Solid–Solid Phase Transitions in [trans-Pt(PMe₃)₂(C \equiv CC₆H₄R)₂]-Containing Materials (R = O(CH₂)_nH; n = 6, 9, 12, and 15)

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S Supporting Information

ABSTRACT: The title complexes were prepared in Hagihara conditions and were investigated by single crystal X-ray crystallography (n = 6, [Pt]C₆; n = 12, [Pt]C₁₂), X-ray powder diffraction (powder XRD), differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA, $[Pt]C_{12}$), and steady-state and time-resolved solid state UV-vis and emission spectroscopy at 298 and 77 K. [Pt]C₆ complex exhibits no phase change with the temperature. Concurrently, $[Pt]C_9$ (n = 9) and $[Pt]C_{12}$ complexes exhibit an irreversible T_{endo} values of 104 and 119 °C, respectively, associated with a thermal annealing. Finally, $[Pt]C_{15}$ (n = 15) complex exhibit a reversible thermal processes with a large hysteresis ($T_{endo} = 126$ °C, $T_{\text{exo}} = 140 \text{ °C}$) followed by a glass transition ($T_{\text{endo}} = 146 \text{ °C}$, $T_{\text{exo}} = 69 \text{ °C}$) as depicted by DSC. These phase changes are accompanied by a decrease in triplet excited state lifetimes upon cycling the sample temperature over and under the transition temperatures. These various thermal processes induce a



significant decrease in emission lifetimes, strongly suggesting the presence of a reorganization of the complexes in the solid state favoring more chain-chromophore contacts, thus promoting nonradiative "knocking" processes.

INTRODUCTION

The trans-bis(ethynylbenzene)bis(trialkylphosphine)platinum-(II) species ([Pt]; alkyl = Me, Et, Bu) are chromophores exhibiting nonlinear optic properties 1 and photonic $\hat{d}\text{evices}$ such as light-emitting diodes² and solar cells³ have also been reported. Concurrently in the field of metallo-mesogens, Pt(II) complexes exhibiting liquid crystal properties are numerous, and can be divided into three distinct categories; *ortho*-metalated,⁵ diimines,⁶ and [Pt].^{7,8} In the last category of metallo-mesogens, only one report indicated the presence of luminescence. Indeed, Cooper et al. prepared two emissive complexes with $P(n-C_8H_{17})_3$ (instead of PMe₃) and R = H and $C \equiv CC_6H_5$ (referring to the title complex [trans-Pt- $(PMe_3)_2(C \equiv CC_6H_4R)_2]$) as viscous liquids at 298 K but could transform into a glass phase upon cooling.⁹ Taking into account the rich photophysical properties of the [Pt] species and the paucity of metalogen properties, it became appropriate to further explore this category of materials. The obvious structural modification is anchoring of long carbon chains on the ethynylbenzene groups. We now report the preparation and characterization of four luminescent X-[Pt]-X complexes where $X = O(CH_2)_n H$ (*n* = 6 ([Pt]C₆), 9 ([Pt]C₉), 12 $([Pt]C_{12})$, and 15 $([Pt]C_{15})$; Chart 1), but no glass transition nor the presence of liquid crystals were observed. However, $[Pt]C_{9}$, $[Pt]C_{12}$, and $[Pt]C_{15}$ complexes exhibit irreversible solid-solid phase transitions above room temperature, which are accompanied by changes in X-ray powder diffraction patterns and photophysical properties. Concurrently, these



$$H(CH_{2})_{n}O - \swarrow Pt - O(CH_{2})_{n}H$$

latter measurements allowed for monitoring of the change in Pt…Pt separations and the relative density of the materials exceeding and returning to the transition temperature. The possible presence of Pt…Pt interactions may generate new excited states of the ${}^{1,3}[d\sigma^*p\sigma]^*$ type when the Pt…Pt separation is short enough (typically below the sum of the van der Waals radii).¹⁰ These emissive states generally exhibit red-shifted and unstructured emission bands.

RESULTS AND DISCUSSION

Synthesis and X-ray Structures. The complexes were synthesized according to well-established procedures under Hagihara conditions¹¹ (Scheme 1; see Scheme S1 for the chemical intermediates). The trans-geometry was confirmed from the ${}^{1}J({}^{31}P-{}^{195}Pt)$ coupling constants^{[2} (Experimental Section), and the X-ray structures for $[Pt]C_{6}$ and $[Pt]C_{12}$ (Figures 1 and 2; see crystallographic data in Table S1). The ¹H and ³¹P NMR, and IR spectra and mass spectrograms of the complexes and intermediates are placed in Figures S1-S36.

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Scheme 1. Synthesis Route for $[Pt]C_{6}$, $[Pt]C_{9}$, $[Pt]C_{12}$, and $[Pt]C_{15}$ (n = 6, 9, 12, and 15)





Figure 1. Top: crystal packing of $[Pt]C_6$ at 172 K. Bottom: space filling model of two neighboring $[Pt]C_6$ complexes in the crystal.



Figure 2. Top: crystal packing of $[Pt]C_{12}$ at 296 K. Bottom: spacefilling model of two neighboring $[Pt]C_{12}$ complexes in the crystal. Note the presence of static disorders of the last three carbons of the C_{12} -chains in the bottom complex.

The X-ray powder diffraction patterns present well-defined diffraction peaks in all cases indicating the presence of a crystalline phase (Figures S37 and 38). The crystal structures for $[Pt]C_6$ and $[Pt]C_{12}$ (Figures 1 and 2) differ in the packing of the long alkyl chains. In the former crystal, one centro-symmetric independent molecule per unit cell is identified (Table S1; relevant structural parameters are placed in Table 1. An exhaustive comparison of all [Pt]-complexes from the literature are also placed in Figure S39 and Table S2.

The dihedral angle made by the C_6H_4 groups and the central square planar PtP₂C₄ unit, θ , is 7.9° and the $\angle C \equiv C-C$ bond angle is 177.0°, indicating that the complex is slightly distorted from an idealized geometry. The C_6H_4 planes are parallel to each other and the resulting interplanar C_6H_4 ... C_6H_4 distance, d, is 0.5 Å. Note that both parameters are identical for both halves. These X-ray data suggest that [**Pt**]**C**₆ is qualitatively a

Table 1. Interplanar C_6H_4 ··· C_6H_4 Distances (d), $\angle C-C \equiv C$, and θ angles for *trans*-Pt(PMe_3)₂(C $\equiv CC_6H_4R)_2$



| d (Å) | ∠C−C≡C (deg) | θ (deg) | R | temp. |
|-------|--------------|----------------|--------------------------|---------------------|
| 0.5 | 177.0 | 7.9 | $O(CH_2)_6H$ | 172 K |
| 0.3 | 179.3 | 28.5 | $O(CH_2)_{12}H$ (mol. 1) | 173 K |
| 0.2 | 177.9 | 26.9 | $O(CH_2)_{12}H$ (mol. 2) | 173 K |
| 0.4 | 177.8 | 28.4 | $O(CH_2)_{12}H$ (mol. 1) | 296 K |
| 0.3 | 178.7 | 29.0 | $O(CH_2)_{12}H$ (mol. 2) | 296 K |
| 0.9 | 176.1 | 30.2 | SCH ₃ | 173 K ¹³ |
| 0.5 | 175.3 | 33.7 | CH ₃ | 120 K ¹⁴ |
| | | | | |

quasi-planar complex but differs significantly from other related complexes reported in this work and from the literature^{13,14} (Table 1). This comparison has a direct consequence on the resulting photophysical properties (described below) as demonstrated in a recent detailed study on related [Pt] complexes.¹⁵ Indeed, the resulting emission lifetimes for this type of complex is found to be a function of its structural parameters and its environment. The $n-(CH_2)_6H$ chains adopt the classic zigzag geometry and the $HC^{--}C-O-CH_2$ skeleton sits on the same plane. The angle formed by the $n-(CH_2)_6H$ chains and $C_6H_4C\equiv C-Pt-C\equiv CC_6H_4$ axis is ~128°, and the three fragments together form a Z-shaped molecule in the crystal. An examination of the crystal packing indicates the presence of close PMe₃...PMe₃ contacts (Figure 1). The adopted Z-shape of $[Pt]C_6$ complex and the presence of obvious PMe3....PMe3 contacts promote tight interlocking interactions preventing any easy sliding of the molecules upon heating (see the thermal behavior below). Moreover, this steric situation may also speculatively correlate with the lower dihedral angle θ .

Complex $[Pt]C_{12}$ exhibits two crystallographically independent molecules per unit cell. The crystal packing also differs from that of $[Pt]C_6$ by the obvious $(CH_2)_{12}H$ chain…chain contacts (Figure 2, top). Some static disorders are also depicted for the last three carbon atoms of the $(CH_2)_{12}H$ chains for one of the two molecules, hence illustrating some chain mobility. The dihedral angle, θ , and $\angle C \equiv C - C$ angles are in the vicinity of $\sim 28 \pm 1^{\circ}$ and $\sim 178 \pm 1^{\circ}$, respectively, and are both temperature-independent between 173 and 296 K (Table 1). These X-ray structural parameters (i.e., θ and $\angle C \equiv$ C-C angles) compare well with those reported for other related trans-Pt(PMe₃)₂(C \equiv CC₆H₄R)₂ complexes where R = alkyl chain (Table 1).^{13,14} The interplanar $C_6H_4\cdots C_6H_4$ distance, d, increases slightly by ~ 0.1 Å going from 173 to 296 K witnessing a slight thermally induced distortion. These distortions stem from the C_6H_4 ...PMe₃ contacts (Figure 2, bottom). Indeed, as the Pt-P bonds vibrate with higher amplitude upon warming, the PMe3 collides with the neighboring C_6H_4 aromatic, thus inducing a slight displacement of the latter in the lattice. This structural trait is also apparent for $[Pt]C_6$ (Figure 1, bottom), but the d value is more pronounced ($d \sim 0.5$ Å) than that of [Pt]C₁₂ (0.2–0.3 Å) at the same temperature (172–173 K).

Thermogravimetric Analysis. The TGA trace was examined for $[Pt]C_{12}$ under an argon atmosphere (Figure S40). The first weight loss associated with a decomposition of the complex occurs near 200 °C. The weight loss continues until the next pseudo plateau at ~300 °C corresponding to a loss of ~14%, which can be attributed to the loss of one PMe₃ ligand (theory = 12%). This is convenient since any decomposition of the samples upon thermal treatment can readily be detected by ³¹P NMR. Upon further heating, another weight loss (of ~38%) occurs and a plateau at 600 °C is depicted corresponding to the two $(CH_2)_{12}H$ chains (theory = 37%). Because the PMe₃ ligand is common to all four complexes, the decomposition temperature is assumed to be about the same (i.e., ~ 200 °C). In light of the thermal decomposition evidenced in the DSC traces, X-ray powder diffraction, and photophysical measurements, the complexes were never exposed to temperatures exceeding 150 °C (except for one case, [Pt]C₉, 175 °C). The structural integrity of the compounds was demonstrated by measuring the ³¹P NMR spectra of the complexes in solution before and after the thermal treatment in the solid state. These spectra are placed in Figures S14, S15, S17-S20, S22, and S23.

Differential Scanning Calorimetry and Powder X-ray Diffraction. The DSC traces of $[Pt]C_6$ exhibit no phase change between 22 and 150 °C. Thus, this material can then serve as a comparison. Concurrently, $[Pt]C_9$ and $[Pt]C_{12}$ exhibit irreversible thermal processes in the 100–120 °C range (Figure 3). Conversely, $[Pt]C_{15}$ shows two reversible



Figure 3. DSC traces of $[Pt]C_{6'}$ $[Pt]C_{9'}$ $[Pt]C_{12'}$ and $[Pt]C_{15}$, in the 20–150 °C range. Scan rate = 10 °C/min. The values in parentheses are the area under the peaks.

thermal processes in the 50–150 °C range (Figure 3). None of these phase changes are due to a melting process, as evidenced by the powder XRD patterns, which indicate the presence of crystalline phases below and above the transition temperatures (Figure 4). [Pt]C₉ and [Pt]C₁₂ exhibit irreversible endothermic processes at 104 and 119 °C, respectively, similar to an annealing process where as for the second scan and the subsequent scans, no thermal behavior is depicted (endo or exo).

The powder XRD patterns for $[Pt]C_9$ and $[Pt]C_{12}$ below and above this transition indicate a phase change going to and



Figure 4. Comparison of the powder XRD patterns for $[Pt]C_9$ and $[Pt]C_{12}$ at below and above the irreversible solid—solid phase change. For $[Pt]C_9$, the 2θ peak is the 001 plane.

from crystalline phases. Interestingly for [**Pt**]**C**₉, the diffraction peak at $2\theta = 4.28^{\circ}$ (interplanar distance, d = 20.63 Å) at 25 °C shifts to 4.14° (d = 21.33 Å) at 120 °C, consistent with a lattice expansion with the temperature.

The monotonic evolution of 2θ (5.80 \rightarrow 5.51 \rightarrow 5.36°; 100 plane) and $d (15.23 \rightarrow 16.00 \rightarrow 16.47 \text{ Å})$ with the temperature (-100 (temperature at which the structure was determined)) $\rightarrow 20 \rightarrow 120$ °C) for [Pt]C₆, a compound where no phase change was observed, is very similar. However, for $[Pt]C_9$, the peak at $2\theta = 4.14^{\circ}$ (d = 21.33 Å) becomes very small and is replaced by a much stronger peak at $2\theta = 4.94^{\circ}$ corresponding to d = 17.87 Å. In a similar manner, 2θ (3.82 \rightarrow 3.74 \rightarrow 3.66° (weak shoulder)) and d (23.11 \rightarrow 23.61 \rightarrow 24.12 Å; 001 plane) exhibit the expected behavior associated with a thermal expansion for $[Pt]C_{12}$ (T = 25 (one temperature at which the structure was determined), 120, and 130 °C, respectively). At the phase transition, a strong new scattering appears at 4.04° (d = 21.85 Å). This decrease in interplanar distance of 3.46 (from 21.33 to 17.87 Å) for [Pt]C₉ and 2.27 Å (from 24.12 to 21.85 Å) for $[Pt]C_{12}$ for their irreversible endothermic process is also consistent with an annealing behavior leading to the formation of a polymorph. The fact that the strongest scattering of the low-temperature phase is still observed in the high temperature phase may be indicative of a slow kinetic conversion. In these cases, this situation provided information on the change in interplanar distances for these two compounds.

Moreover, upon increasing the temperature, the DSC trace for $[Pt]C_{15}$ exhibits two endothermic processes at 126 and 146 °C, appearing as a sharp and a broad peak, respectively, during the first scan. On the return scan, a sharp exothermic peak is recorded at 141 °C, and upon the second cycle another broad one at 69 °C appears. The cycling permits observation of a shift of the first endothermic signal from 126 to 123 °C, whereas the second one remained at 146 °C. Multiple subsequent cyclings do not induce any major progression of the overall shape of the DSC traces and the peak positions (see Supporting Information). The powder XRD patterns were measured before and after these phase transformation (Figure 5).

The patterns at 40, 100, and 135 °C exhibits well-resolved scattering peaks indicating the presence of crystalline phases.



Figure 5. Comparison of the powder XRD patterns for $[Pt]C_{15}$ at selected temperatures between the phase change temperatures.

However, at 155 °C, a large hollow under the sharp signals appears and indicates the presence of an amorphous phase. These measurements allow for an interpretation of the thermal behaviors. The sharp signals with a small hysteresis at T = 123(endo) and 140 °C (exo) is a first-order solid-solid phase transition between two ordered lattices. The broad signal at 146 °C is an order-disorder phase change with a recrystallization at 69 °C (exo). At 40 °C, two scatterings at $2\theta = 3.28$ and 3.70° are evident (d = 26.91 and 23.86 Å, respectively), but the former becomes dominant at 100 $^{\circ}$ C (2 θ = 3.30° and 3.68° ; d = 26.75 and 23.99 Å), and unique at 135 °C ($2\theta = 3.60^{\circ}$; d = 24.52 Å). At 155 °C, only the peak at 3.50° (d = 25.22 Å) is observable. Conclusively, upon the synthesis of $[Pt]C_{15}$ (after purification by column chromatography and solvent evaporation) two crystal lattices are generated. However, upon thermal treatment, one of them $(2\theta = 3.70^{\circ} \text{ at } 40^{\circ} \text{C})$ disappears, while the other one remains with its characteristic thermal behavior (cycle 2 in Figure 3; see Figure S41 for the subsequent cycles). The data before and after thermal annealing of $[Pt]C_{15}$ for 2 h are very different. Interestingly, the patterns after thermal annealing exhibit some striking similarities with those from before $[Pt]C_{12}$ annealing (Figure 6). This comparison is suggestive of isostructurality with the expected difference that the interplanar distances are anticipated to be longer for $[Pt]C_{15}$.

Emission Spectra and Lifetime. trans-Pt(PR₃)₂(C \equiv CC₆H₄)₂ chromophore, [Pt], is well-known to be emissive from its lowest-energy triplet state, which is best described as mostly $\pi\pi^*$ excited state, mixed with a metal-to-ligand charge transfer contribution (see ref 15, its corresponding Supporting Information, and the references therein). Typical emission spectra of the complexes, here [Pt]C₆, under various conditions are presented in Figure 7, whereas the spectra for the other complexes are placed in Figures S42–S57. The characteristic phosphorescence band of the *trans*-Pt-(PR₃)₂(C \equiv CC₆H₄)₂ chromophore¹⁶ is readily observed in the 420–600 nm window in four experimental conditions.

At 298 K in 2MeTHF solution, only a weak fluorescence band at ~365 nm is observed with a fluorescence lifetime, $\tau_{\rm F}$, <90 ps (note that the fwhm of the nanoLED laser is ~90 ps). This fluorescence may also be accompanied by a very weak



Figure 6. Left: comparison of the powder XRD patterns of $[Pt]C_{15}$ at 25 °C before and after ($2\theta = 3.36^\circ$, d = 26.27 Å) keeping the solid at 120 °C for 2 h. Right: comparison of the powder XRD pattern of $[Pt]C_{12}$ at 25 °C after keeping the solid at 120 °C for 2 h with that of $[Pt]C_{15}$ at 25 °C before thermal annealing. Note that the $[Pt]C_{15}$ sample exhibits a different pattern from that shown in Figure 5 stressing the presence of multiple phases after synthesis (and quick precipitation) but is reminiscent of the one recorded at 100 °C at the early stage of the thermal annealing of this sample.

phosphorescence. If the phosphorescence is present, then $\tau_{\rm P}$ < 1 μ s (i.e., within the pulse width of the flash lamp). The fluorescence turns out to be either absent or too weak to be investigated in the solid state (i.e., at 298 and 77 K) and in 2MeTHF solution at 77 K, so only the phosphorescence is studied. During the course of this investigation, the intensity of the excitation light was varied (using neutral density filters), and the observed emission intensity was linear with that of the excitation. In parallel, the emission lifetimes and their relative contributions (described below) remained constant. These tests indicate that under the irradiation conditions used no triplet-triplet annihilation nor photoinduced decomposition takes place. Interestingly, these emissions exhibit multiple phosphorescence lifetimes, τ_p (Tables 2 and 3). The presence of multiple components in the emission decays (i.e., mostly two or three in these cases) is not unprecedented.^{15,17} Various origins of these multiple emissive "species" have been suggested (i.e., O2-quenching,^{17a} two conformers)^{15,17c} but is often not discussed or assessed in detail.

In a recent an detailed investigation on related complexes, it was unambiguously demonstrated that these complexes give rise to multiexponential decays in the solid state and in glassy matices.¹⁵ The reason for this is that depending on the structural distortion (i.e., different θ and $\angle C \equiv C-C$ angles) and the crystal sites (i.e., complexes located at the surfaces versus inside the bulk or unit cells exhibiting two crystallographycally independent molecules with their own θ and $\angle C \equiv C-C$ bond angles) specific emission lifetime are prone to appear for each situation. Since the thermal treatment induces changes in the lattice, then changes in θ and $\angle C \equiv C-C$ angles are expected, and consequently, changes in emission lifetimes are also anticipated. In Table 2, several thermal cycles (from 2 to 4) were performed, but for convenience, only the last one is provided where there are no further changes.

In this work, it became apparent from Table 1 that the dihedral angle made by the C₆H₄ groups and the central square planar PtP₂C₄ unit, θ , can adopt various values from 7 to 33°, and multiple crystalline and amorphous phases exist, so various sites can induce such a behavior. Interestingly, a literature survey on $[trans-Pt(PR_3)_2(C \equiv CC_6H_4X)_2]$ (R = Me, Et, Bu; X = various groups) complexes and analogues indicates that θ can also be highly variable (6° < θ < 89°; 37 entries, see the Supporting Information for details). We also propose that the



Figure 7. Absorption (black), emission (red), and excitation (blue) spectra of $[Pt]C_6$ in the solid state or in 2MeTHF. The signals at ~370 and ~450 nm are fluorescence and phosphorescence, respectively.

| Table 2. Emission | Lifetimes | at 298 | K in t | the | Solid | State | upon |
|-------------------|-----------------|--------|--------|-----|-------|-------|------|
| Thermal Treatmen | nt ^a | | | | | | |

| | [Pt] | C ₆ | | [Pt]C ₉ | | | | |
|----------|----------------------|-----------------|----------|---------------------|---------------------------|------|----------|--|
| | $	au_{ m P}~(\mu s)$ | % | χ^2 | | $	au_{ m P}~(\mu { m s})$ | % | χ^2 | |
| no tr. | 1.97 | 78.8 | 1 172 | no tu | 2.95 | 26.5 | 1.004 | |
| | 7.25 | 21.2 | 1.1/5 | no tr. | 10.2 | 73.5 | 1.000 | |
| | 2.28 | 62.7 | | last tr. | 0.17 | 12.8 | | |
| last tr. | 5 5 2 | 27.2 | 0.998 | | 2.30 | 72.7 | 1.007 | |
| | 3.33 | 37.3 | | | 6.50 | 14.5 | | |
| | [Pt]C | C ₁₂ | | [Pt]C ₁₅ | | | | |
| | $	au_{ m P}~(\mu s)$ | % | χ^2 | | $	au_{ m P}~(\mu s)$ | % | χ^2 | |
| | 1.47 | 26.6 | 1.028 | no tr. | 1.79 | 23.6 | | |
| no tr. | 10.5 | 10.8 | | | 7.43 | 17.8 | 1.066 | |
| | 34.2 | 62.6 | | | 34.8 | 58.5 | | |
| last tr. | 0.59 | 21.0 | | last tr. | 2.28 | 62.7 | | |
| | 2.33 | 17.6 | 1.026 | | 5.53 37.3 | | 0.998 | |
| | 8.76 | 5.7 | 1.026 | | | 37.3 | | |
| | 32.6 | 55.7 | | | | | | |

^{*a*}Tr = treatment. In 2MeTHF solution, $\tau_e(T_1) < 1 \ \mu s$ and $\tau_e(S_1) < 90$ ps for all cases.

resulting $\tau_{\rm P}$ is site-dependent where θ varies with its surroundings in the crystal lattices, as well as the nature of the surroundings. Taking this literature into account and the fact that upon thermal annealing the complex's environment changes, often leading to tighter packing, the closer proximity of the *trans*-Pt(PR₃)₂(C=CC₆H₄)₂ chromophore with its neighbors promotes enhanced nonradiative deactivation of the triplet excited states via collisions. Note again that the flash lamp employed in this work (100 W lamp; fwhm $\approx 1.5 \ \mu$ s) does not generate enough power to induce triplet–triplet annihilation.

Upon subjecting the samples (placed inside a melting point tube) to a higher temperature, just above the first phase transition for $[Pt]C_9$, and $[Pt]C_{12}$ and at 120 °C for $[Pt]C_{15}$ and $[Pt]C_6$ (this sample does not exhibit any phase transition between 20 °C and decomposition temperature), the

phosphorescence lifetimes decrease globally upon repeated thermal treatments and may change the number of components until they do not vary any more (Table 2, Figure 8). Again, the decrease in $\tau_{\rm P}$ values is entirely consistent with an increase in nonradiative processes induced by the effect of thermal annealing where the average distances between the chromophores decrease (as concluded by the powder XRD experiments). These thermal treatments are accompanied by changes in the general shape of the emission spectra as well (Figure 8). This significant change in the spectral fingerprint is associated with a change in crystal site or the direct environment of the chromophore upon thermal annealing. Moreover, the variation of the τ_e values upon the thermal treatment is by far the largest for $[Pt]C_{15}$, in comparison with those for $[Pt]C_6$, $[Pt]C_9$, and $[Pt]C_{12}$ and (Figure 8 and Table)2). This feature suggests that the longest alkyl chains provide greater degrees of freedom for inducing both molecular movements (i.e., better packing) and "knocking" processes.

Finally, the absence of Pt…Pt interactions (as obviously observed in the X-ray structures) precluded the formation of emissive ${}^{1,3}[d\sigma^*p\sigma]^*$ excited states¹⁰ and the corresponding red-shifted and unstructured emission bands. This contrasts with the emission characteristics of the related d^8-d^8 complex Pt₂(dppm)₂(C=CC₆H₅)₂ (dppm = bis(diphenylphosphino)-methane) where the two Pt(II) metals are held face-to-face by the two bridging dppm ligands.¹⁸ In this work, no unstructured emission was detected above 600 nm under any experimental condition used.

CONCLUSION

Prior to this work, only two other reports of phase changes were known. These concern the push-pull organometallic polymer ([*trans*-Pt(PEt₃)₂(C \equiv CC₆H₄)₂](N=C₆(OMe)₄ \equiv N))_n (where N=C₆(OMe)₄ \equiv N = quinone dimine; M_n = 32400; M_w = 68400; polydispersity PD = 2.1; degree of polymerization DP = 38)¹⁹ and the liquid complexes at room temperature reported by Cooper et al.,⁹ for which a glass transition was observed in both cases. To the best of our knowledge, this study reports the first solid-solid phase

| Table 3. Emission | Lifetimes a | t 77 | K in | the Solid | State a | and | 2MeTHF | Glass |
|-------------------|-------------|------|------|-----------|---------|-----|--------|-------|
| | | | | | | | | |

| | [Pt]C ₆ | | | | [Pt]C ₉ | | | |
|--------------|---------------------------|-----------|-------------|---------------------|---------------------------|-------|----------|--|
| | $	au_{ m P}~(\mu { m s})$ | % | χ^2 | | $	au_{ m P}~(\mu s)$ | % | χ^2 | |
| | 26.0 | 32.0 | 1.000 | 2MeTHF 77 K | 15.5 | 6.8 | 1 001 | |
| ZMETHF // K | 41.8 | 68.0 | | | 38.0 | 93.2 | 1.001 | |
| | 1.84 | 19.9 | | | 2.37 | 16.5 | | |
| powder 77 K | 7.57 | 51.5 | 1.010 | powder 77 K | 10.3 | 42.4 | 1.020 | |
| | 19.5 | 28.6 | | | 47.8 | 41.1 | | |
| | [Pt]C ₁₂ | | | [Pt]C ₁₅ | | | | |
| | $	au_{ m P}~(\mu { m s})$ | % | χ^2 | | $	au_{ m P}~(\mu { m s})$ | % | χ^2 | |
| MaTHE 77 V | 6.7 | 11.1 | 1.066 | 2MeTHF 77 K | 14.2 | 6.5 | 1 004 | |
| ZWIETHF // K | 37.8 | 88.9 | | | 37.9 | 93.5 | 1.004 | |
| | 2.06 | 2.6 | | | 2.16 | 1.5 | | |
| novedou 77 V | 6.94 | 1.9 | 1.010 | | 8.58 | 4.6 | 1.020 | |
| powder // K | 51.6 05.4 | 1.010 | powder // K | 46.5 | 72.8 | 1.030 | | |
| | 51.0 | 51.0 95.4 | | | 84.2 | 21.2 | | |

^aNo thermal treatment was applied.



Figure 8. Comparison of the emission decays of $[Pt]C_6$, $[Pt]C_9$, $[Pt]C_{12}$ and $[Pt]C_{15}$ upon thermal treatments.

transition between two ordered phases for luminescent materials built upon the $[trans-Pt(PR_3)_2(C \equiv CC_6H_4)_2]$ chromophore. This luminescence feature was used to obtain information on the molecular behavior upon the thermal annealing, as demonstrated by both variation of the emission

lifetimes and powder XRD scattering peaks upon thermal treatments. Both led to the expected conclusion that the closeness of the packing increases upon promoting more efficient excited states deactivation through intermolecular knockings.

EXPERIMENTAL SECTION

Materials. 4-Iodiophenol (Aldrich), 2-butanone (Anachemia), K_2CO_3 (Anachemia), tetrabutylammonium fluoride (TBAF; Aldrich), MgSO₄ (Fisher), THF (Fisher), DCM (Fisher), *n*-bromohexane (Aldrich), *n*-bromononane (Aldrich), *n*-bromododecane (Aldrich), and *n*-bromopentadecane (Aldrich) were used as received. Diethylamine (Aldrich) was degassed by reflux under argon atmosphere. Cis-Pd(PPh₃)₂Cl₂ was prepared from PdCl₂ and PPh₃ in benzonitrile.²⁰ *cis*-Pt(PMe₃)₂Cl₂ was prepared from K₂PtCl₄, SEt₂, and PMe₃ in water.²¹ The description of the synthesis intermediates starting from commercial compounds is placed in the Supporting Information. These compounds are trivial and are obtained from standard procedures. Only the last step is included in this section, along with their characterization data.

Synthesis of $[Pt]C_{6'}$ $[Pt]C_{9'}$ $[Pt]C_{12'}$ and $[Pt]C_{15'}$. Under argon, *cis*-Pt(PMe₃)₂Cl₂ (1 equiv), CuI (0.01 equiv), and the corresponding [((4-(alkyloxy)phenyl)ethynyl)trimethylsilane] (2 equiv; see the Supporting Information for their syntheses) were added to degassed diethylamine (18 equiv). The mixture was stirred for 24 h at room temperature. The solvent was removed under reduced pressure. The resulting product was purified by column chromatography using hexanes and progressively going to DCM to remove most of the impurities. The product was removed from the column using hexanes mixed with methanol.

 $[Pt]C_6$: Yield = 28%. ¹H NMR (300 MHz, CD₂Cl₂) δ 7.23 (d, J = 8.7 Hz, 4H), 6.78 (d, J = 8.8 Hz, 4H), 3.95 (t, J = 6.6 Hz, 4H), 1.88-1.67 (m, 22H), 1.54–1.42 (m, 4H), 1.42–1.28 (m, 8H), 0.94 (t, J = 6.9 Hz, 6H). ³¹P NMR (300 Hz; CD₂Cl₂) δ -20.70 (¹J₃₁_{P-195}_{Pt} = 2308 Hz). IR (ν (C=C)) 2107 cm⁻¹. Elem. Anal. (theory): C, 54.46; H, 6.99; O, 4.27; (found) C, 53.93; H, 6.91; O, 4.26. [Pt]C₉: Yield = 60%. ¹H NMR (300 MHz, CD_2Cl_2) δ 7.19 (d, J = 8.7 Hz, 4H), 6.74 (d, J = 8.8 Hz, 4H), 3.91 (t, 4H), 1.86–1.64 (m, 22H), 1.44 (m, 5H), 1.29 (m, 19H), 0.89 (m, 6H). ³¹P NMR (300 Hz; CD_2Cl_2) δ -20.70 $({}^{1}J_{P_{-}}{}^{_{1}}P_{-} = 2308 \text{ Hz})$. IR ($\nu(C\equiv C)$) 2108 cm⁻¹. Elem. Anal. (theory): C, 57.61; H, 7.74; O, 3.84; (found): C, 57.65; H, 7.68; O, 4.05. $[Pt]C_{12}$: Yield = 45%. ¹H NMR (300 MHz, CDCl₃) δ 7.25 (s, 4H), 6.77 (d, J = 8.8 Hz, 4H), 3.93 (t, J = 6.6 Hz, 4H), 1.92-1.64 (m, 22H), 1.37 (d, J = 50.7 Hz, 36H), 0.90 (t, J = 6.7 Hz, 6H). ³¹P NMR (300 Hz; CDCl₃) δ -20.60 (¹J₃₁_{P-195}_{Pt} = 2314 Hz). IR (ν (C=C)) 2111 cm⁻¹. Elem. Anal. (theory): C, 60.18; H, 8.34; O, 3.49; (found): C, 60.19; H, 8.34; O, 3.67. [Pt]C₁₅: Yield 69%. ¹H NMR (300 MHz, CDCl₃) δ 7.25 (d, 4H), 6.77 (d, J = 8.8 Hz, 4H), 3.93 (t, J = 6.6 Hz, 4H), 1.78 (m, J = 10.5, 6.6 Hz, 20H), 1.46 (s, 6H), 1.28 (s, 44H), 0.89 (d, J = 6.8 Hz, 6H). ³¹P NMR (300 Hz; CD₂Cl₂) δ -20.70 (¹J³¹ $_{P}$ -¹⁹⁵ $_{Pt}$ = 2308 Hz). IR (ν (C=C)) 2109 cm⁻¹. Elem. Anal. (theory): C, 62.31; H, 8.85; O, 3.19; (found): C, 62.00; H, 8.84; O, 3.61.

Instruments. Solid state UV-vis spectra were recorded on a Varian Cary 50 spectrophotometer at 298 K and 77K using raisedangle transmittance apparatus and a homemade 77K sample-holder. Steady-state emission and excitation spectra were measured on a Edinburgh Instruments FLS980 Phosphorimeter equipped with single monochromators. The steady state emission spectra were recorded using capillaries for the solid state, an NMR tube for the 77 K measurements, and an airtight 1 cm cuvette for measurements in solution at 298 K, which were prepared in a glovebox. These spectra were corrected for instrument response. The phosphorescence lifetime measurements were performed with an Edinburgh Instruments FLS980 Phosphorimeter equipped with "flash" pulsed lamp. The frequency of the pulse was be adjusted from 1 to 100 Hz. All lifetime values were obtained from deconvolution and distribution lifetime analysis and multiexponential analysis for comparison purposes. The TGA traces were acquired on a PerkinElmer TGA 7 apparatus between 20 and 950 °C at 10 °C/min under argon atmosphere. The DSC traces were acquired using a DSC Q200 spectrometer equipped with a RCS 90 model from TA Instruments.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.8b00304.

Absorption, emission, and excitation spectra; emission decays, best fits, and residuals of the title complexes in 2MeTHF or in the solid state at 298 and 77 K; table comparing the θ values for the titles complexes and related complexes from the literature (PDF)

Accession Codes

CCDC 1811412–1811414 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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