Polymorph-Dependent Phosphorescence of Cyclometalated Platinum(II) Complexes and Its Relation to Non-covalent Interactions

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ABSTRACT: Cyclometalated platinum(II) complexes [Pt(ppy)Cl(CNAr)] (ppy = 2-phenylpyridinato-C6H4; Ar = C6H4-2-I 1, C6H4-3-I 2, C6H4-2-F-4-I 3, and C6H4-2,4-I-3 4) bearing ancillary isocyanide ligands were obtained by the bidge-splitting reaction between the dimer [Pt(ppy)(μ-Cl)] and 2 equiv any one of the corresponding CNAr. Complex 2 was crystallized in two polymorphic forms, namely, 2H and 2F, exhibiting green (emission quantum yield of 0.5%) and orange (emission quantum yield of 12%) phosphorescence, respectively. Structure-directing non-covalent contacts in these polymorphs were verified by a combination of experimental (X-ray diffraction) and theoretical methods (NCIplot analysis, combined electron localization function (ELF), and Bader quantum theory of atoms in molecules (QTAIM analysis)). A noticeable difference in the spectrum of non-covalent interactions of 2H and 2F is seen in the Pt···Pt interactions in 2H and absence of these metallophilic contacts in 2F. The other solid luminophores, namely, 1, 3H, 4, and 4-CHClCH2 exhibit green luminescence; their structures include intermolecular C–I···Cl···Pt halogen bonds as the structure-directing interactions. Crystals of 1, 2H, 3H, 3F, 4, and 4-CHClCH2 demonstrated a reversible mechanochromic color change achieved by mechanical grinding (green to orange) and solvent adsorption (orange to green).

1. INTRODUCTION

Transition metal-based luminescent materials are a subject of rapidly growing interest in view of their applications for design and fabrication of solid-state lighting devices,1–7 in chemo-sensing,8–11 and as photocatalysts.12–15 Efficient room temperature (RT) phosphorescence of transition-metal species is conventionally attributed to the heavy atom effect that induces strong spin–orbit coupling, which facilitates both fast intersystem crossing and the formally spin-forbidden triplet radiative decay.16–19 The photophysical and photochemical properties of transition-metal species, particularly those of platinum(II), have been analyzed in a number of reviews.16,17,19–25

The luminescent properties of metal complex-based materials are closely associated with their molecular conformations and also with crystal packing determined in particular by intermolecular interactions;24–28 thus, different polymorphs of the same compound could exhibit different photophysical properties. The control over the formation of polymorphs is challenging because of the complexity of multiple molecule–molecule and molecule–solvent interactions that occurred on crystallization. In contrast to octahedral d6-RuII and d6-IrIII complexes, d6-PtII-based species usually adopt a square-planar coordination geometry with open axial coordination sites facilitating non-covalent binding to PtII centers. These non-covalent linkages can significantly alter both ground and excited-state properties of PtII-based systems and, hence, photophysical parameters.20,27–31

Thus, metallophilic interactions and intermolecular π-stacking strongly change the emission profile and shift the radiation to the red region, which can be explained by the change in the nature of the excited state from an MLCT to MMLCT.22–26 At the same time, aggregation due to other contacts, for example, halogen bonding or dπ3–π-hole interactions, as a rule does not lead to a change in the emission color but can be accompanied by an increase in the emission quantum yield (hereinafter abbreviated as EQY) of luminescence.37–40

Significant differences in the luminescence EQYs for polymorphs of platinum(II) complexes have been detected in only few cases.29,41,42 In two out of three reports, a polymorph exhibiting short Pt···Pt contacts displayed 2H and 12-fold29.
greater-phosphorescence EQYs than those measured for the other polymorph—without Pt···Pt metallicophilic interactions. In the third study, one out of three obtained polymorphs does not exhibit luminescence, while the other two emissive polymorphs exhibit a sixfold difference of their EQYs. The latter two polymorphs do not display Pt···Pt contacts and, as indicated by the original authors, “different quantum yields may be ascribed to the different local packings of the independent molecules in the polymorphs.”

In this study, the complexes [Pt(ppy)Cl(CNAr)] (ppy = 2-phenylpyridinato-C,2,N; Ar = C6H4-2-I, C6H4-4-I, C6H4-2-F-4-I, and C6H4-2-4-I) were crystallized under different conditions. In the case of 2, two polymorphic forms exhibiting a 24-fold difference in EQYs and also different emission profiles were obtained. We analyzed structure-directing non-covalent contacts by experimental and theoretical methods and hypothesized which intermolecular forces could lead to this polymorph-dependent phosphorescence. All our data are consequently detailed in the following sections.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Crystal Growth. Cyclometalated platinum(II) complexes bearing ancillary isocyanide ligands are promising candidates for optoelectronic applications since they exhibit strong RT phosphorescence in combination with useful properties such as thermal and chemical stability (for recent reports, see refs 43–46). Cyclometalated species 1–4 were prepared and isolated in moderate to high yields (61–94%) by the bridge-splitting reaction between the dimer [Pt(ppy)(μ-Cl)]2 and 2 equiv any one of the corresponding isocyanides: CNC6H4-2-X=4-X, X1 = H, F; I; X2 = H, I; reflux for 3 h in MeCN). The structures of 1–4 were confirmed by IR and 1H, 13C(1H), and 195Pt(1H) NMR spectroscopy, mass spectrometry, and single-crystal X-ray diffraction (XRD). For details, see Sections S3–S5.

Complexes 1–4 were crystallized under different conditions including solvent, temperature, and concentration variations (Experimental Section). In the case of 1, only one type of crystal was obtained, while the crystallization of 2–4 gave two polymorphs (denoted as 2-I and 3-II for 2 and 3, respectively) or a solvent-free form (4) and crystal solvate (4·CHCl3) of high quality and homogeneity; all these species were characterized by XRD (Section 2.2). We observed that all crystals (apart from orange polymorph 2II) are yellow, which is typical for [Pt(ppy)Cl(CNAr)]-type complexes.

2.2. Structure-Directing Non-covalent Interactions.

Inspection of the XRD data combined with the Hirshfeld surface analysis (for the Hirshfeld diagrams, see Section S6) revealed and visualized the structure-directing intermolecular non-covalent contacts such as C–I···Cl–Pt halogen bonding (abbreviated as HaB; found in all structures) and metallicophilic Pt···Pt interactions (observed exclusively for polymorph 2I).

Since polymorphs 2I and 2II exhibit different photophysical properties (Figure 2, detailed in Section 2.3), we attempted to highlight their structural features and speculate how they might be related to the different luminescent properties of the polymorphs.

The asymmetrical unit of 2I contains four crystallographically independent molecules in two conformations (two 2I-a and two 2I-b; Figure 3), which differ from each other by the orientation of the isocyanide aryl relatively the Pt coordination plane. For 2I-a, the isocyanide aryl group is almost coplanar with the Pt(C=N, C, Cl) plane (4.1(2)° for 2I-aI and 11.42(18)° for 2I-a2; Table S5.3), whereas in 2I-b the angle between the coordination plane (C=N, C, Cl) and the isocyanide aryl plane is much larger (55.29(17)° for 2I-b1 and 67.29(18)° for 2I-b2). The C–I···Cl–Pt HaBs (0.90–0.91 ΣvdW Bondi48 0.87–0.88 ΣvdW Alvarez49) is formed by the interaction between the σ(1)-hole of coplanar 2I-a and a Cl atom of twisted 2I-b. The Pt···I–C semicoodination bonds (1.01–1.03 ΣvdW Bondi48 0.87–0.88 ΣvdW Alvarez49) are formed by the interaction between the Pt atom of coplanar 2I-a and an electron belt of the I atom of another neighboring twisted 2I-b. Simultaneously, the twisted 2I-b is a face-to-face dimer that formally occurred by the symmetric C–I···I–C interaction between two arene iodine centers, and these contacts are attributed to type I halogen–halogen contact.

Table S6.2. Accordingly, the pair of C–I···Cl–Pt HaBs and the symmetric C–I···I–C short contact link two coplanar 2I-a and two twisted 2I-b to a tetrameric supramolecular architecture.

In contrast to 2I, the structure of 2II contains only one type of crystallographically independent planar molecule (the dihedral angle is 6.39(11)°), which is arranged in the helical chain held by HaB (Figure 4). In 2II, we observed short [3.2058(3) Å 0.93 ΣvdW Bondi48 0.70 ΣvdW Alvarez49] Pt···Pt separations between planes of 2I in the dimeric structure, which then forms the supramolecular double zigzag via the system of the HaB and Pt···Pt interactions.

The structures of 1, 3I, 3II, 4, and 4·CHCl3 contain one type of crystallographically independent complex, where an interplay between σ(1)-hole and a chloride accomplishes a head-to-tail supramolecular dimer (3I; Figure S9A), 1D supramolecular...
polymers with a 1D zigzag arrangement (1 and 4; Figure 5B), or a helical chain held by HaB (3II and 4·CHCl3; Figure 5C). These crystals display intermolecular Pt···Pt separations of >4.0 Å, which is significantly larger than the Bondi Pt + Pt van der Waals radius’s sum (3.44 Å), and this comparison indicates the absence of any meaningful contacts between two Pt centers. The structural features of these species are detailed in Section S6. Thus, the absence of metallophilic interactions in the structures of 1, 3I, 3II, 4, and 4·CHCl3 is their common feature, which is the same as that for the 2I polymorph.

2.3. Solid-State Luminescence Properties. 2.3.1. Solid-State Luminescence. In general, all our solid species are emissive materials (Table S7.1 and Figure 6), but efficiency of luminescence is different, particularly for polymorphs 2I and 2II. Yellow crystals of 2I and all crystalline forms of the other species, namely, 1, 3I, 3II, 4, and 4·CHCl3, exhibit a green emission ($\lambda_{\text{max}}$ of 509–522 nm; Figure 6) with very similar luminescence spectra profiles. The solid-state luminescence spectra of 1, 2I, 3I, 3II, 4, and 4·CHCl3 are similar to those observed for 1–4 in CH2Cl2 solutions (the photophysical properties in solution are detailed in Section S7), thus providing evidence favoring the absence of any metal···metal short contacts in all these structures.

In contrast to green-emissive yellow polymorph 2I ($\lambda_{\text{max}}$ of 522 nm; $\Phi_{\text{em}}$ of 0.5%), orange polymorph 2II displayed an unstructured band in the orange region ($\lambda_{\text{max}}$ 586 nm) with a 24-fold higher EQY ($\Phi_{\text{em}}$ of 12%). This strong 24-fold increase of the EQY in 2II compared to 2I is probably associated with an increase in structural rigidity upon the formation of a supramolecular double-zigzag due to the synergistic combination of HaB and Pt···Pt interactions (Figure 4). Note that, in this context, a few previous reports29,30 indicated an efficiency of solid-state luminescence for those polymorphs that exhibit Pt···Pt interactions, and EQY enhancement was attributed to “inhibition of the thermal dispersion of photoenergy from the excited state”32 or by “inhibition of vibrational quenching by the formation of the rigid dimer” 29.

2.3.2. Mechanochromic Behavior. Some phosphorescent PtI complexes could also display mechanochromic luminescence behavior (for relevant reviews, see refs 52 and 53). The luminescent mechanochromism was observed for all yellow crystals (namely, 1, 2I, 3I, 3II, 4, and 4·CHCl3), but it was not detected for orange crystals of 2II. Grinding of these yellow crystals results in their color change from yellow to orange; the color change is reversed on treatment with a solution or even vapors of CH2Cl2. Irradiation of the finely ground orange 1, 2I, 3I, 3II, 4, and 4·CHCl3 with 365 nm UV light leads to orange luminescence (564–601 nm; Figure 7.3 and Table S7.2), which is close to the emission profile of orange crystals of 2II ($\lambda_{\text{max}}$ of 586 nm). In contrast to 2I, grinding of orange crystals 2II in an agate mortar does not lead to any visible changes in the photoluminescence; ground powders of 2II display an identical emission with that of ground powder of 2I. In all cases, grinding led to a decrease in the luminescence emission quantum yields (Table S7.2).
The powder X-ray diffraction (PXRD) studies of finely ground \(2^I\) and \(2^\text{II}\) show only low-intensity diffraction peaks from the starting crystals, indicating the amorphization upon grinding (Figures S5.8 and S5.9). We assumed accordingly that the mechanochromism of \(2^I\) is based on crystalline-to-amorphous phase transitions. On grinding, the color and luminescence of \(2^\text{II}\) was not changed, although the PXRD data indicate the change from a crystalline state to an amorphous phase (Figure S5.9). The mechanical grinding-triggered luminescence switches of some solid platinum(II) complexes have previously been reported.\(^{46,54-59}\) In all these studies, a structure-less emissive band and red shift of the emissive maxima after grinding were assigned to the occurrence of emissive aggregates packed in close proximity through Pt···Pt and/or \(\pi\cdots\pi\) interactions. The mechanochromic luminescence of ground samples of \(1, 2^I, 3^I, 3^\text{II}, 4,\) and 4-CHCl\(_3\) exhibiting orange luminescence can be reversed either by addition to the ground powders of a few drops of CH\(_2\)Cl\(_2\) or by exposure to dichloromethane vapor; the reversible mechanochromic behavior, illustrated in Figure 7, is similar to that observed recently for the [Pt(ppy)Cl(CNC\(_6\)H\(_4\)-2,6-Me\(_2\))] complex.\(^{30}\)

Thus, we demonstrated that six \(1, 2^I, 3^I, 3^\text{II}, 4,\) and 4-CHCl\(_3\) out of seven studied structures exhibited similar green emission under 365 nm UV irradiation at RT, while only \(2^\text{II}\) is an orange emitter. The longer wavelength and the non-structured emission of \(2^\text{II}\) are consistent with low-lying spin-forbidden triplet metal–metal-to-ligand-charge transfer (\(^3\text{MMLCT}\)) transitions;\(^{60}\) these transitions are in agreement with the identified Pt···Pt short contact.

**2.4. Theoretical Studies of Non-covalent Interactions.**

It is undoubtedly attractive to associate the solid-state phosphorescence with the presence of a certain type (or certain system) of non-covalent interaction(s). However, by having only one example of differing photophysical properties of polymorphs, it is hardly possible to reveal the underlying factors of such distinct behavior. To reveal these factors, an extensive set of statistical data is needed, which, we hope, will be gradually accumulated in the literature.

At this stage, one can only examine the existing structure-determining interactions to simplify the analysis of polymorph-dependent phosphorescence for future relevant studies. Therefore, we left aside the puzzle of multiple hydrogen bonds—the fraction of which is significant in almost all organometallic systems—and focused on the study of halogen bonding and metallophilic interactions in the two polymorphs.
of 2. The Hirshfeld surface analysis (Section S6) indicates that these interactions, in addition to the hydrogen bond, greatly contribute to the stabilization of both crystal structures. An additional factor, which stimulated our interest in studying these types of intermolecular interactions, is based on the previous reports that verified the strong effect of HαB\textsuperscript{37–39} and metallophilic interactions\textsuperscript{33,35} on the photophysical characteristics of platinum(II) complexes (see the Introduction).

Several approaches, such as analysis of the molecular electrostatic potential (MEP),\textsuperscript{61−63} NCIplot\textsuperscript{64,65} analysis, combined electron localization function (ELF),\textsuperscript{66−68} and Bader’s quantum theory of atoms in molecules (QTAIM analysis),\textsuperscript{69} were applied to reveal structure-determining non-covalent interactions in the two phosphorescent polymorphs.

2.4.1. MEP Analysis. The MEP surfaces of all our structures were computed in order to study the most electron-poor and electron-rich regions of this molecules (Figure 8 and Figures S8.1 and S8.2). An analysis of the MEP surfaces reveals that the MEP maximum is located at the $\sigma$-hole of the I-substituent of arene from isocyanides (HαB donors), ranging from +27.6 to +32.6 kcal/mol. Notably, the value of the $\sigma$-hole in different conformers, that is, coplanar $2^1$–$a^1$ (+27.7 kcal/mol) and twisted $2^1$–$b^2$ (+27.6 kcal/mol) are slightly different, which indicates the little effect of conformation on the value of the $\sigma$-hole. The MEP minimum is located at the coordinated chloride in compounds 1–4, ranging from $-41.9$ to $-39.5$ kcal/mol. This result strongly agrees with the occurrence of HαBs in the solid state.

2.4.2. Combined QTAIM and NCIplot Analysis. We evaluated energetically the non-covalent interactions using DFT calculations and also characterized them by a combination of QTAIM and NCIplot analyses (Figure 9 and Figures S8.3–S8.12). In all model clusters, the non-covalent interactions are characterized by the $(3, -1)$ bond critical points (BCPs) and bond paths connecting the atoms. The QTAIM parameters at the bond CPs are gathered in Tables S8.1–S8.4.

2.4.3. Analysis of ELF and ED/ESP Minima. The philicities of non-covalently interacting partners can be determined by ELF projections with critical points and bond paths from a QTAIM electron density topology, which were drawn for both crystal and cluster models. For C–I–Cl–Pt interactions on ELF projections, the $I$–$\cdot$–$Cl$ bond paths go through the lone-pair orange areas of Cl with high ELF values and blue-ish areas with low ELF values around I corresponding to a $\sigma$-hole, which confirms the HαB nature of the discussed non-covalent interaction (Figure 10 and Figures S8.3–S8.12).\textsuperscript{72−75} The analysis of the 1D profiles of electron density (ED) and
electrostatic potential (ESP) functions along the I···Cl bond paths shows a clear shift of the ESP minimum toward the nucleophilic Cl atom, whereas the ED minimum shifts toward the electrophilic I atom in all cases (Figure 11 and Figures S8.3−S8.12). This data confirmed the nucleophilic nature of the chloride ligand and the electrophilic character of I centers of arene isocyanides.

In the structure of 2\textsuperscript{i}, the Pt···I bond path on the ELF projections passes through the area that corresponds to the region of lone electron pairs of the I atoms and through the area of Pt atoms with a smaller ELF value than that for the I atoms. Analysis of these values verified the nucleophilicity of the I atom toward the Pt center. Thus, the Pt atom functions as an electrophile, while the I center acts as a nucleophile, and consequently, the Pt···I interaction should be treated as the semicoordination.

ELF analysis indicated the nonpolar non-covalent nature of the I···I and Pt···Pt interactions. Further confirmation of the nonpolar nature of the metallophilic interactions is provided by the 1D profiles of the ED and ESP functions along the Pt···Pt bond paths where ED and ESP minima overlap in both cases (Figure 11).

3. CONCLUSIONS

In this study, we prepared four new cyclometalated platinum(II) complexes (1−4) whose solid-state luminescence depend on the aggregation motifs. Complex 2, which was crystallized in two polymorphic forms 2\textsuperscript{i} and 2\textsuperscript{II}, shows green and orange phosphorescence, respectively. The other studied solid luminophores, namely, 1, 3\textsuperscript{i}−3\textsuperscript{II}, 4, and 4·CHCl\textsubscript{3}, exhibit green luminescence. All yellow crystals (1, 2\textsuperscript{i}, 3\textsuperscript{i}−3\textsuperscript{II}, 4, and 4·CHCl\textsubscript{3}) demonstrated a reversible mechanochromic green-to-orange color change achieved by mechanical grinding (green-to-orange) and solvent adsorption (orange-to-green).

The most interesting finding of this work is that orange polymorph 2\textsuperscript{II} exhibits a significantly higher EQY (12%), while 2\textsuperscript{i} is a very weak emitter (0.5%). One of most significant differences in the structure-determining non-covalent interactions between the two polymorphs, that is 2\textsuperscript{i} and 2\textsuperscript{II}, is seen in the availability of Pt···Pt interactions in 2\textsuperscript{II} and absence of

Figure 10. ELF projections (contour lines with a 0.05 step), bond paths (white lines), zero-flux surface projections (black lines), bond CPs (blue dots), nuclear CPs (brown dots), and ring CPs (orange dots) for the I···Cl HaBs in 2\textsuperscript{i} (a) and 2\textsuperscript{II} (d); Pt···I semicoordination in 2\textsuperscript{i} (b); and I···I interactions in 2\textsuperscript{i} (c) and Pt···Pt interactions in 2\textsuperscript{II} (e) in the crystal (left) and cluster (right) models.

Figure 11. ED (black) vs ESP (red) minima along the bond paths for the I···Cl HaBs in 2\textsuperscript{i} (a) and 2\textsuperscript{II} (b), I···I interactions in 2\textsuperscript{i} (c), and Pt···Pt interactions in 2\textsuperscript{II} (d).
these metallophilic contacts in 2\textsuperscript{I}. Based on our data and previous observations,\textsuperscript{25,30,42} considered in the Introduction, we hypothesized that the 24-fold difference in the phosphorescence EQYS between polymorphs 2\textsuperscript{I} and 2\textsuperscript{II} could be related to the presence and absence of Pt···Pt interactions; these metallophilic interactions are accompanied by the reduction of vibrational relaxation due to the formation of a rigid supramolecular structure.

We hope that our results, in conjunction with relevant data of the other studies focused on packing effects in emission performance properties,\textsuperscript{36,40} add to the modulation of photophysical properties of organometallic luminescent materials by planned selection of non-covalent interactions.

4. EXPERIMENTAL SECTION

4.1. Materials and Instrumentation. For details, see Section S1. The latter includes the reagents and materials used, photophysical data, X-ray structure determination, and computation details.

4.2. Synthesis of 1–4. \([\{\text{Pt}([\text{ppy})_2(\mu-\text{Cl})]\}_2]\) (50 mg, 0.065 mmol) was suspended in MeCN (2 mL), whereupon a solution of isocyanide (0.130 mmol) in MeCN (2 mL) was added dropwise. The reaction mixture was refluxed at 90 \(\degree\)C for 3 h. During this period, the reaction mixture gradually turned from a yellow suspension to a light yellow solution (for 1–3) or a yellow suspension (for 4). After refluxing for 3 h followed by cooling to RT, Et\(_2\)O (3 mL) was added to the reaction mixture, and then it was left to stand without stirring for 3 days at RT. In each case, the formed solid was separated by centrifugation, washed with three 3 mL portions of Et\(_2\)O, and dried in air at RT. Complexes 1–4 are shelf-stable at RT; they are soluble in aprotic solvents such as CH\(_2\)Cl\(_2\) and CHCl\(_3\).

4.3. Characterization. Characterization and elemental analyses (C, H, and N), high-resolution ESI-MS, IR, and \(^1\)H, \(^13\)C(\(^{1}\)H), and \(^{199}\)Pt(\(^{1}\)H) NMR spectroscopy are included in Section S2.

4.4. Crystal Growth. Crystals of 1 were obtained by slow evaporation of its CH\(_2\)Cl\(_2\) solution at RT; they were also obtained by slow evaporation of their CHCl\(_3\), MeCN, or EtCN solutions at RT. Crystals of 2\textsuperscript{I} were obtained by slow evaporation of solution of 2 in CH\(_2\)Cl\(_2\) at RT. Crystals of 2\textsuperscript{II} were obtained by slow evaporation of solution of 2 in EtCN solutions at RT. Crystals of 3\textsuperscript{I} were obtained by slow evaporation of solution of 3 in MeCN at 60 \(\degree\)C. Crystals of 3\textsuperscript{II} were obtained by slow evaporation of solution of 2 in CH\(_2\)Cl\(_2\)/MeNO\(_2\) (3:1, v/v) solvent mixture at RT. Crystals of 4 were obtained by slow evaporation of solution of 4 in a CH\(_2\)Cl\(_2\)/hexane (3:1, v/v) solvent mixture at RT. Crystals of 4-CHCl\(_3\) were obtained by slow evaporation of a solution of 4 in CHCl\(_3\) at RT. Slow evaporation of solutions of 3 or 4 in EtCN gives only oily samples, and all our attempts to obtain crystals suitable for XRD studies failed.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c04110.

Experimental section and spectra, X-ray diffraction, and photophysical data, experimental data and structural-feature discussion, and theoretical calculations (PDF).

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Notes

The authors declare no competing financial interest.

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