, NEt₂) and [PtCl₄(R'CN)₂] (R' = Ph, NEt₂), respectively, by Kukushkin, Pombeiro and their co-workers.^{12,13} Although the photophysical properties of some of them have also been reported, most of the data are limited to the solution state, in which the bis(imidoamidinato) Pt(II) complexes exhibit weak luminescence.¹³ We have succeeded in the synthesis of a series of Pt(II) complexes consisting of 2,2'-bipyridine (bpy) and imidoamidinate {NH=C(pz)NC(R)=NH} (R = Me, Et, Ph), which exhibit drastic color change of luminescence upon grinding. This phenomenon is known as mechanochromism. It reflects a grinding-induced structural rearrangement, which results in the change of Pt•••Pt interactions. However, the number of the Pt(II) complexes showing mechanochromism is still limited.¹⁴⁻¹⁹ We report here the



Scheme 1 Synthesis of [Pt(bpy){NH=C(pz)NC(R)=NH}]X (R = Me, Et, Ph; X⁻ = BF₄⁻, PF₆⁻)

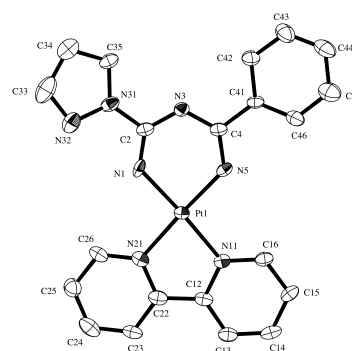


Fig. 1 ORTEP drawing of the complex cation of [3Y]BF₄ with the atom numbering scheme (50% probability ellipsoids).

crystal structures and photophysical properties of (2,2'-bipyridine)(imidoylamidinato)Pt(II) complexes in the solid state.

The (2,2'-bipyridine)(imidoylamidinato)Pt(II) complexes, [Pt(bpy){NH=C(pz)NC(R)=NH}X (R = Me, Et, Ph; X⁻ = BF₄⁻ or PF₆⁻), were prepared by the treatment of [PtCl₂(bpy)] with AgBF₄ or AgPF₆ in acetonitrile, propionitrile and benzonitrile, respectively, followed by the reaction with 1*H*-pyrazole-1-carboxamide hydrochloride in the presence of triethylamine under refluxing for 24h (Scheme 1). Recrystallization of the methyl derivative (R = Me) of imidoylamidinato Pt(II) complex, [1Y]PF₆, from acetonitrile as well as methanol gave a crystal phase, which exhibits yellow luminescence (Type I, *vide infra*). However, recrystallization of the ethyl (R = Et) and phenyl (R = Ph) derivatives afforded two crystal phases, which exhibit yellow luminescence (Type I; [2Y]BF₄ (minor phase) and [3Y]BF₄ (major phase)) and yellow-green luminescence (Type II; [2G]BF₄ (major phase) and [3G]BF₄ (minor phase)). The ¹H NMR spectra of Type I and Type II crystals of each complex are very similar to each other. Among them, we have succeeded in the X-ray structural analyses of [1Y]PF₆, [2G]BF₄, [3Y]BF₄ and [3G]BF₄•H₂O, which enabled us to compare the crystal structures of Type I and Type II phases.

The structure of the complex cation of phenyl derivative [3Y]BF₄ is shown in Fig. 1 as a representative (the structures of [1Y]⁺, [2G]⁺, [3G]⁺ are shown in Figs. S1-S3).[†] The complex cation [3Y]⁺ consists of Pt(II) ion, bpy, and imidoylamidinate formed by the coupling of amidine group with benzonitrile used as a reaction solvent, and it takes planar structure (Fig. S7). Atoms of the metallacycle lie in one plane with a mean deviation of 0.013 Å. The N=C bond lengths [N1-C2 1.284(9) and N5-C4 1.321(9) Å] and N-C bond lengths [N3-C2 1.325(9) and N3-C4 1.338(9) Å] in the metallacycle in [3Y]⁺ agree well with those observed in [1Y]⁺, [2G]⁺ and [3G]⁺ (Table S1) and have values typical for the corresponding bonds in imidoylamidinato Pt(II) complexes reported previously, which exhibit a small degree of delocalization in the ring.^{12,13} The

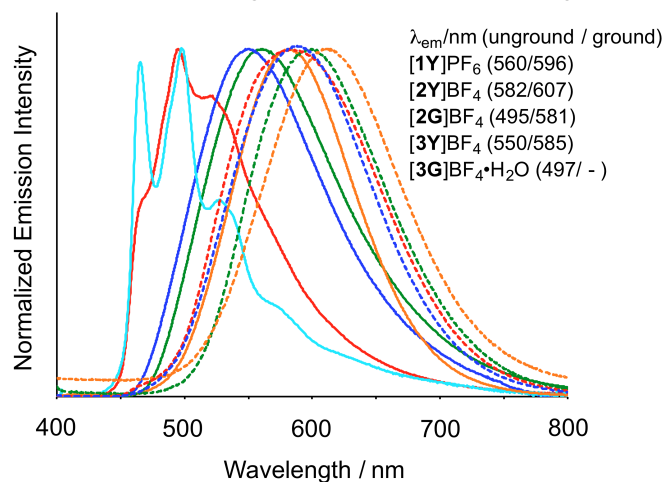


Fig. 2 Normalized emission spectra of [1Y]PF₆ (—), [2Y]BF₄ (---), [2G]BF₄ (---), [3Y]BF₄ (---) and [3G]BF₄•H₂O (---) in the solid state at 295 K ($\lambda_{\text{ex}} = 355$ nm). Solid lines and dashed lines correspond to the spectra of unground and ground samples, respectively.

remarkable difference in crystal structure between two phases of [3]BF₄ is the absence ([3Y]BF₄) and presence ([3G]BF₄•H₂O) of water molecule as a solvent for crystallization. The corresponding metric parameters of [3Y]⁺ and [3G]⁺ are very similar to each other (Table S1). Both [3Y]BF₄ and [3G]BF₄•H₂O crystallize in an antiparallel fashion, which is also seen in the crystal structures of [1Y]PF₆ and [2G]BF₄. The intra-dimer Pt...Pt separation in [3Y]BF₄ (3.7147(7) Å) is shorter than that in [3G]BF₄•H₂O (4.3970(8) Å).

The solid state emission spectra of [1Y]PF₆, [2Y]BF₄, [2G]BF₄, [3Y]BF₄ and [3G]BF₄•H₂O (measured under benzonitrile vapor) can be classified into two groups (Fig. 2, Table 1). The broad emission spectra (Type I) are observed for [1Y]PF₆ ($\lambda_{\text{max}} = 560$ nm, $\Phi = 0.47$), [2Y]BF₄ ($\lambda_{\text{max}} = 582$ nm, $\Phi = 0.38$) and [3Y]BF₄ ($\lambda_{\text{max}} = 550$ nm, $\Phi = 0.38$), while the structured emission spectra (Type II) are observed for [2G]BF₄ ($\lambda_{\text{max}} = 495$ nm, $\Phi = 0.44$) and [3G]BF₄•H₂O ($\lambda_{\text{max}} = 497$ nm).²⁰ The different features of the emission spectra indicate that the emissive states of [1Y]PF₆, [2Y]BF₄ and [3Y]BF₄ and those of [2G]BF₄ and [3G]BF₄•H₂O are different. The lifetimes of [1Y]PF₆, [2Y]BF₄ and [3Y]BF₄ (Type I phase) are similar to each other, while the lifetime of [2G]BF₄ (Type II phase) is about 10 times longer than that of Type I phase. The different features of the lifetimes of two phases may also reflect the different extent of intermolecular interactions among complex cations and counter anions.

To shed light on the absorption spectra of [1]PF₆, [2]BF₄ and [3]BF₄, the absorption bands of these complexes were theoretically investigated with the time-dependent density functional theory (TD-DFT) method. Although the molar absorptivity of each complex is slightly different, the features of the absorption spectra as well as the diffuse reflectance spectra of these complexes are very similar to each other. Calculated transition energies agree well with the experimental results in Table S2. The molecular orbitals, which contribute to the excitations in Table S2, are depicted in Figure S21. Orbital composition percentages of these orbitals are listed in Table S4. These data imply that the lowest energy absorption bands of [1]PF₆, [2]BF₄ and [3]BF₄ are assigned to the combination of the ligand-to-ligand charge-transfer (LLCT) and metal-to-ligand charge-transfer (MLCT) transitions. The optimization of the triplet excited state also revealed that the emission of these three complexes could be attributed to phosphorescence from mixed ³LLCT/³MLCT manifold. The calculated energies of emission agree well with

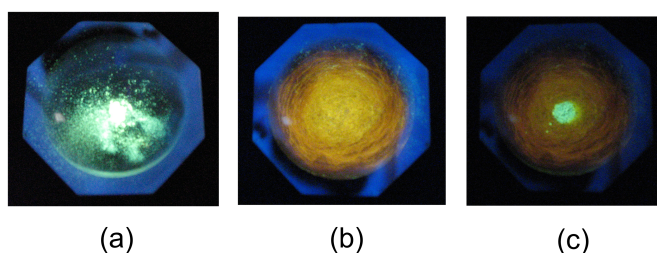


Fig. 3 Photographic images of [2G]BF₄ in response to mechanical grinding under UV light irradiation (365 nm): (a) unground sample, (b) completely ground sample, (c) ground sample with a drop of acetonitrile added.

experimental values for Type I emission of unground samples, respectively (Table S3). Actually this tendency is consistent with the observation that the XRD patterns of the rapidly precipitated sample obtained from acetonitrile solution of [2G]BF₄ by addition of diethyl ether are similar to those of [2Y]BF₄, which indicates that the crystal structure of the former is similar to that of the latter (Fig. 2). On the other hand, the longer Pt...Pt separation and intermolecular interaction with neighboring counter anions may play an important role for Type II emission though the assignment of Type II emission is not available at the present stage.

Interestingly, when crystalline samples [1Y]PF₆, [2G]BF₄, and [3Y]BF₄ are ground in a mortar, the broad yellow emission (Type I) of [1Y]PF₆ and [3Y]BF₄ and structured yellow-green emission (Type II) of [2G]BF₄ both changed to broad structureless orange emission (Figs. 2, 3). The XRD patterns for crystalline [1Y]PF₆, [2G]BF₄ and [3Y]BF₄, respectively, almost disappeared when the samples were thoroughly ground. However, new XRD patterns, which are similar but different from those of corresponding unground samples, were observed for each complex when a drop of acetonitrile was added to each ground powder sample (Figs. S15-S17). The emission spectrum of ground [1Y]PF₆ with a drop of acetonitrile added as well as those corresponding to [2G]BF₄ and [3Y]BF₄ are also different from the emission spectra of corresponding unground samples, respectively, as shown in Figs. S11, S13 and S14, respectively. Furthermore the emission spectra and XRD patterns of the second cycle of grinding and addition of a drop of acetonitrile to the ground samples almost coincide with those of the first cycle of grinding and addition of acetonitrile to the ground samples, respectively. These observations imply that a conversion from the crystalline state to the amorphous phase occurs for each complex when the sample is thoroughly mechanically ground. However, the addition of a drop of acetonitrile converts the amorphous phase to a crystalline state, which is slightly different from the unground original crystalline state. Although several Au(I)^{14,21} and Pt(II)¹⁴⁻¹⁹ complexes showing mechanochromic behavior have already been reported, the addition of solvent to the ground sample usually convert to the original crystalline state. Thus it is interesting that the reversible conversion between another crystalline state and amorphous phase was observed for the imidoamidinato platinum complexes.

In conclusion, we have succeeded in the synthesis of a series of imidoamidinato Pt(II) complexes by the reaction of [Pt(bpy)(RCN)₂]²⁺ generated in nitrile solution with a pyrazole derivative bearing amidine group. The key of the formation of imidoamidinate is the coupling of coordinated nitriles with pyrazolecarboxamide. The imidoamidinato Pt(II) complexes exhibit bright luminescence in the solid state and interesting mechanochromic behavior. These properties may be originated from one-dimensional stacking of the highly planar Pt(II) complexes, in which bpy and imidoamidinate ligands stack alternately.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details of the preparation of the new compounds and photophysical data. CCDC 1023400-1023403. For ESI and crystallographic data in CIF or other electronic format, see DOI: 10.1039/c000000x/

‡ [1Y]PF₆: C₁₆H₁₆F₆N₇Pt, *M* = 646.40, monoclinic, *a* = 7.050(3) Å, *b* = 21.060(9) Å, *c* = 13.409(7) Å, β = 104.882(8)°, *V* = 1924(2) Å³, *T* = 93(1) K, space group *P*2₁/*c*, *Z* = 4, μ(MoKα) = 7.424 mm⁻¹, 15662 reflections measured, 4345 independent reflections (*R*_{int} = 0.0399). The final *R*_i values were 0.0326 (*I* > 2σ(*I*)) and 0.0495 (all data). The final *wR*(*F*²) values were 0.0749 (all data). The goodness of fit on *F*² was 0.971. CCDC number CCDC 1023400. [2G]BF₄: C₁₇H₁₈BF₄N₇Pt, *M* = 602.27, monoclinic, *a* = 8.173(5) Å, *b* = 16.645(9) Å, *c* = 14.314(7) Å, β = 105.822(9)°, *V* = 1874(2) Å³, *T* = 93(1) K, space group *P*2₁/*n*, *Z* = 4, μ(MoKα) = 7.519 mm⁻¹, 15362 reflections measured, 4291 independent reflections (*R*_{int} = 0.0481). The final *R*_i values were 0.0328 (*I* > 2σ(*I*)) and 0.0461 (all data). The final *wR*(*F*²) values were 0.0559 (all data). The goodness of fit on *F*² was 1.041. CCDC number CCDC 1023401. [3Y]BF₄: C₂₁H₁₈BF₄N₇Pt, *M* = 650.31, monoclinic, *a* = 7.585(2) Å, *b* = 13.848(3) Å, *c* = 20.627(4) Å, β = 94.433(3)°, *V* = 2160.2(8) Å³, *T* = 93(1) K, space group *P*2₁/*n*, *Z* = 4, μ(MoKα) = 6.529 mm⁻¹, 17643 reflections measured, 4934 independent reflections (*R*_{int} = 0.0418). The final *R*_i values were 0.0426 (*I* > 2σ(*I*)) and 0.0520 (all data). The final *wR*(*F*²) values were 0.0972 (all data). The goodness of fit on *F*² was 1.128. CCDC number CCDC 1023402. [3G]BF₄·H₂O: C₂₁H₂₀BF₄N₇OPt, *M* = 668.33, monoclinic, *a* = 7.669(2) Å, *b* = 21.278(5) Å, *c* = 13.326(4) Å, β = 90.037(5)°, *V* = 2174.5(9) Å³, *T* = 93(1) K, space group *P*2₁/*n*, *Z* = 4, μ(MoKα) = 6.493 mm⁻¹, 17722 reflections measured, 4948 independent reflections (*R*_{int} = 0.0414). The final *R*_i values were 0.0322 (*I* > 2σ(*I*)) and 0.0415 (all data). The final *wR*(*F*²) values were 0.0692 (all data). The goodness of fit on *F*² was 1.056. CCDC number CCDC 1023403.

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