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Acetylides With Aromatic Stacking**

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Turning on Solid-State Phosphorescence of Platinum Acetylides With Aromatic Stacking

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Neat solids that phosphoresce under ambient conditions are rare due to aggregation-caused quenching. This communication describes a platinum acetylide (PtPE) that phosphoresces as a solid due to programmed aromatic stacking interactions of pendant groups that prevent intermolecular aggregation.

Phosphorescent materials offer advantages in many optoelectronic applications.¹ In sensing, the long excited state lifetimes of phosphors present favorable kinetics for signal transduction events to modify triplet excited states.^{2–4} In electroluminescent devices, phosphors harness triplet excitons that comprise the majority of excited states generated upon electron-hole recombination.^{5–7} Organometallic phosphors containing iridium,⁸ rubidium,⁹ gold,^{10,11} and platinum¹² have figured prominently in photoluminescent and electroluminescent materials, as have metal-free phosphors that contain heavy atoms.^{13–15} However, quenching of long-lived triplet excited states often limits phosphorescence efficiency.¹⁶ Strategies to prevent quenching include exclusion of O₂ and encapsulation in glassy matrices.^{17–19} Neat, solid phosphors exacerbate this challenge as the resulting interchromophore interactions induce “aggregation-caused” quenching.

Numerous groups have reported molecules that show room-temperature phosphorescence (RTP). Su and coworkers demonstrated aggregation induced phosphorescent emission (AIPE) of cationic Ir(III) complexes,²⁰ while Zhao and coworkers observed similar phenomena in a series of Pt(II) complexes that

were non-emissive in solution, but strongly phosphorescent as crystals.²¹ While these findings indicate that molecular self-assembly can enable phosphorescence, the extent to which solid-state phosphorescence can be designed rationally using chemical structure remains unclear.

Platinum acetylides are important phosphors with structures analogous to metal-free organic phenylene-ethynylenes (PE).^{22–26} Although their simple architecture allows for tuning of their optoelectronic properties through changing either the PE backbone or dative ligands, their phosphorescence properties are highly susceptible to quenching in the solid state.^{27–29} To ameliorate this challenge of poor solid-state phosphorescence, several groups have used molecular “jackets” to prevent intermolecular aggregation and quenching of solid platinum acetylides. Building on the well-known poly(phenylene ethynylene) compounds of Yang and Swager,³⁰ Schanze and coworkers installed bulky pentiptycene groups into the backbone of a Pt-acetylide polymer to yield thin films with improved phosphorescence quantum yields.³¹ More recently, Masai and coworkers used cyclodextrin-based rotaxanes around linear Pt-acetylide polymers to prevent interchromophore stacking and preserve phosphorescence.³²

We have previously reported a strategy for controlling the luminescence of conjugated solids with PE linkages using discrete non-covalent interactions of pendant aromatic rings.^{33,34} In particular, the co-facial interactions of fluoroarene pendants with arenes of the PE chromophores can prevent aggregation and increase solid-state fluorescence.³⁵ In addition, these intramolecular interactions twist the PE backbones out of planarity (torsional angles 55–85°). As a result, these specific and tunable stacking interactions between fluoroaromatic pendants and main chain arenes prevent both the bathochromic shifting and the quenching that often characterizes solid phenylene-ethynylene solids. Our objective in this study, was to determine if this design motif, combining intermolecular and intramolecular fluoroarene-arene stacking could program solid-state phosphorescence in otherwise non-emissive materials by preventing intermolecular aggregation.

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† Electronic Supplementary Information (ESI) available: Details regarding synthesis, characterization, optical spectroscopy, and X-ray crystallography (PDF). Crystallographic information files for the four single crystal X-ray structures discussed (CIF). See DOI:

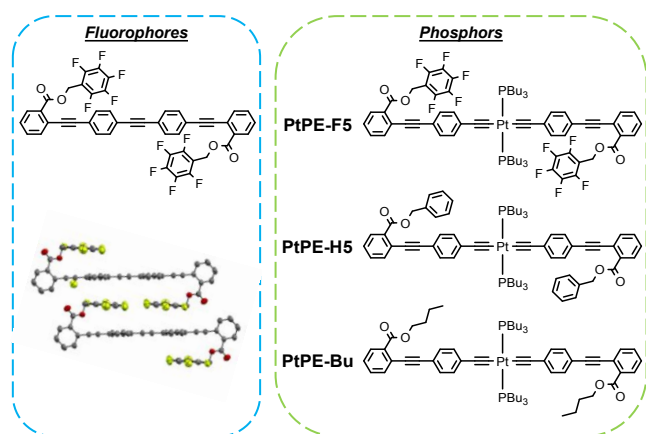


Figure 1: Prior fluorophore design and current phosphor design.

We tested our strategy by comparing the optical properties of three PtPE analogs. The chemical structures of the π -conjugated “main chains” of these complexes are identical, comprising a tetracoordinated Pt(II) center bound to two diphenylacetylenes in *trans* stereochemistry, with two tri-*n*-butylphosphines occupying the remainder of the square planar environment. The terminal conjugated arenes bear *ortho* benzoate esters, the alkoxy groups of which are the only differences between these three structures, as either *n*-butyl esters (**Pt-Bu**), benzyl esters (**Pt-H5**), or pentafluorobenzyl esters (**Pt-F5**) (Figure 1). Our preparation of these three complexes (see ESI) followed literature precedent³⁶: Acylation of 2-iodobenzoic acid produced the target benzoate esters, which we further elaborated with two successive Sonogashira cross-coupling/deprotection reaction sequences to yield the terminal alkyne ligands. Coupling between these alkynes and dichlorobis(tri-*n*-butylphosphine)platinum afforded the targets.

Given that the pendants of these molecules are not formally conjugated with the chromophore backbone, we predicted that their optical properties would resemble each other and previously reported analogs.^{17,37,38} The absorbance and emission spectra of these complexes in chloroform conform to this expectation (Figure 2). The absorbance spectra of these three complexes comprise a broad band ($\lambda_{\text{max}} = 375$ nm) with similar extinction coefficients. Under ambient conditions, solutions of these complexes have quantum yields $\Phi_{\text{em}} \leq 0.01$,

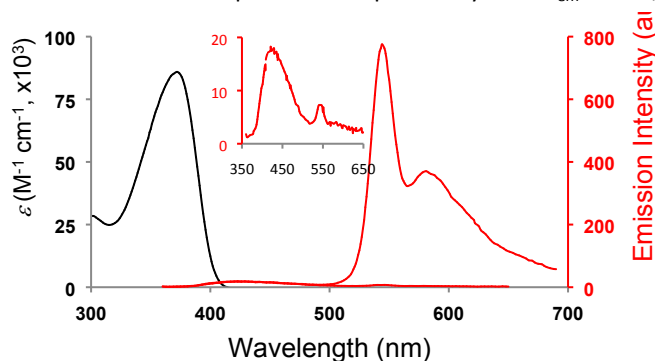


Figure 2: Absorbance (black, solid), and emission spectra in aereated (red, dashed), and deoxygenated solution (red, solid) of PtPE-F5.

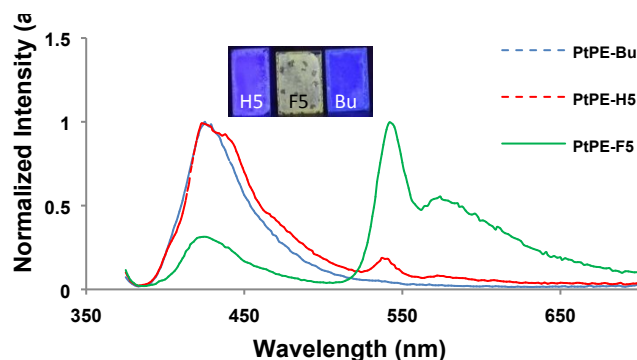


Figure 3: Emission spectra of neat PtPE films. The inset photograph shows the films themselves upon excitation with 365nm light.

with a dominant band at 390 nm and a much smaller peak at 540 nm. Deoxygenation of these solutions increases Φ_{em} at 540 nm dramatically to 0.10-0.15. The emission at 540 nm also dominates the emission spectra of any of these complexes when doped into a thin film of poly(methyl methacrylate), PMMA (see ESI). We estimated the energy levels of the S^1 and T^1 states to be 2.95 eV and 2.30 eV, respectively, from the fluorescence and phosphorescence maxima of these compounds. Time-resolved emission spectroscopy shows that the lifetime of the emission at 540 nm in PMMA is 2.9-3.6 μs . Altogether, these observations support assigning this yellow emission at 540 nm to phosphorescence enabled by the efficient spin-orbit coupling of platinum.

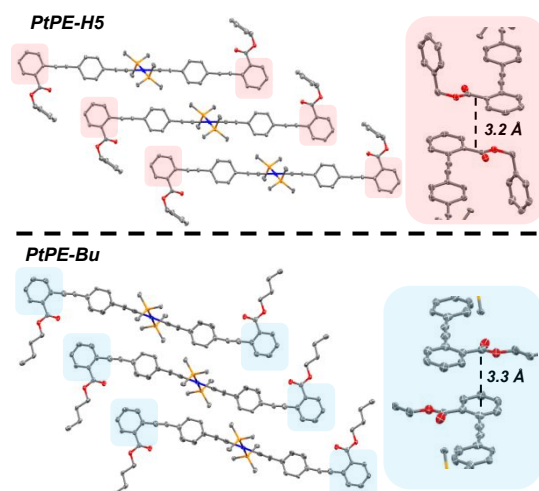


Figure 4: Crystal packing of PtPE-H5 (top) and PtPE-Bu (bottom). Shaded boxes highlight cofacial stacking in each structure. Interchromophore distances are given. Phosphine groups are truncated and hydrogen atoms are omitted for clarity; thermal ellipsoids are shown at 50% probability.

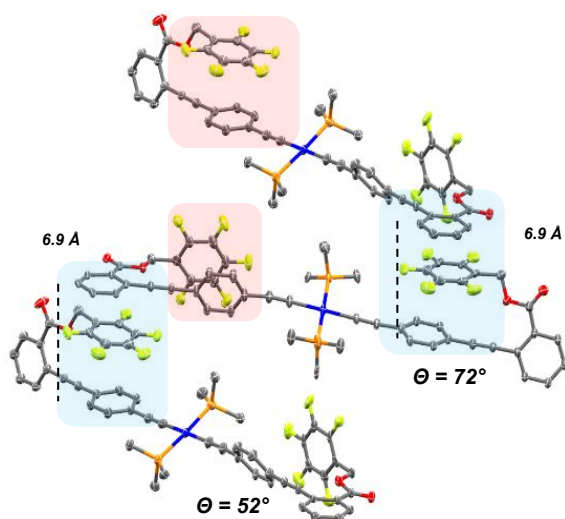


Figure 5: PtPE-F5 polymorph G, with boxes highlighting intramolecular (red) and intermolecular stacking (blue). θ represents torsional angle between adjacent arene rings in the backbone. Interchromophore distances are given. Phosphine ligands are truncated and hydrogen atoms are omitted for clarity; thermal ellipsoids are shown at 50% probability.

Unlike their behavior in degassed fluid solution or rigid matrices, neat solid films of these three complexes display dramatically different luminescence. Emission at 420 nm dominates the spectra of neat films of **PtPE-Bu** and **PtPE-H5** (Figure 3). As is typical, we attributed the lack of competitive phosphorescence in these solids, especially in contrast to their behavior in fluid or solid solution, to aggregation-caused quenching. In contrast, neat films of **PtPE-F5** display dual emission, with phosphorescence at 540 nm outcompeting fluorescence at 420 nm by a 4:1 ratio. We measured the solid state quantum yields of PtPE-F5, PtPE-H5, and PtPE-Bu as powders to be .01, \leq .01, and .01, respectively. While the quantum yield of PtPE-F5 is low, the emission spectrum is dominated by 540 nm phosphorescence, which is absent in the other compounds. **PtPE-Bu** and **PtPE-H5** remain fluorescent under a nitrogen atmosphere, indicating that aggregation itself plays a more vital role than oxygen in quenching of phosphorescence in the control complexes (ESI). Time-resolved luminescence of neat **PtPE-F5** films (average lifetime of 4.5 μ s at 540 nm) further supports assigning its yellow emission to phosphorescence. Doping phosphors into rigid polymer matrices allows for observation of phosphorescence by minimizing non-radiative decay through aggregation and oxygen quenching. Our results suggest that the perfluorinated ester pendants of **PtPE-F5** in part accomplish these same objectives, as it is the only neat complex for which phosphorescence dominates under ambient conditions

We therefore determined single crystal X-ray structures of each complex to understand how the different ester alkoxy substituents influence the conformations and packing of the platinum acetylide chromophores. Colorless prisms of **PtPE-H5** and **PtPE-Bu** grew by slow diffusion of hexanes into a solution of each compound in chloroform. As expected, based on the similarity of their optical spectra and appearance of their single crystals, the crystal structures of **PtPE-H5** and **PtPE-Bu** share

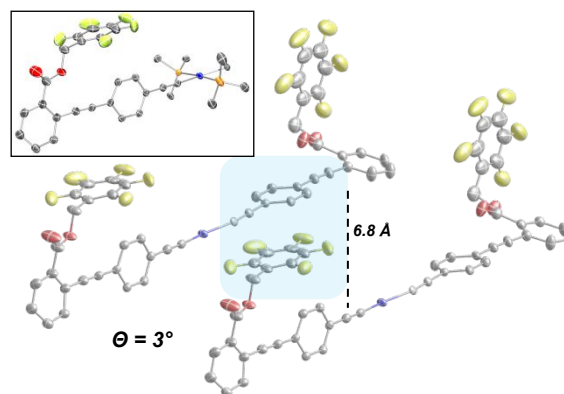


Figure 6: PtPE-F5 polymorph Y, with blue boxes highlighting intermolecular stacking. θ represents torsional angle between adjacent arene rings in the backbone. Interchromophore distances are given. Inset shows positioning of phosphines (truncated). Hydrogen atoms are omitted for clarity; thermal ellipsoids are shown at 50% probability.

some key features (Figure 4). Each of the molecules has nearly planar PE backbones, with torsional angles between all chromophore rings less than 8° . The *n*-butyl phosphine ligands of both molecules lie perpendicular to the faces of the rings in the PE backbones. Moreover, neither the *n*-butyl nor the benzyl pendants interact directly with other parts of the same molecule to which they are attached. The butyl ester substituent of **PtPE-Bu** shows no notable intermolecular interactions, while the phenyl substituents of **PtPE-H5** participate in intermolecular edge-face interactions with the inner conjugated arenes of neighboring molecules. The most striking feature of both structures are head-to-tail cofacial stacking interactions between the terminal arenes of the phenylacetylene ligands, which yield C...C distances as close as 3.2 Å. We conclude that this cofacial arrangement of the chromophores facilitates intermolecular electronic coupling, which can lead to non-radiative decay of excited triplet states. Among other potential quenching mechanisms, one possibly would be triplet-triplet annihilation, supported by our estimation of the energy levels of the S^1 and T^1 states.³⁹

Slow evaporation of a concentrated acetone solution of **PtPE-F5** gave green-emitting polymorph **G** (emission onset 480 nm), while slow diffusion of hexanes into a chloroform solution gave polymorph **Y** (emission onset 510 nm). The visual appearance and spectrum of emission of polymorph **Y** resembles more closely those of the solution-cast thin films, although green-emitting domains also appear in thin films. In contrast to **PtPE-H5** and **PtPE-Bu**, non-covalent interactions of the perfluorinated pendants in both polymorphs of **PtPE-F5** prevent inter-chromophore aggregation. Polymorph **G** (Figure 5) shows each of the fluorinated arenes stack intramolecularly with the phenylene rings closest to platinum, with inter-ring distances of 3.5 Å. As we have observed previously in organic PEs, these interactions twist all PE linkages with 50° - 80° torsional angles between the inner and outer conjugated rings. This twisting reduces intramolecular electronic coupling and shifts the phosphorescence (see ESI for spectra) of polymorph **G** from polymorph **Y** hypsochromically. In addition, both fluorinated rings of polymorph **G** interact cofacially with

terminal rings on nearby molecules and prevent interchromophore aggregation. The fluorinated pendants of polymorph **Y** also prevent interchromophore aggregation, with one ArF ring stacking with the inner ring of an adjacent molecule, separating the chromophores by 6.8 Å (Figure 6), and the second generating a repeating column of ArF-ArH stacking interactions that insulate each platinum acetylide chromophore. The positions of the n-butyl phosphine ligands of both polymorphs lie in similar perpendicular arrangements as our control complexes, indicating little impact on the solid state emission. Therefore, the proclivity of ArF rings to stack cofacially with other arenes, prevents interchromophore aggregation and preserves phosphorescence as the dominant mode of radiative decay of **PtPE-F5** solids.

We also measured the electroluminescence of these compounds as neat films using simple devices (ITO/PEDOT:PSS/**PtPE**/TPBi/Ca/Ag, see ESI for details). These devices all showed electroluminescence matching the PL spectrum of a neat **PtPE-F5** film at 540 nm, even though the films of **PtPE-Bu** and **PtPE-H5** show nearly only fluorescent PL. This result suggests that under the aggressive operating conditions required to observe luminescence, EL may not come from the bulk, but an interfacial region, or alternatively creation of a energy band level alignment that readily forms triplet excitons on the PtPE molecules.

In conclusion, phosphorescence dominates the photoluminescence of solid-state **PtPE-F5**, while fluorescence dominates the emission of solid **PtPE-H5** and **PtPE-Bu**. Cofacial interactions between perfluorinated arene pendants and main chain PE rings prevent aggregation. We conclude that ArF-ArH interactions enable solid state phosphorescence by insulating the chromophores from aggregation. This work impacts optoelectronics by demonstrating that specific interactions of pendant groups, which are often a design afterthought, can enable technologically critical solid-state phosphorescence.

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