ORGANOMETALLICS

Efficient Electroluminescence of Two Heteroleptic Platinum Complexes with a 2-(5-Phenyl-1,3,4-oxadiazol-2-yl)phenol Ancillary Ligand

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Supporting Information

ABSTRACT: Two new platinum(II) cyclometalated complexes with 2phenylpyridine (**Pt1**) and 2-(4-trifluoromethyl)phenylpyridine (**Pt2**) as the main ligands and 2-(5-phenyl-1,3,4-oxadiazol-2-yl)phenol (pop) as the electron-transporting ancillary ligand were developed. The photoluminescence quantum efficiency yields of both green **Pt1** and **Pt2** phosphors (λ_{max} 490 and 496 nm) are 20.0% and 31.0% in CH₂Cl₂ solutions, respectively. Efficient OLEDs (organic light emitting diodes) of ITO/TAPC (bis[4-(*N*,*N*ditolylamino)phenyl]cyclohexane, 40 nm)/**Pt1** or **Pt2** (5 wt %):TCTA (4,4',4"-tri(carbazoyl-9-yl)triphenylamine, 10 nm)/**Pt1** or **Pt2** (5 wt %):2,6DCzPPy (2,6-bis(3-(carbazol-9-yl)phenyl)pyridine, 10 nm)/TmPyPB (1,3,5-tris(*m*-pyrid-3-ylphenyl)benzene, 40 nm)/LiF (1 nm)/Al (100 nm) were fabricated. Particularly, device G1 based on complex **Pt1** with 5 wt % doped concentration showed superior performance with a maximum current



efficiency $(\eta_{\text{max,c}})$ of 55.6 cd A⁻¹, a maximum power efficiency $(\eta_{\text{max,p}})$ of 52.2 lm W⁻¹, and a maximum external quantum efficiency (EQE_{max}) of 18.0%. Device G2 with the **Pt2** emitter displayed lower efficiency rolloff with η_c values of 48.5 and 43.1 cd A⁻¹ as the luminance reached 5000 and 10000 cd m⁻², respectively. These research results demonstrate that the Pt(II) complexes with an ancillary ligand attached with the 1,3,4-oxadiazole group have promising applications in efficient OLEDs.

■ INTRODUCTION

Because of the spin-orbit coupling $(SOC)_{t}^{1}$ transition-metal complexes have been identified as potential emitters for POLEDs (phosphorescent organic light emitting diodes), which possess excellent photophysical properties. Especially, much attention has been attracted by iridium² and platinum³ complexes in recent years owing to their outstanding photophysical properties.⁴ Extensive studies of the photophysical properties of these complexes by modifications of the phenylpyridine ligands have been carried out by introducing electron-withdrawing or electron-donating units to the phenyl or pyridine rings. Furthermore, the good electron-transporting properties of these emitters are also important for efficient OLEDs in view of the better hole-transporting ability of the hole-transporting material in comparison to the electrontransporting ability of the electron-transporting material. Many research groups have reported efficient devices based on complexes containing cyclometalated and ancillary ligands with nitrogen, oxygen, phosphorus, sulfur, and boron heterocyclic derivatives for better electron mobility.⁵ For example, some high-performance phosphorescent OLEDs were reported by our group employing Ir(III) emitters with tetraphenylimidodiphosphinate derivatives as ancillary ligands, which have P=O units.

Furthermore, 1,3,4-oxadiazole derivatives also have been studied extensively in optoelectronic materials because of their

good electron-injecting and -transporting ability.⁷ Over the past few years, in order to enhance the electron-transporting ability of Ir(III) complexes and improve the device efficiency, several research groups have introduced the 1,3,4-oxadiazole derivatives into the main ligands.8 As far as we know, Pt(II) complexes using ancillary ligands with 1,3,4-oxadiazole derivatives have been rarely reported for efficient OLEDs. On this basis, as is shown in Scheme 1, two new heteroleptic Pt(II) complexes containing the main ligands 2-phenylpyridine (ppy) and 2-(4-trifluoromethylphenyl)pyridine (4-tfmppy) and the ancillary ligand 2-(5-phenyl-1,3,4-oxadiazol-2-yl)phenol (pop) were synthesized. The trifluoromethyl moiety at the 4-position on the phenyl does not change the emission color of the complexes on the basis of ppy, but the device performances were improved greatly.^{6a-d} Here, the synthetic process, structure identification, thermal stability, photophysical properties, theoretical calculations, and OLED performances of both Pt(II) complexes are described in detail.

EXPERIMENTAL SECTION

The general information on the preparation and measurements of the materials, procedures and methods of the single-crystal analysis, and

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Scheme 1. Synthetic Routes of Ligands and Complexes Pt1 and Pt2



OLED fabrication and measurements are included in the Supporting Information.

General Syntheses of Complexes Pt1 and Pt2. K_2PtCl_4 (0.415 g, 1 mmol) and 1.2 equiv of the cyclometalated ligand (1.2 mmol) were added to a 2-ethoxyethanol and water mixture. Then, the solution was heated for 16 h at 80 °C. After the addition of water, the precipitated yellow greenish powder was filtered and reacted with K(pop) without further purification for another 16 h at 80 °C. After it was cooled, the solution was concentrated and the resulting residue was purified by silica gel column chromatography (CH₂Cl₂/petroleum ether 1/2 (v/v)); vacuum sublimation gave yellow crystals.

Pt1: yield 40.0%. ¹H NMR (500 MHz, CDCl₃): δ 9.44 (d, J = 5.58 Hz, 1H), 8.67 (d, J = 7.85 Hz, 1H), 8.22–8.25 (m, 2H), 8.06 (d, J = 6.03 Hz, 2H), 7.96 (d, J = 9.71 Hz, 1H), 7.72 (d, J = 3.93 Hz, 3H), 7.65 (s, 1H), 7.46 (d, J = 6.85 Hz, 2H), 7.20 (d, J = 8.15 Hz, 1H), 7.09 (dd, J = 7.94, 13.63 Hz, 2H), 6.70 (t, J = 7.26 Hz, 1H). HR-MS (electrospray, m/z): calcd for C₂₅H₁₇N₃O₂Pt [M + H]⁺ 587.1047, found 587.1050. Anal. Calcd for C₂₅H₁₇N₃O₂Pt: C, 51.20; H, 2.92; N, 7.16. Found: C, 51.12; H, 2.84; N, 7.06%.

Pt2: yield 45.0%. ¹H NMR (500 MHz, CDCl₃): δ 9.55 (d, J = 6.20 Hz, 1H), 9.22 (s, 1H), 8.20 (dd, J = 2.45, 7.33 Hz, 2H), 7.87–7.83 (m, 2H), 7.72 (d, J = 7.93 Hz, 1H), 7.64–7.57 (m, 4H), 7.38 (ddd, J = 6.95 Hz, 3H), 7.10 (d, J = 8.59 Hz, 1H), 6.68 (t, J = 7.39 Hz, 1H). HR-MS (electrospray, m/z): calcd for C₂₆H₁₆F₃N₃O₂Pt [M + H]⁺ 655.0921, found 655.0917. Anal. Calcd for C₂₆H₁₆F₃N₃O₂Pt: C, 47.71; H, 2.46; N, 6.42. Found: C, 47.48; H, 2.41; N, 6.33%.

RESULTS AND DISCUSSION

Preparation and Characterization of Compounds. The platinum complexes were synthesized by the reaction of $[(C^N)Pt(\mu-Cl)]_2$ chloride-bridged dimers with the pop potassium salt (K(pop)) (Scheme 1). The crude products **Pt1** and **Pt2** were purified by silica chromatography and further refined by sublimation under 10⁻⁷ Torr vacuum. Both Pt(II) complexes were identified by elemental analyses, ¹H NMR, and HR-MS.

X-ray Crystallographic Analysis. Figure 1 shows the ORTEP (Oak Ridge thermal ellipsoid plot) diagram of the Pt2 single crystal. The crystallographic data and the selected bond lengths/angles are summarized in Tables S1 and S2 in the Supporting Information, respectively. The Pt2–C1 bond length is 1.997 Å, which is slightly shorter than the Pt2–N1 and Pt2–N2 bond lengths (2.010 and 2.000 Å, respectively). The Pt2–O1 bond length is 2.068 Å. The average dihedral angle among planes [C1–Pt2–N1], [N1–Pt2–O1], and [O1–Pt2–N2] is 179.06°, which suggests that they maintain a good square planar coordination geometry. The bond lengths and angles of



Figure 1. ORTEP diagram of Pt2 (CCDC No. 1495292) with the atom-numbering schemes. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level.

the complex are in good agreement with the few previously published structures of this type.⁹ Additionally, **Pt2** exhibits a different packing in the crystal (Figure S1 in the Supporting Information), in which the molecules are stacked in a head-totail fashion. Due to the attachment of the bulky trifluoromethyl, the closest Pt…Pt distance (6.22 Å) is outside the range of 2.7– 3.5 Å for any metallophilic interaction.^{3d} Furthermore, the presence of the bulky groups effectively inhibits intermolecular $\pi-\pi$ stacking interactions, in which there is a separation of about 3.36 Å between the only partially overlapping ppy and pop rings, suggesting only weak $\pi-\pi$ interactions between the **Pt2** units.

Thermal Stability. To fabricate stable OLEDs, the thermal stability of the emitters is also very important. Therefore, differential scanning calorimetry (DSC) and thermogravimetric (TG) measurements were applied to characterize the thermal properties of both platinum complexes under a nitrogen atmosphere. As observed from Figure 2a, the DSC curves give the melting points of Pt1 and Pt2 as 295 and 311 °C, respectively. TG curves suggest that the decomposition temperatures of Pt1 and Pt2 (5% loss of weight) are as high as 347 and 358 °C, respectively, indicating that the melting



Figure 2. DSC (a) and TG (b) curves of complexes Pt1 and Pt2.



Figure 3. UV-vis absorption (a) and emission (b) spectra of complexes Pt1 and Pt2 in degassed dichloromethane (5 \times 10⁻⁵ M) at room temperature.

Table 1. Photophysical Data of Pt1 and Pt2 in CH₂Cl₂ Solution

compd	$T_{\rm d}^{\ a}$ (°C)	absorption ^b λ (nm)	emission ^b λ_{max} (nm), 298 K	$ au_{298\mathrm{K}}^{b}(\mu\mathrm{s})$	$\Phi_{\mathrm{P}}{}^{c}$ (%)	$HOMO/LUMO^{d}$ (eV)
Pt1	347	305/394/452	490/510	1.7	20.0	-5.63/-2.84
Pt2	358	307/391/460	496/528	1.8	31.0	-5.67/-2.96

^{*a*}Decomposition temperature. ^{*b*}Measured in degassed CH₂Cl₂: ^{*c*} Φ denotes emission quantum yields, calculated with *fac*-Ir(ppy)₃ standard in degassed CH₂Cl₂ solution. ^{*d*}HOMO (eV) = $-(E_{ox} - E_{1/2,Fc}) - 4.8$; LUMO (eV) = HOMO + $E_{band gap}$.

point and decomposition temperature will be improved by the introduction of $-CF_3$ in **Pt2**.

Electronic Spectroscopy. Figure 3 shows the absorption and photoluminescence (PL) spectra of Pt1 and Pt2 in CH₂Cl₂ at room temperature, and Table 1 collects the photophysical data of both complexes. The intense absorption bands below 350 nm in Figure 3a should belong to the $\pi \to \pi^*$ transitions of the cyclometalated main ligand and ancillary ligand. However, the lower-energy absorption bands (350-460 nm) can be assigned to the mixed ¹MLCT and ³MLCT (metal-to-ligand charge-transfer) states or LLCT (ligand-to-ligand chargetransfer) transition through strong spin-orbit coupling of platinum atoms.¹⁰ In comparison with complex Pt1, which has a peak emission at 490 nm with a weak band (510 nm) (Figure 3b), complex Pt2 shows a red-shifted emission peak at 496 nm with a shoulder emission (528 nm). Additionally, the PL quantum yields for Pt1 and Pt2 are 20.0% and 31.0%, respectively. The results suggest that the -CF₃ moiety has an

effect on the emitting properties of Pt(II) complexes because the molecular packing can be affected by the bulky CF₃ substituents on the phenyl rings of ppy and the self-quenching behavior can be effectively inhibited by the steric protection around the metal.¹⁰ Furthermore, the lifetimes are in the range of microseconds for the two complexes (1.7 μ s for **Pt1** and 1.8 μ s for **Pt2**, respectively) (Figure S2 in the Supporting Information). The short lifetimes would improve the spinstate mixing and suppress the exciton annihilation.

Theoretical Calculations. To investigate the electronic states and orbital distributions, density functional theory (DFT) calculations for both Pt(II) complexes employing Gaussian09 software with the B3LYP functional were conducted.¹¹ The 6-31G(d,p) basis set was used for C, H, N, O, and F atoms, while the LanL2DZ basis set was employed for Pt atoms.¹² The CH₂Cl₂ effect was taken into consideration by using the polarizable continuum model (C-PCM) conductor.¹³

The optimized HOMO/LUMO structures of both complexes are clearly shown in Figure 4.



Figure 4. Isodensity surface plots and HOMO/LUMO orbital levels of Pt1 and Pt2: black line, calculated values; red line, experimental values.

With regard to energy levels and compositions, electronic structures of HOMOs are wholly different from those of LUMOs in both complexes. The HOMOs of both **Pt1** and **Pt2** correspond to an admixture of pop ligand (62.0–68.0%) and Pt d orbitals (22.4–25.2%) with minor contribution from the ppy substituents (9.4–12.7%). However, the LUMOs are quite different from the HOMOs of **Pt1** and **Pt2** concerning the composition. For **Pt1**, the electron cloud density of the LUMO is mainly distributed over the pop ligand (92.34%) with

negligible contribution from Pt d orbitals (0.99%) and the main ligand (6.62%). However, for **Pt2**, the LUMO is distributed mainly over the π orbitals of the main ligand (88.24%) and rarely located on Pt d orbitals (4.97%), which illustrates that the attachment of the $-CF_3$ group with high electron affinity on the phenyl rings significantly affects the unoccupied frontier molecular orbitals. In addition, the results fit well with the calculated LUMO energy levels.

OLED Performances. To study the electroluminescence performances of complexes Pt1 and Pt2, the OLEDs of ITO/ TAPC (bis[4-(N,N-ditolylamino)phenyl]cyclohexane, 40 nm)/ Pt1 or Pt2 (5 wt %):TCTA (4,4',4"-tris(carbazol-9-yl)triphenylamine, 10 nm)/Pt1 or Pt2 (5 wt %):2,6DCzPPy (2,6-bis(3-(9H-carbazol-9-yl)phenyl)pyridine, 10 nm)/ TmPyPB (1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene, 40 nm)/ LiF (1 nm)/Al (100 nm) were fabricated (Scheme 2). The devices using Pt1 and Pt2 emitters are denoted G1 and G2. respectively. Due to its high hole mobility $(1 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1})$ s^{-1}) and high-lying LUMO level (-1.8 eV), TAPC was used as both hole-transporting and electron-blocking layer. However, TmPvPB was applied as both hole-blocking and electrontransporting layer because of its low-lying HOMO level (-6.7)eV) and high electron mobility $(1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$.¹⁴ The bipolar material 2,6DCzPPy and p-type material TCTA were used as double-emitting host materials, respectively. Figure 5 displays the EL spectra, luminance (L) versus voltage (V), current efficiency (η_c) versus luminance, and power efficiency $(\eta_{\rm p})$ versus luminance characteristics of the optimized devices. In addition, Table 2 collects most key EL data.

In theory, the gradually changed HOMO energy levels of TAPC (-5.5 eV), TCTA (-5.7 eV), and 2,6DCzPPy (-6.1 eV) are beneficial for the hole injection and transport. Similarly, these levels are also beneficial for the injection and transport of electrons owing to the gradually changed LUMO energy levels

Scheme 2. Energy Level Diagram of HOMO and LUMO Levels of Materials Investigated^a and Their Chemical Molecular Structures



^aThe dotted line represents the HOMO/LUMO energy levels of dopants.



Figure 5. Characteristics of devices with configuration ITO/TAPC (40 nm)/Pt1 or Pt2:TCTA (10 nm, 5 wt %)/Pt1 or Pt2:2,6DCzPPy (10 nm, 5 wt %)/TmPyPB (40 nm)/LiF (1 nm)/Al (100 nm): (a) EL spectra; (b) L-V curves; (c) η_c-L curves; (d) η_p-L curves for G1 and G2.

Table 2. Key EL Data of Devices G1 and G	y EL Data of Devices G1 and	ey EL Data of Devices G1 and	Gź
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device	$V_{\text{turn-on}}^{a}$ (V)	$L_{\max} (voltage)^b$ (cd m ⁻² (V))	$\eta_{ m p,max} \; ({ m voltage})^c \; ({ m lm \; W}^{-1} \ ({ m V}))$	$\eta_{ m c,max}(m voltage)^d \ (m cd~A^{-1}~(V))$	$\eta_{\rm c,5000,10000}^{e} ~({\rm cd}~{\rm A}^{-1})$	$EQE_{max}^{f}(\%)$	CIE (x,y)
G1	3.4	31494 (8.7)	52.2 (3.7)	55.6 (3.7)	49.2/36.5	18.0	(0.24,0.59)
G2	3.1	52435 (9.1)	42.5 (4.4)	50.5 (4.2)	48.5/43.1	17.2	(0.32,0.60)
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 ${}^{a}V_{\text{turn-on}}$ denotes the turn-on voltage recorded at a luminance of 1 cd/m². ${}^{b}L_{\text{max}}$ denotes the maximum luminance. ${}^{c}\eta_{\text{p,max}}$ denotes the maximum power efficiency. ${}^{d}\eta_{\text{c,max}}$ denotes the maximum current efficiency. ${}^{e}\eta_{c,5000}$ denotes the current efficiency at 5000 cd/m², and $\eta_{c,10000}$ denotes the current efficiency at 10000 cd/m². ${}^{f}\text{EQE}_{\text{max}}$ denotes the maximum external quantum efficiency.

of TmPyPB (-2.7 eV), 2,6DCzPPy (-2.6 eV), and TCTA (-2.4 eV). Thus, holes and electrons will be distributed in a more balanced device and the exciton recombination zone is expected to be broadened. Furthermore, the HOMO energy level of 2,6DCzPPy is 0.6 eV higher than that of TmPyPB and the LUMO energy level of TCTA is 0.6 eV lower than that of TAPC, which will result in excitons (hole-electron pair) well conformed within emissive layers and triplet exciton quenching effectively avoided. In addition, because the Pt1 or Pt2 HOMO and LUMO levels (-5.63/-5.67 eV and -2.84/-2.96 eV, respectively) are all within those of 2,6DCzPPy and TCTA, it is conceivable that carrier (holes and electrons) trapping is the dominant mechanism of electroluminescence in G1 and G2 devices. Additionally, the reverse energy transferred from dopant to host materials can be effectively avoided because of the higher triplet energies of 2,6DCzPPy (2.71 eV) and TCTA (2.83 eV) in comparison to those of Pt1 or Pt2 (2.53/2.50 eV). In these devices, the optimized Pt(II) complexes with 5 wt % doped concentration in TCTA and 2,6DCzPPy, respectively, were used as the two emitting layers. Usually, the carrier recombination region can be broadened by the adoption of double emitting layers, which can improve the hole–electron utilization ratio, causing the increased EL performance and impressed efficiency roll-off. The EL emissions of devices G1 and G2 peak at 495/523 and 507/534 nm (Figure 5a) with Commission Internationale de l'Eclairage (CIE) coordinates of (0.24, 0.59) and (0.32, 0.60), respectively, are very similar to the PL spectra of the complexes measured in CH₂Cl₂, which indicates that the EL derives from the triplet excited states of the complexes. Furthermore, the disappearance of the TCTA and 2,6DCzPPy emission suggests that almost complete energy transferred from the hosts to the emitter in the device.

Both OLEDs display good EL performances with low turnon voltages ($V_{turn-on}$) (G1, 3.4 V; G2, 3.1 V) and high maximum brightness (G1, 31494 cd m⁻²; G2, 52435 cd m⁻²). The $\eta_{c,max}$ (maximum current efficiency), EQE_{max} (maximum external quantum efficiency), and $\eta_{p,max}$ (maximum power efficiency) values of G1 and G2 are 55.6/50.5 cd A⁻¹, 18.0/17.2%, and 52.2/42.5 lm W⁻¹, respectively. The performances are close to those with similar Pt(II) complexes,³ but are still lower than those of present state of the art OLEDs using green Pt(II) complexes containing a single, tetradentate, robust chelating ligand, which always show high EQE values of above 25%.¹⁵ Furthermore, both devices demonstrate low-efficiency rolloff. For device G1, the current efficiencies (η_c) can still be obtained as 49.2 and 36.5 cd A⁻¹ when the luminance reaches 5000 and 10000 cd m⁻², respectively. The G2 device shows even lower efficiency rolloff with current efficiencies of 48.5 cd A⁻¹ at the brightness of 5000 cd m⁻² and 43.1 cd A⁻¹ at that of 10000 cd m⁻², respectively.

The good device properties may be ascribed to the following facts. First, the electron transport ancillary ligand pop is applied in Pt(II) complexes. Because the hole mobility of TAPC (1 \times 10^{-2} cm² V⁻¹ s⁻¹) is much higher than the electron mobility of the TmPyPB $(1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ and the high LUMO energy barrier between TmPyPB and 2,6DczPPy, the excitons are expected to accumulated near the interface of (Pt complexes (5 wt %):2,6DCzPPy)/TmPyPB, which is inclined to lead to the severe triplet-polaron annihilation (TPA), triplet-triplet annihilation (TTA), high-efficiency rolloff.^{14,16} Thus, the enhanced electron-transporting ability of the dopants can increase the excitation lifetime of the OLEDs. In this work, the $-CF_3$ group and the 1,3,4-oxadiazole unit are introduced into the framework of the main ligand, which can lower the LUMO energy levels and benefit the electron transport properties. Though the maximum efficiency of G2 is lower than that of G1, the introduction of the CF₃ unit in the Pt(II) complex results in low-efficiency rolloff. Second, the stepwise changes in HOMO/LUMO energy level of all layers is beneficial for the injection and transport of both holes and electrons, which will result in high-performance green OLEDs. Finally, the broad recombination zone, good balanced distribution, and improved trapping of carriers caused by double light-emitting layers are adopted in this device, which showed higher current efficiency, higher brightness, and slower efficiency rolloff.¹⁷

CONCLUSION

In conclusion, two green cyclometalated Pt(II) complexes Pt1 and Pt2 using 2-(5-phenyl-1,3,4-oxadiazol-2-yl)phenol ancillary ligand have been successfully prepared with photoluminescence quantum efficiency yields of 20.0% and 31.0% in CH₂Cl₂ at room temperature. EL devices with ITO/TAPC (40 nm)/Pt1 or Pt2 (5 wt %):TCTA (10 nm)/Pt1 or Pt2 (5 wt %):2,6DCzPPy (10 nm)/TmPyPB(40 nm)/LiF (1 nm)/Al (100 nm) displayed promising performances with a $\eta_{c,max}$ value of 55.6 cd A⁻¹, a maximum EQE value of 18.0%, and a peak η_p value of 52.2 lm W⁻¹. This study suggests that Pt(II) complexes containing the electron-transporting pop ancillary ligand have potential applications in OLEDs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.6b00851.

Details of materials and measurements, synthesis details of 2-[4-(trifluoromethyl)phenyl]pyridine and 2-(5-phenyl-1,3,4-oxadiazol-2-yl)-phenol ligands, details of X-ray crystallography and electrochemical tests, procedures and methods of OLED fabrication and measurements, crystallographic data, selected bond lengths and angles, and the crystal-packing diagram of **Pt2**, and selected lifetime curves and cyclic voltammograms of Pt1 and Pt2 (PDF)

Crystallographic data for Pt2 (CIF)

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Notes

The authors declare no competing financial interest.

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