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Tunable and Efficient White Light Phosphorescent Emission Based on Single Component N-Heterocyclic Carbene Platinum(II) Complexes

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S Supporting Information



ABSTRACT: A new class of cyclometalated pyridine N-heterocyclic carbene (NHC) Pt(II) complexes with electronically different alkyne derivatives ($C \equiv CR$; $R = C_6H_4C(CH_3)_3$ (1), C_6H_5 (2), C_6H_4F (3), $C_6H_3(CF_3)_2$ (4)) as ancillary ligands were synthesized, and the consequences of the electronic properties of the different substituted phenylacetylene ligands on the phosphorescent emission efficiencies were studied, where $C \equiv CC_6H_4C(CH_3)_3 = 4$ -tert-butylphenylacetylene, $C \equiv CC_6H_5 =$ phenylacetylene, $C \equiv CC_6H_4F = 4$ -fluorophenylacetylene, and $C \equiv CC_6H_3(CF_3)_2 = 3,5$ -bis(trifluoromethyl)phenylacetylene. Structural characterization, electrochemistry, and photophysical investigations were performed for all four compounds. Moreover, the emission quantum efficiencies and wavelength emission intensities of the complexes were also recorded in different weight percents in poly(methyl methacrylate) films (PMMA) and evaluated in the CIE-1931 chromaticity diagram. The square planar coordination geometry with the alkynyl ligands was corroborated for complexes 1, 2, and 3 by single crystal X-ray diffraction studies. These complexes show tunable monomeric high energy triplet emission and an additional concentration-dependent low-energy excimer-based phosphorescence. While adopting weight percent concentrations between 15 and 25%, the two emission bands covering the entire visible spectrum were obtained with these particular complexes displaying the properties of an efficient white light triplet emitter with excellent CIE-1931 coordinates (0.31, 0.33). On the basis of the high luminescent quantum efficiency of over 50% for white light emission, these compounds could be potentially useful for white organic light-emitting diodes (WOLEDs) based applications.

INTRODUCTION

New efficient light-emitting materials have attracted a broad range of potential applications in the fields of sensors, storage, photoelectronic devices, and optical devices. Transition metal complexes with suitable ligands allow tailoring the properties for a specific application that requires light emission. In particular, extensive investigations on transition metal complexes as triplet emitters for application in organic light emitting devices (OLEDs) have been carried out. Owing to the interesting photophysical properties of iridium(III) and platinum(II) complexes, they have been the most widely investigated metal centers. Although there has been significant progress made toward obtaining highly efficient as well as stable green and red emitters, much progress is desired in the area of blue and white light emitting complexes because of its necessity in creating full-colored OLED displays and WOLEDs for solidstate lighting appliances.

Hence, the investigations into white-light emitting materials have increasingly gained attention.¹ Most of the materials to obtain white light emission reported to date consist of a multicomponent system of various emitters like red, green, and blue or blue and orange to cover the entire visible electromagnetic spectrum.² The disadvantage of such white light emitting systems involves the complicated mixing or doping processes, which may cause problems such as color aging, formulation issues, and complicated device engineering.³ In contrast to the multicomponent system, the use of a single-compound entity to yield direct white-light emission has been demonstrated to improve the negative aspects of the different mixing and doping procedures of combined emitters, leading to a simplified production of efficient high quality white light.⁴ For

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Scheme 1. Synthetic Pathway for Complexes 1-4

Article



this reason, the investigations of new single component emitters that can directly generate white light are highly desired.

In order to realize white light emission based on a single component, the propensity of complexes to form excimers could be utilized. In particular, the square planar geometry of bipyridine Pt(II) bisalkyne complexes has been shown to promote excimer formation resulting in an emission at lower energy.^{4c,5} Earlier studies on biscyclometalated Pt(II) complexes bearing strong donor ligands exhibit white light emission through controlled intramolecular-intermolecular interactions. They display low-energy metal-metal to ligand charge transfer (MMLCT) or $\pi(\text{ligand})\cdots\pi(\text{ligand})$ excimeric excited states, leading to bathochromic shifts in emission energies of excimers compared to the monomeric species.⁶ Pt(II) bisalkyne complexes bearing phosphine and bipyridine ligands have been previously shown to possess luminescent properties in solution at room temperature in the green and red region of the electromagnetic spectrum and have been investigated for OLED and solar cell applications.^{5a-c} In particular, bipyridine bound Pt(II) bisalkyne complexes show excimer formation that results in emission properties dictated by the electronics of the bipyridine as well as the alkynes. These complexes display emission only in the green and red parts of the electromagnetic spectrum.^{5a-c} In order to obtain a white light emission, it is required to have part of the emission in the blue region of the electromagnetic spectrum in addition to the red/orange region. To accomplish the targeted white light emission, we sought to replace the bipyridine and phosphine ligands with a chelating pyridine NHC ligand. Such an excimeric based white light emission has been scarcely observed in the case of monocyclometalated compounds bearing NHC.7 Pyridine NHC ligands were chosen since the strong σ -donor property of the NHC ligands was expected to be effective in separating the nonradiative d-d states from the radiative states as well as in conjunction with the pyridine moiety destabilizing the LUMO, thereby resulting in a deep blue emission for the complex without any excimer formation.^{6e} Previous studies with Ru(II) and Ir(III) complexes bearing pyridine NHC ligands show a considerable blue shift in the emission energies and significant enhancements in emission efficiencies in comparison to the corresponding bipyridine analogues.⁸

In this context, we sought to utilize the Pt(II) bisalkyne motif to achieve white light emission based on excimer formation. Although transition metal bisalkyne complexes have been investigated for their interesting redox and luminescent properties, there are no reports of them displaying any white light emission until now. The alkyne ligand is expected to play the role of a chromophore that allows tuning the emission color as well as to effectively control the steric requirements. In addition, the square planar geometry of Pt(II) was expected to pave the way to intermolecular interactions, resulting in aggregation and leading to lower energy emission induced by excimer formation that could be effectively controlled by variation of the concentration to further shift the emission properties from cold (2500–3000 K) to warm (4000–5000 K) white light depending on the requirement.⁹ Such a design strategy was assumed to result in an overall phosphorescence emission in the high-energy and low-energy spectral regions covering the entire visible spectrum leading to a single molecule white light triplet emitter.

Herein, we report a new series of pyridine NHC platinum complexes supported by electronically different acetylide ligands to tune and control the emission efficiency as well as color purity of the resulting white light emission. The complexes show high quantum efficiencies with precise tunability of emission energies of the monomer and excimer emission, which could make these compounds suitable for application in solution processed WOLEDs.

RESULTS AND DISCUSSION

Synthesis and Characterization. Compounds 1-4 were synthesized as yellowish solids in 41-77% yields starting from the different cyclooctadiene-Pt(II)-bisacetylene derivatives and successive substitution of the 1,5-cyclooctadiene (COD) with [1-isopropyl-3-(2-pyridyl)-imidazole-2-ylidene] silver(I) iodide according to the synthetic strategy shown in Scheme 1. All the compounds were characterized by ¹H, ¹³C, and ¹⁹F NMR; IR; and elemental analysis. The ¹H NMR signals of the cyclometalating moiety of complexes 1-4 displayed only marginal deviations in the chemical shifts relative to their electron withdrawing character of the ancillary acetylene derivatives. In a comparison between the unbound ligand and the final metal complexes, the two imidazole protons showed an upfield shift ($\delta\Delta$) from 8.32 and 7.48 ppm to 7.55–7.63 and 7.15–7.21 ppm, respectively. A downfield shift ($\delta\Delta$) was observed for the α proton of the pyridyl unit from 8.56 ppm in the free ligand to a range from 9.63 to 9.83 ppm for the final complexes. The ¹³C NMR spectrum of 1 revealed a characteristic signal for the quaternary carbon of the carbene-metal bond attached to the platinum center at 174.7 ppm, while the greatest shift of this corresponding resonance was found for 4 at 173.6 ppm. The ¹⁹F NMR studies of 3 revealed the resonances for the two monofluorinated acetylene derivatives standing trans to two different ligands as two multiplets at -116.7 and -117.2 ppm. Owing to the presence of two chemically inequivalent 3,5-bis(trifluoromethyl)-

Table 1. Crystal Data and Structure Refinements for 1-3

	1	2	3
CCDC number	1039496	1039497	1039498
empirical formula	$C_{35}H_{39}N_3Pt$	$C_{27}H_{23}N_3Pt$	$C_{27}H_{21}F_2N_3Pt$
formula weight	696.78	584.57	620.56
temperature/K	183(1)	183(1)	183(1)
cryst syst	monoclinic	orthorhombic	triclinic
space group	P2 ₁ /c	Pbca	PĪ
a/Å	14.83670(12)	10.2144(3)	12.2534(4)
b/Å	14.15225(10)	16.6314(6)	14.7691(5)
c/Å	15.38219(11)	26.3951(8)	14.9032(4)
α/\deg	90	90	112.588(3)
β /deg	106.7338(8)	90	105.915(3)
γ/deg	90	90	97.166(3)
volume/Å ³	3093.06(4)	4484.0(2)	2312.91(14)
Ζ	4	8	4
$ ho_{\rm calcd}$, g/cm ³	1.496	1.732	1.782
μ/mm^{-1}	4.563	6.277	6.102
F(000)	1392.0	2272.0	1200.0
cryst size/mm ³	$0.15 \times 0.13 \times 0.02$	$0.47 \times 0.19 \times 0.03$	$0.28 \times 0.19 \times 0.13$
radiation	Mo K α (λ = 0.71073)	Mo K α (λ = 0.71073)	Mo K α (λ = 0.71073)
2Θ range for data collection/ deg	4.426-54.97	4.928-52.744	5.22-61.014
index ranges	$-19 \le h \le 19, -18 \le k \le 18, -19 \le l \le 19$	$-12 \le h \le 12, -20 \le k \le 20, -32 \le l \le 32$	$-17 \le h \le 17, -21 \le k \le 21, -21 \le l \le 21$
reflections collected	60807	36605	52346
independent reflections	7098 [$R_{\rm int} = 0.0278, R_{\rm sigma} = 0.0147$]	4582 $[R_{int} = 0.0496, R_{sigma} = 0.0279]$	14118 [$R_{\text{int}} = 0.0433, R_{\text{sigma}} = 0.0413$]
data/restraints/params	7098/0/360	4582/6/282	14118/0/599
goodness-of-fit on F^2	1.114	1.239	1.054
final R indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0264, wR_2 = 0.0555$	$R_1 = 0.0464, wR_2 = 0.0782$	$R_1 = 0.0291, wR_2 = 0.0594$
final R indexes [all data]	$R_1 = 0.0310, wR_2 = 0.0577$	$R_1 = 0.0572, wR_2 = 0.0817$	$R_1 = 0.0454, wR_2 = 0.0668$
largest diff. peak/hole/e Å ⁻³	3.17/-1.70	2.02/-1.48	1.98/-0.98

phenylacetylene ligands, two resonances at -63.8 and -63.9 ppm were observed as singlets.

Crystal Structure Determination. Suitable single crystals appropriate for X-ray diffraction analysis of 1-3 were obtained via slow diffusion of hexane into a dichloromethane (CH_2Cl_2) solution containing small amounts of the compound. Detailed crystallographic analyses and further information on data collections are summarized in Table 1. Selected bond angles and distances are provided in Table S1 (Supporting Information). The obtained Pt(II) complexes possess a square-planar geometry with a small distortion that could be attributed to the steric encumbering of the ligand (Figure 1). The Pt-N and Pt- $C_{carbene}$ bond lengths were found in the narrow ranges 2.084(5)-2.089(3) Å and 1.997(6)-2.017(4) Å, which indicate that the bonds are not significantly influenced by the electronically different alkyne ligands. On the other hand, the Pt-C bond length between the metal and the acetylide ligand trans to the carbene (1.992(6)-2.037(4) Å) is significantly longer in all structures than the one involving the other acetylide trans to the nitrogen atom (1.938(7) -1.952(3) Å). This trans effect leads to a difference of 0.064(5)Å in 1, 0.054(9) Å in 2, and 0.071(5)-0.085(5) Å in 3 (two crystallographically independent molecules) between the Pt-C_{alk} bonds. These bond distances correspond well to those found in the literature. Indeed, in the crystal structures of bipyridine bisacetylide Pt(II) complexes, the $Pt-C_{alk}$ bond distances range from 1.925(11) to 1.977(7) Å (70 over 77 hits used, obtained from the Cambridge Structural Database) while in the seven previously reported crystal structures of biscarbene bis-acetylide Pt(II) complexes showing *trans* carbeneacetylide moieties, the Pt– C_{alk} bond distances are longer in the range 1.990(9)–2.026(10) Å.¹⁰ The triplet excimer formation in platinum-based phosphors has been theoretically investigated using density functional theory (DFT) and time-dependent DFT by Bredas and Kim.¹¹ It could be assumed that the Pt…Pt bimetallic interactions play a critical role in the triplet excimer formation of Pt(II) molecules and that the interligand $\pi \cdots \pi$ interactions are important in the ground state dimer structure. Our complexes exhibit modest $\pi \cdots \pi$ and Pt \cdots Pt interactions as indicated by the shortest intermolecular $\pi \cdots \pi$ interaction of 3.551(2) Å and the shortest Pt…Pt distance of 5.6856(4) Å both observed in the crystal structure of 3 (see Table S2 in the Supporting Information). The lack of intermolecular interactions in the crystal structures of our compounds does not necessarily state that the formation of a ground-state dimer or excimer is prohibited. Due to the square-planar geometry of the complexes and coplanarity of the ligands, we can even assume that under some conditions intermolecular $\pi \cdots \pi$ and Pt \cdots Pt interactions may exist in the solid state for such compounds. The three polymorphs we recently reported for the same Au(III) compound showing various cell parameters, crystal systems, space groups, and consequently different molecular packings are a good example to not draw definitive conclusions only based on crystal structures.¹²

Photophysical Properties. The UV/vis absorption spectra of 1-4 in CH₂Cl₂ at 298 K are shown in Figure 2. All four complexes display a strong band at wavelengths below 300 nm and a moderate intense absorption band at 320–420 nm. On the basis of the spectroscopic studies and the DFT and TDDFT calculations, the high energy absorption bands are





3 (two crystallographically independent molecules per asymmetric unit)

Figure 1. Molecular structures of 1-3, with displacement ellipsoids drawn at the 30% probability level. Selected hydrogen atoms are omitted for clarity.



Figure 2. UV/vis spectra of 1 ($c = 1.62 \times 10^{-5}$ M), 2 ($c = 4.58 \times 10^{-5}$ M), 3 ($c = 1.87 \times 10^{-5}$ M), and 4 ($c = 3.39 \times 10^{-5}$ M) in CH₂Cl₂.

assigned to a mixture of metal-perturbed ¹ILCT[$\pi_{alk} \rightarrow \pi_{alk}^*$] and ¹LLCT[$\pi_{alk} \rightarrow \pi_{alk}^*$] transitions and the lower energy band mainly to ${}^{1}LLCT[\pi_{alk} \rightarrow \pi_{N^{\wedge}C}^{*}]$ and ${}^{1}MLCT[d \rightarrow \pi_{N^{\wedge}C}^{*}]$ transitions. The edge of the low energy absorption in 2-4 are slightly blue-shifted by 10-20 nm in comparison to 1, which is consistent with the nature of the electronic substituents attached at the alkyne ligand. Solvent dependent UV/vis absorption studies carried out on the exemplary complex 4 revealed a negative solvatochromic behavior of the lowest energy absorption band strongly suggestive of different ground and excited-state dipole moments (see Figure S1 in the Supporting Information). This observation is similar to the behavior reported for the bipyridine Pt(II) dialkyne complexes.^{5a-c} While 1 wt % of 1-4 in poly(methyl methacrylate) (PMMA) films showed broad and structureless emission bands with λ_{max} in the range 459–480 nm with emission quantum yields of 51-59%, the complexes displayed no luminescence in solution at room temperature (Table 2, Figure S2 in the Supporting Information). This nonemissive behavior in solution at room temperature is in contrast to the property previously reported for bipyridine Pt(II) and bisNHC Pt(II)

	2.		,			
	absorption (CH ₂ Cl ₂)		emis	sion (in PMMA)	
complex	$\lambda_{\rm max}/{\rm nm}~(\varepsilon/{\rm M}^{-1}{\rm cm}^{-1})$	concentration	$\lambda_{\rm max}/{\rm nm}~(\tau/\mu { m s})$	$\phi_{ m em}/\%$	$k_{\rm r}/$ $ imes$ 10 ⁵ s ⁻¹	$k_{\rm nr}/$ $ imes$ 10 ⁵ s ⁻¹
1	266 (26586), 362 (8038)	1 wt %	480 (1.59)	57.5	3.61	2.67
		3 wt %	479	33.3		
		10 wt %	483	13.0		
		15 wt %	482	7.5		
		20 wt %	488	9.6		
		50 wt %	487	5.6		
		80 wt %	494, 577 (0.51)	1.8		
2	272 (38390), 367 (12215)	1 wt %	468 (1.23)	50.9	4.14	4.00
		3 wt %	472	43.1		
		10 wt %	474	20.8		
		15 wt %	476	15.3		
		20 wt %	478, 580	48.2		
		50 wt %	486, 594	33.6		
		80 wt %	594 (0.43)	23.9		
3	268 (31563), 365 (9629)	1 wt %	465 (1.52)	53.2	3.50	3.08
		3 wt %	467	28.2		
		10 wt %	470	19.1		
		15 wt %	473	16.5		
		20 wt %	476	23.1		
		50 wt %	485, 585	24.3		
		80 wt %	485, 589 (0.59)	13.1		
4	281 (41532), 360 (15611)	1 wt %	459 (5.72)	58.6	1.02	0.72
		3 wt %	460	41.5		
		10 wt %	460	27.3		
		15 wt %	460, 572	17.6		
		20 wt %	462, 576	22.3		
		50 wt %	461, 581	12.8		
		80 wt %	463, 587 (0.60)	12.5		

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Table 2. Photophysical Data Including Radiative and Non-Radiative Decay Rates of 1-4 at 298 K



Figure 3. Concentration dependent emission spectra of complexes 1 (top left), 2 (top right), 3 (bottom left), 4 (bottom right) in PMMA films.



Figure 4. CIE-1931 diagrams of 1-4 at different concentrations in PMMA. a = 1 wt %, b = 3 wt %, c = 10 wt %, d = 15 wt %, e = 20 wt %, f = 50 wt %, g = 80 wt %.

complexes. 5a-c,10a The thermal quenching of the emission in solution at room temperature could be caused by the solvent molecules.^{5g} The excited state lifetimes for the complexes are similar to those of other Pt complexes reported in the literature.^{5a,c,13} The measured monomer and excimer lifetimes differ by a factor between 3 and 10, and both emission lifetimes are located in the lower microsecond time range (Table 2). The origin of the monomeric emission in PMMA is tentatively assigned to come from an excited state composed of an admixture of ¹LLCT, ³LLCT, ¹MLCT, and ³MLCT. This is similar to the earlier assignments made for related complexes.¹⁴ As expected, upon increasing the weight percentage of the complex in the PMMA films, a low-energy emission was observed. Figure 3 illustrates that the high-energy emission band at 460–480 nm decreases in intensity, while a low-energy emission band at around 575-595 nm developed as the concentration of the complex was increased from 10-80 wt % with respect to the PMMA. While a maximum emission QY was obtained at 20 wt %, self-quenching was observed upon further increasing of the concentration.¹⁵ Due to the fact that the excitation spectrum for the monomeric emission at 1 wt % in PMMA remains the same as the one from the red-shifted orange emission in 80 wt % PMMA, it can be assumed that the low-energy emission arises from an excimer rather than a ground-state dimer that is based on strong metal-metal interactions (see Figure S3 in the Supporting Information). An additional confirmation for the lack of metal-metal interactions leading to the observed excimer formation lies in the absence of additional low-energy absorption bands in the UV/vis measurements that correspond to metal to metal ligand

charge transfer (MMLCT) upon increasing the concentration of the complex.

To further study the excimer-induced behavior of the complexes, the excitation spectra and photoluminescence spectra were determined in PMMA spin coated films at different weight concentrations. Upon reaching 10 wt %, the films exhibited two emission bands with λ_{max} at approximately 460 and 570 nm. They showed a bright white photoluminescence covering the entire visible spectrum due to the presence of monomeric and excimeric emission. From the emission spectra intensities, the CIE-1931 diagrams with its coordinates were determined for all four complexes (Figure 4 and Table S3). For complex 4 at a concentration of 20 wt % in PMMA, CIE coordinates of x = 0.31 and y = 0.33 were obtained, which are very close to the intended pure white light (x = 0.33, y = 0.33). Moreover, the CIE coordinates were found to be tunable depending on the weight percentage of the respective complexes doped in the PMMA matrix.

DFT and TD-DFT Calculations. The absorption and emission properties of the new series of compounds were investigated by DFT and TDDFT using the hybrid functional PBE1PBE in conjunction with the Stuttgart/Dresden effective core potentials (SDD) basis set for the Pt center and the standard 6-31+G(d) basis set for the remaining atoms (for details, see the Supporting Information). The TDDFT calculations based on the DFT optimized ground state geometries S₀ are summarized in Table 3. For all complexes, the S₀ \rightarrow S₁ transition (HOMO \rightarrow LUMO excitation), which corresponds to an admixture of ligand-to-ligand charge transfer (¹LLCT) and metal-to-ligand charge transfer (¹MLCT) Table 3. Selected TD-DFT/CPCM Singlet (S_n with n = 1-25) and Triplet (T_m with m = 1-2) Excited States (in Dichloromethane) with Vertical Excitation Energies (nm), Transition Coefficients c (with c > 0.2), Orbitals Involved in the Transitions, and Oscillator Strengths f (with f > 0.05, except for S_1) for Compounds 1–4

	1	2	3	4
exp. abs., λ_{\max}^{a}	266, 362 nm	272, 367	268, 365	281, 360
singlet excited states S_n^{b}	n = 1	n = 1	n = 1	n = 1
	417.2 $(f = 0.071)$	$403.5 \ (f = 0.016)$	$405.8 \ (f = 0.048)$	367.6 (f = 0.063)
	$H \rightarrow L (c = 0.68)^f$	$H \rightarrow L (c = 0.69)$	$H \rightarrow L (c = 0.69)$	$H \rightarrow L (c = 0.69)$
	n = 2	n = 4	n = 2	n = 3
	385.3 (0.144)	336.3 (0.264)	376.6 (0.113)	334.9 (0.231)
	H-1→L (0.67)	H-3→L (0.64)	H-1→L (0.65)	H-2→L (0.64)
	n = 4	n = 10	n = 4	n = 4
	332.5 (0.126)	277.0 (0.248)	330.3 (0.113)	324.8 (0.092)
	H-3→L (0.62)	$H \rightarrow L+2 (0.59)$	H-3→L (0.53)	H-3→L (0.61)
	n = 6	n = 11	H-4→L (0.43)	H-4→L (0.30)
	327.9 (0.103)	275.6 (0.469)	n = 9	n = 11
	$H \rightarrow L+1 (0.53)$	H-1 \rightarrow L+2 (0.47)	280.2(0.381)	288.4 (0.238)
	n = 9	n = 12	$H \rightarrow L+2 (0.64)$	$H-1 \rightarrow L+1 (0.50)$
	286.2 (0.482)	2/1.5 (0.15/)	n = 12	$H \rightarrow L + 4 (0.21)$
	$H \rightarrow L+2 (0.65)$	$H_{-}/\rightarrow L(0.50)$	2/2.2 (0.10/)	$H-3 \rightarrow L+5 (0.20)$
	n = 12	$H \rightarrow L+3 (0.29)$	H-S→L (0.50)	$H-2 \rightarrow L+1 (0.20)$
	2/1.8 (0.309)	$H-1 \rightarrow L+2 (0.22)$	n = 15	n = 12
	$H^{-1} \rightarrow L^{+2} (0.43)$	n = 13 270.7 (0.140)	$U_{200.7}(0.239)$	283.8 (0.344)
	$H \rightarrow I + 3 (0.29)$	$H \rightarrow I + 3 (0.39)$	n = 16	n = 13
	n = 13	$H_{-2} \rightarrow L_{+2} (0.22)$	n = 10 2657 (0.066)	n = 13 281 2 (0.165)
	n = 13 270.2 (0.175)	n = 14	$H_{-2} \rightarrow L_{+3} (0.41)$	$H \rightarrow L + 4 \ (0.58)$
	$H \rightarrow L+3 (0.52)$	268.2(0.108)	$H \rightarrow L+3 (0.25)$	n = 17
	n = 14	$H-2 \rightarrow L+3 (0.45)$	$H^{-3} \rightarrow L^{+2} (0.23)$	271.4 (0.175)
	267.2 (0.118)	$H-1 \rightarrow L+3 (0.34)$	n = 18	$H-2 \rightarrow L+4 (0.42)$
	H-2→L+2 (0.38)	<i>n</i> = 18	261.8 (0.358)	H→L+5 (0.22)
	H-2→L+3 (0.25)	260.3 (0.294)	H-1→L+2 (0.48)	H-5→L (0.20)
	H-5→L (0.23)	H-1 \rightarrow L+2 (0.38)	H-2→L+2 (0.33)	<i>n</i> = 19
	n = 18	H-3→L+2 (0.28)	<i>n</i> = 19	268.2 (0.114)
	264.9 (0.191)	H→L+3 (0.22)	257.7 (0.135)	H-3→L+1 (0.41)
	H-2→L+3 (0.36)	n = 21	H-1→L+3 (0.56)	n = 21
	n = 19	254.7 (0.101)	H→L+6 (0.29)	264.1 (0.137)
	260.7 (0.156)	H-1→L+3 (0.53)		H-5→L (0.51)
	H-1→L+3 (0.53)	H→L+6 (0.22)		H-3→L+1 (0.44)
	H→L+6 (0.20)	n = 25		
	n = 21	245.5 (0.067)		
	258.7 (0.073)	H-1→L+6 (0.47)		
	H-6→L (0.31)	H-2 \rightarrow L+2 (0.26)		
	$H-1 \rightarrow L+4 (0.30)$			
	H-5→L (0.28)			
	n = 23			
	251.3(0.051)			
	$H-9 \rightarrow L (0.49)$			
) <i>C</i>	H-8→L (0.30)	460	165	450
exp. em., λ_{max}	480 nm	408	405	439
exp. em., λ_{max}	494, 377	394	403, 309	403, 387
triplet excited states T b	$\frac{494}{2.31}$ eV	(2.53 eV)	(2.30 eV)	408 (2.03 eV) m = 1
upper excited states T_m	451 7 nm	432.2	439.5	437.4
	$H \rightarrow L (0.57)$	H-1→L (0.44)	$H \rightarrow L (0.54)$	$H \rightarrow L + 5 (0.46)$
	$H \rightarrow L+2 (0.24)$	m = 2	$H \rightarrow L+2 (0.25)$	m = 2
	m = 2	418.1	H-1→L+3 (0.23)	426.7
	435.0	H→L+3 (0.42)	m = 2	H-1→L+4 (0.40)
	H-1→L (0.47)	H→L (0.28)	426.1	H→L+4 (0.22)
	H→L+3 (0.32)		H-1→L (0.42)	. ,
	H-1→L+2 (0.30)		H→L+3 (0.35)	
	• •		H-1→L+2 (0.31)	

Table 3. continued

^{*a*}Recorded at room temperature in CH_2Cl_2 . ^{*b*}TDDFT on the DFT optimized ground state geometry. ^{*c*}Recorded at room temperature at 1 wt % in PMMA. ^{*d*}Recorded at room temperature at 80 wt % in PMMA. ^{*c*}Solvent-corrected (CH₂Cl₂) energy difference between the optimized ground state and lowest triplet state (ZPE included). ^{*f*}H = HOMO, L = LUMO.



Figure 5. Spatial plots of selected frontier orbitals of the DFT optimized ground state of 2 (solvent effect included).

Table 4. Frontier	Orbitals of the	DFT Optimized	d Ground State	(S_0)	Structures	of 1–4:	Energy	Levels and	Compositio	ns
(Solvent Effect In	cluded)	-							-	

			1				2					
			composition ^a (%)			-		composi	tion (%)			
	МО	energy (eV)	N^C	alk1	alk2	Pt	energy (eV)	N^C	alk1	alk2	Pt	
ground-state	L+3	-0.46	1	24	72	3	-0.51	2	0	94	4	
	L+2	-0.62	16	60	11	13	-0.65	10	81	1	8	
	L+1	-1.28	98	0	0	2	-1.29	98	0	0	2	
	LUMO	-1.95	85	4	1	10	-1.96	86	4	0	10	
	НОМО	-5.71	2	20	62	16	-5.84	3	13	68	16	
	H-1	-5.91	6	63	23	8	-6.00	5	67	17	11	
	H-2	-6.30	6	25	36	33	-6.39	5	25	41	29	
	H-3	-6.54	17	31	28	24	-6.50	20	32	19	29	
				3					4			
				composi	tion (%)				composi	tion (%)		
	МО	energy (eV)	N^C	alk1	alk2	Pt	energy (eV)	N^C	alk1	alk2	Pt	
ground-state	L+3	-0.52	1	20	72	7	-1.31	7	91	2	0	
-	L+2	-0.65	17	61	10	12	-1.34	1	1	98	0	
	L+1	-1.30	98	0	0	2	-1.38	85	12	1	2	
	LUMO	-1.98	85	4	1	10	-2.08	84	3	4	9	
	НОМО	-5.84	2	21	61	16	-6.32	3	13	62	22	
	H-1	-6.04	6	61	24	9	-6.49	9	54	14	23	
	H-2	-6.38	7	27	32	34	-6.65	21	48	9	22	
	H-3	-6.60	18	27	30	25	-6.78	8	12	55	25	
and (1 1.1	1. 1	11 1 11	1. 1.	1 .			1 11 2 6 1	11 1.	1		•.	

"N^C for the bidentate ligand, alk1 for the alkyne ligand *trans* to the N^C carbon atom, and alk2 for the alkyne ligand trans to the N^C nitrogen atom.

characters, is relatively weak ($f \le 0.07$) since the overlap between the molecular orbitals involved in the transition is small: HOMO (H) is localized on the alkynyl ligands (75–

82%) and the Pt metal center (16–22%), while the LUMO (L) is mainly localized on the monocyclometalated pyridine N^{Λ}C (84–86%) and on the Pt metal center (9–10%; Figure 5 for 2,



Figure 6. Spin density surface (left) and singly occupied molecular orbitals (obtained by a restricted open-shell single point calculation on the optimized triplet state geometry, solvent effect included) of the triplet state of 2 (middle, SOMO; right, SOMO-1).

Table 4, Figures S4-S6, see in the Supporting Information). The first significant absorption in the spectra is $S_0 \rightarrow S_2$ for 1 (oscillator strength f = 0.14) and 3 (f = 0.11), $S_0 \rightarrow S_3$ for 4 (f = 0.14) 0.23), and $S_0 \rightarrow S_4$ for 2 (f = 0.26). The corresponding singlet excited states have a similar ${}^{1}LLCT[\pi_{alk} \rightarrow \pi_{N^{\wedge}C}^{*}]/{}^{1}MLCT[d \rightarrow$ $\pi_{N^{\wedge}C}^{*}$ character as the lowest singlet excited state S₁, but the occupied molecular orbitals involved in the transitions (H-1 for 1 and 3, H-2 for 4, and H-3 for 2), even similar to HOMOs, are also slightly localized on the pyridine ligand (6-21%) which provide a larger spatial overlap of the π and π^* (LUMO for all complexes) orbitals and consequently a small intraligand ¹IL character to the excited states. The largest oscillator strengths observed in the 25 lowest singlet-singlet transitions (0.38 < f <0.54) correspond to the excited singlet states S_9 for 1 and 3, S_{11} for 2, and S_{12} for 4 with vertical energies in the range of 275– 286 nm. A detailed analysis of the π and π^* orbitals involved in these excited states (H \rightarrow L+2 for 1 and 3, H-1 \rightarrow L+2 for 2, and $H \rightarrow L+5$) reveal that the frontier orbitals are largely localized on the alkynyl ligands (71-84%), mainly on the alkynyl ligand trans to the N^C carbon atom in the π orbitals and on the alkynyl ligand *trans* to the N^AC nitrogen atom in the π^* orbitals, with participation of the metal and to a lesser extent of the pyridine N^C ligand. The intense and broad absorption bands experimentally observed between 267 and 280 nm can be mainly attributed to ${}^{1}ILCT[\pi_{alk} \rightarrow \pi_{alk}^{*}]$ and metal-perturbed ¹LLCT[$\pi_{alk} \rightarrow \pi_{alk'}^*$] transitions. Nevertheless, among the calculated singlet excited states with a vertical excitation energy below 300 nm, many of them exhibit significant oscillator strengths: five singlet states for 1, four states for 2 and 4, and three states for 3 with f greater than 0.15. Other transitions like metal-to-ligand ¹ML and ligand-to-ligand ¹LL[$\pi_{N^{\wedge}C} \rightarrow \pi_{alk}^{*}$] transitions also participate in these broad absorption bands (see Figure S7 in the Supporting Information).

The singlet-triplet vertical excitations T_1-S_0 obtained by CPCM/TDDFT calculations on the gas phase optimized ground state structures S_0 are given in Table 3. The lowest energy triplet excited state T_1 consists of ${}^3LL[\pi_{alk} \rightarrow \pi_{N^{\wedge}C}^*]$. CT/ ${}^3ML[d \rightarrow \pi_{N^{\wedge}C}^*]$ CT character for each compound arising mainly from HOMO \rightarrow LUMO or HOMO-1 \rightarrow LUMO one-electron excitations, π orbitals of the alkynyl ligands, and π^* orbitals. The low-lying DFT optimized triplet state structures obtained by unrestricted open-shell calculations are in agreement with the T_1-S_0 transitions. The most significant structural variations in the triplet state in comparison with the corresponding singlet ground state of each compound are mainly observed in the coordination sphere of the Pt center with shorter Pt-N and Pt-C_{alkynyl} bonds, but also with longer

alkynyl C C triple bonds (bonding C C character in π , nonbonding in π^*) leading to a relative reorientation of the alkynyl benzene rings as a main consequence (Figures S8 and S9, Table S4 in the Supporting Information). Indeed, the benzene rings become more coplanar with the pyridine ligand as indicated by the dihedral angles between the mean planes calculated in the ranges of 54-84° and 0-28° for the ground state and triplet state structures, respectively (Table S5 in the Supporting Information). It is worth it to note that for compound 4 the benzene ring of the alkynyl group *trans* to the N[^]C carbon atom remains almost perpendicular to the pyridine ligand (83.7 vs 81.1°) with no changes in the bond lengths while the second benzene ring (from the alkynyl *trans* to the N^C nitrogen atom) becomes perfectly coplanar with the pyridine ligand in the triplet state $(61.2 \text{ vs } 0.5^{\circ})$. The calculated vertical energies of the T1-S0 transitions underestimate the experimental results recorded at room temperature at 1 wt % in PMMA by about 30-40 nm. Interestingly, the emission maxima computed as the solvent-corrected energy difference between the DFT optimized singlet ground states (S_0) and the emitting triplet states (T_1) only overestimate the same experimental data by 9 to 22 nm. Furthermore, the relative emission variations are better reproduced with the vertical energies, which is another good indication that the open-shell DFT calculations provide reliable emissive triplet state structures. The spin density surfaces of the lowest triplet states and the SOMOs obtained from restricted open-shell calculations reveal the origin of the emission and confirm the ${}^{3}LLCT[\pi_{alk} \rightarrow \pi_{N^{\wedge}C}^{*}]/{}^{3}MLCT[d \rightarrow \pi_{N^{\wedge}C}^{*}]$ character of the emission process (Figure 6 for 2, Figures S10-S12 in the Supporting Information).

Electrochemical Properties. Cyclic voltammetry studies carried out for all four complexes in DMF at room temperature showed a quasi-reversible reduction peak in the range -2.240 to -2.006 V (vs Fc⁰/⁺ couple) and an irreversible oxidation peak in the range 0.533-0.712 V (Table 5 and Figures S13-S16 in the Supporting Information). The quasi-reversible reduction peak corresponds to the addition of an electron to an

Tab	le	5.	Cy	clic	Vo	ltammetr	y Dat	a of	С	ompl	lexes	$1 - 4^{\circ}$	*
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complex	$E_{\rm ox}/{ m V}$	$E_{\rm Red}/{ m V}$
1	0.533	-2.240
2	0.534	-2.006
3	0.544	-2.222
4	0.712	-2.125

^{*a*}Scan rate = 100 mV s⁻¹ in 0.1 M $[nBu_4N][PF_6]$ (carbon electrode; E⁰ vs Fc⁺/ Fc; 20 °C; DMF).

orbital composed of the NHC-pyridine ligand, the metal and to a lesser extent also the alkyne ligands. This is consistent with the significant changes in the reduction potentials observed with different electronic substituents on the alkyne. While the substitution with the electron donating *t*-butyl group at the 4position of the alkyne ligand strongly shifts the reduction to more negative values, the electron withdrawing fluorine group results in a less negative reduction potential. The irreversible oxidation event is assigned to a HOMO centered process involving metal and the acetylide ligands, which was found to decrease with increasing electron density of the acetylide and is in line with the observed shift in the absorption spectra as well as the change in the energy of the emission wavelength. These observations and assignments compare well with the previously reported bipyridine Pt(II) bisalkyne complexes.^{5a-c}

CONCLUSION

In conclusion, we have successfully designed and accomplished white light emission with high quantum yields and tunability from a single-component triplet emitter. To the best of our knowledge, these are the first Pt(II) bisalkyne complexes that offer exquisite control over the color purity of the white-light emission induced by excimer based phosphorescence. DFT and TDDFT calculations qualitatively confirmed the influence of the alkyne ligands as well as the NHC pyridine ligand and the platinum center on the excited state of the monomer emission. The strong excimer formation of this class of complexes in addition to the fine-tuning of the emission leading to high quantum yields achieved through precise electronic control of the substituents on the alkynes makes these complexes highly promising for single component triplet emitter based WOLEDs.

EXPERIMENTAL SECTION

General Procedure.^{10b,16} All manipulations requiring inert atmosphere were carried out using standard Schlenk techniques under N₂ gas. ¹H, ¹³C{¹H}, and ¹⁹F NMR spectra were performed using Bruker 400 and 500 MHz spectrometers. Chemical shifts (δ) are given in parts per million (ppm). Residual proton (¹H NMR experiments) and carbon (¹³C NMR experiments) solvent peaks were used as internal standards referenced to tetramethylsilane (δ 0.00 ppm). Fluorine (¹⁹F NMR experiments) spectra were referenced to $CFCl_3$ (δ 0.00 ppm). Coupling constants (J) are reported in Hertz (Hz) using the following abbreviations for signal multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), m (multiplet). The assignments were done either with routine 1D or 2D NMR spectroscopies. Infrared (IR) spectra were recorded on a Perkin-Elmer SpectrumTwo FT-IR Spectrometer equipped with a Specac Golden GateATR (attenuated total reflection) accessory. The samples were measured neat, and the frequencies $(
u_{\max})$ are given in wavenumbers (cm⁻¹). Samples for elemental microanalysis were examined on a Leco CHNS-932 analyzer. For TLC analysis, precoated Merck Silica Gel60F254 slides were used, and visualization was done by luminescence quenching either at 254 or 365 nm. Column chromatographic purification (length 15.0 cm; diameter 1.5 cm) of the products was accomplished with silica gel 60, 230-400 mesh. The UV/vis absorption measurements were performed on a PerkinElmer Lambda 35 UV/vis spectrophotometer. Emission spectra were recorded on an Edinburgh FLS920 spectrometer. As an excitation source, a 450 W xenon lamp was used to excite at the lowest-energy absorption maxima with an excitation slit width of 3-5 nm and emission slit width of 5–10 nm. Absolute quantum yields $\phi_{\rm em}$ were measured using a F-M01 integrating sphere assembly with doped poly(methyl methacrylate) (PMMA) thin films at 298 K (estimated uncertainty \pm 15%; with YAG:Ce powder as calibration reference: ϕ_{em} = 97%). Phosphorescence lifetimes for monomeric emissions in PMMA films were measured with an Edinburgh laser flash photolysis spectrophotometer LP920. As an excitation source, a Nd:YAG laser (355 nm) equipped with a single monochromator was used. Phosphorescence lifetimes for excimeric emissions in thin films were measured on the Edinburgh picosecond pulsed diode laser EPL-375 with 371.2 nm and 83.7 ps as excitation source. Photo excited emission color CIE-1931 chromaticity diagrams were determined using normalized emission spectra and the ColorCalculator Version 5.31 from Osram Sylvania. Cyclic voltammetry measurements were performed with a Methrom 757 VA Computrace using a glassy carbon electrode (d = 2 mm) with a Pt counter electrode versus Ag/AgCl reference electrode.

All starting materials were obtained from commercial suppliers and used as received unless otherwise stated. Chemicals that were used are of reagent grade, and the solvents for synthesis were of analytical grade.

Preparation. The ligands 1-isopropyl-3-(2-pyridyl)-imidazolium iodide,¹⁷ [1-isopropyl-3-(2-pyridyl)-imidazole-2-ylidene] silver(I) iodide,¹⁷ 3,5-bis(trifluoromethyl)phenylethynyltrimethylsilane,¹⁸ 3,5-bis(trifluoromethyl)phenylacetylene,^{18,19} and precursors [Pt(COD)(C \equiv CC₆H₄(¹Bu))₂]²⁰ (a), [Pt(COD)(C \equiv CC₆H₅)₂]²⁰ (b), and [Pt-(COD)(C \equiv CC₆H₄F)₂]^{10b} (c) were synthesized according to the reported literature.

General Procedure for the Synthesis of a-d. A total of 2 equiv (with respect to the platinum precursor) of elemental sodium was dissolved in dry EtOH (10 mL) under a nitrogen atmosphere. After complete solvation, 2 equiv of the acetylene ligand was added with a syringe. Under stirring and cooling in a cooling bath (liquid nitrogen in EtOH/MeOH solution), 1 equiv of Pt(COD)Cl₂ was added. After addition, the cooling bath was removed and left to stir for 1 h. The solvent was evaporated under reduced pressure. To the crude product a small amount of CH₂Cl₂ was added to dissolve the product. After adding hexane and sonication of the mixture, the product was purified by precipitation and filtration. The resulting product was washed with EtOH.

[*Pt*(*COD*)(*C*≡*CC*₆*H*₃(*CF*₃)₂), *d*. A brown solid was obtained. Yield: 58%. ¹H NMR (500.25 MHz, CD₂Cl₂, 278 K): δ (ppm) 7.80 (s, 4H, aromatic (arom.) *o*-CH) 7.68 (s, 2H, arom. *p*-CH), 5.77–5.68 (m, 4H, CH=CH), 2.67–2.57 (m, 8H, aliphatic CH₂). ¹³C{¹H}-NMR (125.78 MHz, CD₂Cl₂, 278 K): δ (ppm) 132.0 (d, arom. *o*-CH), 131.6 (q, ²*J*_{CF} = 32.7, arom. *m*-CH), 128.9 (s, Pt–C≡C), 123.8 (q, ¹*J*_{CF} = 272.9, CF₃), 120.2 (sept, ³*J*_{CF} = 3.8, arom. *p*-CH), 106.5 (d, CH of COD), 105.2 (Pt–C≡C), 100.2 (s, Pt–C≡CC), 30.8 (t, CH₂ of COD). ¹⁹F-NMR (470.61 MHz, CD₂Cl₂, 298 K): δ (ppm) −63.8 (s, 6F, CF₃). IR (ATR, cm⁻¹): ν(C≡C) 2147, 2120. Elemental analysis calcd (%) for C₂₈H₁₈F₁₂Pt: C, 43.25; H, 2.33. Found: C, 42.77; H, 2.26%.

General Procedure for the Synthesis of 1–4. One equiv of $Pt(COD)(C \equiv CR)_2$ was dissolved in dry CH_2Cl_2 (50 mL) under a nitrogen atmosphere. One equiv of [1-isopropyl-3-(2-pyridyl)-imidazole-2-ylidene] silver(I) iodide was added to the solution under exclusion of light. The reaction progress was monitored by TLC. The crude products were purified by column chromatography on silica gel. The product was obtained by evaporation of the solvent under reduced pressure.

[*Pt(iPrPyIm)*(*C*≡*CC*₆*H*₄(^{*I*}B*u*))₂], **1** (*iPrPyIm* = 1-*I*-*IsopropyI*-3-(2*pyridyI*)-*imidazole*). A yellow solid was obtained. Eluent: pure EtOAc. Yield: 77%. ¹H NMR (500.25 MHz, CD₂Cl₂, 278 K): δ (ppm) 9.84–9.83 (m, 1H, Pt–NCH), 8.13–8.10 (m, 1H, Im– CCHCH), 7.55 (d, 1H, ³J_{HH} = 2.0, py–NCH), 7.49–7.48 (m, 1H, Im–CCH), 7.42 (d, 2H, ³J_{HH} = 8.5, arom. *o*-CH), 7.42–7.40 (m, 1H, Pt–NCHCH), 7.30 (d, 2H, ³J_{HH} = 8.5, arom. *m*-CH), 7.28 (s, 4H, arom. *o*-CH and arom. *m*-CH), 7.18 (d, 1H, ³J_{HH} = 2.0, iPr–NCH), 6.38 (sept, 1H, ³J_{HH} = 7.0, CH(CH₃)₂), 1.54 (d, 6H, ³J_{HH} = 7.0, CH(CH₃)₂), 1.32 (s, 9H, Ph–C(CH₃)₃), 1.31 (s, 9H, Ph–C(CH₃)₃). ¹³C{¹H}-NMR (125.78 MHz, CD₂Cl₂, 278 K): δ (ppm) 174.7 (s, carbene), 153.2 (s, Im–CC₄H₄N), 151.8 (d, Pt–NCH), 148.8 (d, arom. *p*-CH), 148.4 (d, arom. *p*-CH), 141.1 (d, Im–CCHCH), 131.5 (d, arom. *o*-CH), 131.2 (d, arom. *o*-CH), 125.9 (s, Pt–C≡CC), 125.8 (s, Pt–C≡CC), 125.4 (s, Pt–C≡C), 125.3 (s, Pt–C≡C), 125.2 (d, arom. *m*-CH), 125.2 (d, arom. *m*-CH), 123.5 (d, Pt–NCHCH), 119.0 (d, iPr–NCH), 115.7 (d, py–NCH), 110.6 (d, Im–CCH), 52.2 (d, CH(CH₃)₂), 34.7 (s, C(CH₃)₃), 34.7 (s, C(CH₃)₃), 31.4 (q, C(CH₃)₃), 23.1(q, CH(CH₃)₂). IR (ATR, cm⁻¹): ν (C=C) 2118, 2108. Elemental analysis calcd (%) for C₃₅H₃₉N₃Pt: C, 60.33; H, 5.64; N, 6.03. Found: C, 60.49; H, 5.56; N, 5.84%.

 $[Pt(iPrPyIm)(C \equiv CC_6H_5)_2]$, 2. A yellow solid was obtained. Eluent: EtOAc/Hexane 4:1. Yield: 41%. ¹H NMR (500.25 MHz, CD₂Cl₂, 278 K): δ (ppm) 9.80–9.78 (m, 1H, Pt–NCH), 8.14–8.10 (m, 1H, Pt– NCHCH), 7.59 (d, 1H, ${}^{3}J_{HH}$ = 2.5, py–NCH), 7.53–7.51 (m, 1H, Im-CCH), 7.49-7.47 (m, 2H, arom. o-CH), 7.42-7.39 (m, 1H, Im-CCHCH), 7.36-7.34 (m, 2H, arom. o-CH), 7.28-7.22 (m, 4H, arom. m-CH), 7.19-7.11 (m, 3H, iPr-NCH and arom. p-CH), 6.31 (sept, 1H, ${}^{3}J_{HH} = 7.0$, CH(CH₃)₂), 1.52 (d, 6H, ${}^{3}J_{HH} = 7.0$, CH(CH₃)₂). ¹³C{¹H}-NMR (125.78 MHz, CD₂Cl₂, 278 K): δ (ppm) 174.5 (s, carbene), 153.2 (s, Im-CC₄H₄N), 151.7 (d, Pt-NCH), 141.2 (d, Im-CCHCH), 131.8 (d, arom. o-CH), 131.6 (d, arom. o-CH), 129.3 (s, $Pt-C \equiv CC$), 128.8 (s, $Pt-C \equiv C$), 128.5 (s, $Pt-C \equiv CC$), 128.3 (s, Pt−C≡C), 128.2 (d, arom. *m*-CH), 128.2 (d, arom. *m*-CH), 125.8 (d, arom. p-CH), 125.5 (d, arom. p-CH), 123.5 (d, Pt-NCHCH), 119.0 (d, iPr-NCH), 115.8 (d, py-NCH), 110.7 (d, Im-CCH), 106.5 (s, $Pt-C\equiv C$), 105.8 (s, $Pt-C\equiv C$), 52.2 (d, $CH(CH_3)_2$), 23.2 (q, $CH(CH_3)_2$). IR (ATR, cm⁻¹): $\nu(C\equiv C)$ 2117, 2107. Elemental analysis calcd (%) for C₂₇H₂₃N₃Pt: C, 55.47; H, 3.97; N, 7.19. Found: C, 55.88; H, 4.34; N, 6.96%.

 $[Pt(iPrPyIm)(C \equiv CC_6H_4F)_2]$, 3. A yellow solid was obtained. Eluent: pure EtOAc. Yield: 70%. ¹H NMR (500.25 MHz, CD₂Cl₂, 278 K): δ (ppm) 9.72-9.71 (m, 1H, Pt-NCH), 8.13-8.10 (m, 1H, Im-CCHCH), 7.63 (d, 1H, ${}^{3}J_{HH} = 2.5$, py–NCH), 7.58–7.56 (m, 1H, Im-CCH), 7.45-7.43 (m, 2H, arom. o-CH), 7.41-7.38 (m, 1H, Pt-NCHCH), 7.32–7.29 (m, 2H, arom. o-CH), 7.15 (d, 1H, ³J_{HH} = 2.0, iPr-NCH), 6.98-6.92 (m, 4H, arom. *m*-CH), 6.24 (sept. 1H, ${}^{3}J_{HH} = 6.5$, CH(CH₃)₂), 1.49 (d, 6H, ${}^{3}J_{HH} = 6.5$, CH(CH₃)₂). ${}^{13}C{}^{1}H{}$ -NMR (125.78 MHz, CD₂Cl₂, 278 K): δ (ppm) 174.1 (s, carbene), 161.1 (d, ${}^{1}J_{CF} = 244.8$, arom. *p*-CF), 160.9 (\bar{d} , ${}^{1}J_{CF} = 244.1$, arom. *p*-CF), 153.0 (s, Im-CC₄H₄N), 151.4 (d, Pt-NCH), 141.2 (d, Im-CCHCH), 133.3 (d, arom. *o*-CH), 132.9 (d, arom. *o*-CH), 129.2 (s, Pt−C≡C), 128.8 (s, Pt-C≡C), 124.8 (s, Pt-C≡CC), 124.3 (s, Pt-C≡CC), 123.4 (d, Pt-NCHCH), 118.9 (d, iPr-NCH), 115.9 (d, py-NCH), 115.1 (d, arom. m-CH), 115.0 (d, arom. m-CH), 110.8 (d, Im-CCH), 105.1 (s, Pt-C \equiv C), 104.3 (s, Pt-C \equiv C), 52.1 (d, CH(CH₃)₂), 23.1 (q, CH(CH₃)₂). ¹⁹F-NMR (470.61 MHz, CD₂Cl₂, 298 K): δ (ppm) $-116.7 \text{ (m, } C_6H_4F), -117.2 \text{ (m, } C_6H_4F). \text{ IR (ATR, } cm^{-1}): \nu(C \equiv C)$ 2126, 2102. Elemental analysis calcd (%) for C₂₇H₂₁F₂N₃Pt: C, 52.26; H, 3.41; N, 6.77. Found: C, 51.95; H, 3.46; N, 6.51%.

 $[Pt(iPrPyIm)(C \equiv CC_6H_3(CF_3)_2)_2]$, 4. A yellow solid was obtained. Eluent: EtOAc/CH2Cl2 1:1. Yield: 59%. ¹H NMR (500.25 MHz, CD₂Cl₂, 278 K): δ (ppm) 9.64-9.63 (m, 1H, Pt-NCH), 8.19-8.16 (m, 1H, Im-CCHCH), 7.92 (s, 2H, arom. o-CH), 7.79 (s, 2H, arom. o-CH), 7.66 (s, 1H, arom. p-CH), 7.63 (s, 1H, arom. p-CH), 7.58 (d, 1H, ${}^{3}J_{HH} = 2.5$, py–NCH), 7.54 (d, 1H, ${}^{3}J_{HH} = 8.0$, Im–CCH), 7.49– 7.46 (m, 1H, Pt–NCHCH), 7.21 (d, 1H, ${}^{3}J_{HH} = 2.5$, iPr–NCH), 6.09 (sept, 1H, ${}^{3}J_{HH} = 6.5$, CH(CH₃)₂), 1.52 (d, 6H, ${}^{3}J_{HH} = 6.5$, CH(CH₃)₂). ${}^{13}C{}^{1}H$ -NMR (125.78 MHz, CD₂Cl₂, 278 K): δ (ppm) 173.6 (s, carbene), 153.0 (s, Im-CC₄H₄N), 151.6 (d, Pt-NCH), 141.7 (d, Im-CCHCH), 131.8 (d, arom. o-CH), 131.5 (d, arom. o-CH), 131.1 (m, 2Pt−C≡CC and 4 arom. *m*-CH), 130.3 (s, Pt−C≡ C), 130.0 (s, Pt–C \equiv C), 123.8 (d, Pt–NCHCH), 123.7 (q, ${}^{1}J_{CF}$ = 272.7, 4CF₃), 119.2 (d, iPr-NCH), 118.9 (d, arom. p-CH), 118.6 (d, arom. p-CH), 115.9 (d, py-NCH), 110.8 (d, Im-CCH), 104.1 (s, Pt- $C \equiv C$), 103.1 (s, Pt-C $\equiv C$), 52.4 (d, CH(CH₃)₂), 23.1 (q, CH(CH₃)₂). ¹⁹F-NMR (470.61 MHz, CD₂Cl₂, 298 K): δ (ppm) -63.8 (s, 3F, CF₃), -63.9 (s, 3F, CF₃). IR (ATR, cm⁻¹): ν (C=C) 2134, 2103. Elemental analysis calcd (%) for $C_{31}H_{19}F_{12}N_3Pt$: C, 43.47;

H, 2.24; N, 4.91. Found: C, 43.23; H, 2.28; N, 4.88%. **Crystal Structure Determinations.**^{10b,16} Single-crystal X-ray diffraction data for 1 were collected at 183(1) K on an Agilent Technologies SuperNova Atlas area-detector diffractometer and for 2 and 3 on an Agilent Technologies Xcalibur Ruby area-detector diffractometer using a single wavelength Enhance X-ray source with Mo K α radiation ($\lambda = 0.71073$ Å)²¹ from a microfocus X-ray source and an Oxford Instruments Cryojet XL cooler. The single crystals that were selected carefully were mounted using polybutene oil on a flexible loop fixed on a goniometer head and immediately transferred to the diffractometer. Pre-experiment, data collection, data reduction, and analytical absorption correction²² were carried out with the program CrysAlisPro.²³ Using Olex2,²⁴ the crystal structures were solved with the ShelXS²⁵ program using Direct Methods and refined with SHELXL2013²⁵ by full-matrix least-squares minimization on F². PLATON²⁶ was used to check the results of the X-ray studies. Crystallographic data (excluding structure factors) for the structures of compounds 1, 2, and 3 reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-1039496 (1), 1039497 (2), and 1039498 (3). Copies of data can be obtained free of charge at http://www.ccdc.cam. ac.uk/products/csd/request/. **Computational Details.**^{10b,16} The luminescent properties of

compounds 1-4 were evaluated by density functional theory (DFT) calculations using the Gaussian 03 program package.²⁷ The hybrid functional PBE1PBE²⁸ together with the Stuttgart/Dresden effective core potentials (SDD) basis set²⁹ for the Pt center augmented with one f-polarization function ($\alpha = 0.993$) and the standard 6-31+G(d) basis set³⁰ for the remaining atoms were used in all calculations. The molecular structures of the ground states and lowest triplet states of compounds 1-4 were fully optimized by DFT calculations in the gas phase (restricted method for the ground states, unrestricted open shell calculations for the triplet states). On the basis of the optimized ground-state S₀ geometries, time-dependent DFT (TD-DFT) calculations³¹ combined with the conductive polarizable continuum model $(CPCM)^{32}$ were used to produce the first 25 lowest singletsinglet and the first two singlet-triplet vertical excitations in the gas phase or in dichloromethane with the corresponding energies, transition coefficients, and oscillator strengths. Full geometry optimizations without symmetry constraints were carried out in the gas phase. The DFT optimized geometries were confirmed to be potential energy minima by vibrational frequency calculations at the same level of theory, as no imaginary frequency was found. All molecular orbital and spin density plots presented in the manuscript and in the Supporting Information take the solvent effect (CPCM, dichloromethane) into account.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b02962.

Crystal data and refinement details of complexes 1–3, Cartesian coordinates and energies for all optimized molecules, spatial plots of selected frontier orbitals of the optimized ground state of 1–4, computational details, photophysical data, CIE-1931 plots with coordinates and CV data (PDF)

X-ray crystallographic data of complex 1 (CIF)

X-ray crystallographic data of complex 2 (CIF)

X-ray crystallographic data of complex 3 (CIF)

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[†]The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. These authors contributed equally.

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Notes

The authors declare no competing financial interest.

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