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A near-infrared phosphorescent probe for F⁻ based on a cationic iridium(III) complex with triarylboron moieties

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In this work, a near-infrared (NIR) phosphorescent probe for F^- based on a cationic Ir(III) complex [Ir(Bpq)₂(quqo)]PF₆ (1) with dimesitylboryl (Mes₂B) groups on the cyclometalated C^N ligands (Bpq) and 2-(quinolin-2-yl)quinoxaline (quqo) as N^N ligand was designed and synthesized. The excited state properties of 1 were investigated in detail using molecular orbital calculations and experimental methods. Upon excitation, complex 1 shows NIR phosphorescent emission around 680 nm. Interestingly, the complex can be excited with long wavelength around 610 nm. Such long-wavelength excitation can reduce the background emission interference and improve the signal-to-noise ratio. Furthermore, the selective binding between boron atom and F⁻ can give rise to the quenching of emission and realize the near-infrared phosphorescent sensing for F⁻. We wish that the results reported herein will be helpful for the further design of excellent near-infrared phosphorescent probes based on heavy-metal complexes.

F⁻ sensor, iridium(III) complex, NIR-infrared, phosphorescent, triarylboron

1 Introduction

Fluoride ion (F) plays an essential role in the health, medical, and environmental sciences [1–6]. Hence, it is very important to develop excellent probes for F⁻. Up to now, a large number of fluorescent probes based on organic luminophores have been designed to detect this important analyst [7–13], owing to its high sensitivity, easy visualization, and short response time for detection. In most cases, the binding sites of the probes for F⁻ consist of amide, urea, thiourea, guanidinium, or pyrrole functionalities that are capable of hydrogen bonding with F⁻ [14–17]. The selectivity of the probes based on this strategy is, however, often not good. Thus, it is very meaningful to exploit new strategies to design fluorescent probes for sensing F⁻ with high selectivity. And some excellent F^- receptors and probes have been reported [18–21]. Due to the Lewis acidity of boron center, triarylboranes with bulky aryl substitutes can react with small nucleophilic anions including F^- to afford fluoroborate anions. The bulky aryl substitutes, such as mesityl group, play a very important role in governing the selectivity of triarylborane receptors for small F^- . In addition, triarylborane derivatives exhibit relatively intense fluorescent characteristics due to the conjugation of $p_{\pi}(B)$ with the π -electron system in the aryl group ($p_{\pi}(B)$ - π conjugation), giving rise to unique electronic structures. In view of these, luminescent triarylborane derivatives as F^- probes have received widespread research interest recently [22–24].

Up to now, the signal of most reported fluorescent probes is visible light. As we all know, the probes with a nearinfrared (NIR) optical response could avoid interference from endogenous chromophores and would be more useful in complex systems, such as biological system [25, 26].

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Moreover, they can be operated with inexpensive and compact NIR diodes, lasers or light-emitting diodes [26]. When applied in biological systems, the light in NIR region around 650–900 nm is poorly absorbed by biomolecules, and it can penetrate deeply into tissues. Furthermore, there is also less autofluorescence in this region, and so the characteristics of these dyes are favorable for *in vivo* imaging. Hence, it is a very important topic to develop NIR dyes applied in sensing and bioimaging.

Currently, most reported or commercial NIR probes are based on organic luminophores. In addition to organic luminophores, luminescent metal complexes are another important class of probe materials [27-33]. Among them, heavy-metal complexes with phosphorescent emission are one important kind of luminescent metal complexes due to their advantageous photophysical properties, such as the sensitivity of emission properties to changes in the local environment, evident Stokes shifts for easy separation of excitation and emission, significant single-photon excitation in the visible range and relatively long lifetimes compared to those of purely organic luminophores. The advantageous phosphorescent emission is beneficial for chemical or biological detection. Introducing dimesitylboryl (Mes₂B) groups into the ligands of heavy-metal complexes can realize phosphorescent detection for F^- through the specific interaction of boron atoms with F⁻, which can induce variations in the excited state properties of heavy-metal complexes. More recently, several phosphorescent probes for F⁻ based on heavy-metal complexes, such as Ir(III), Pt(III) and Re(I) complexes containing Mes₂B group have been reported by us and other groups [34–41]. However, no NIR phosphorescent probe for F^- based on this design strategy has been reported up to now.

In order to realize the near-infrared phosphorescent F probe, two points should be considered. One is that the probe should contain the receptor for F⁻, such as Mes₂B group. The other is that the conjugation length of ligands should be increased in order to shift the emission wavelength to the NIR region. Cationic Ir(III) complexes with two cyclometalated C^N ligands and one neutral N^N ligand are excellent phosphorescent materials. Their excited state properties can be determined by both C^N and N^N ligands. Thus, it is very convenient to design NIR phosphorescent probe based on cationic Ir(III) complexes by modifying the chemical structures of both C^N and N^N ligands. The excited state energy level of complexes can be decreased by extending the conjugation length of both C^N and N^N ligands, inducing the significant red-shift of emission wavelength. In addition, the receptor for the analyte can be introduced into C^N or N^N ligands to realize the detection. Herein, we designed and synthesized a novel cationic Ir(III) complex $[Ir(Bpq)_2(quqo)]PF_6$ (1) with Mes₂B groups on the C^N ligands (Bpq) (see Scheme 1). On the one hand, Mes₂B groups can act as the receptor for F⁻. On the other hand, the conjugation length of C^N ligand can be increased through the $p_{\pi}(B)$ - π conjugation, inducing the decrease of energy level and red-shift of emission wavelength. Furthermore, 2-(quinolin-2-yl)quinoxaline (quqo) with low energy level was chosen as N^N ligand in order to



Scheme 1 The synthetic route of complex 1.

shift the emission wavelength to the longer region [42]. Because of the synergetic effect of N^N ligand quqo and C^N ligand Bpq, complex **1** showed a near-infrared phosphorescent emission. The selective interaction of boron and F^- can induce the variation in emission, realizing the NIR phosphorescent probe for F^- .

2 Experimental

2.1 General

NMR spectra were recorded on a Bruker Ultra Shield Plus 400 MHz NMR instruments (¹H: 400 MHz, ¹³C: 100 MHz). Mass spectra were obtained on a Thermo Scientific ESI-MS spectrometer. The UV-vis absorption spectra were recorded on a Shimadzu UV-3600 UV-vis-NIR spectrophotometer. Lifetime studies were performed by an Edinburgh LFS-920 spectrometer with a hydrogen-filled excitation source. The data were analyzed by iterative convolution of the luminescence decay profile with the instrument response function using a software package provided by Edinburgh Instruments. Photoluminescent spectra were measured using a RF-5301PC Spectrofluorophotometer. The elemental analysis was performed using Vario Macro apparatus (Germany). The quantum efficiency was determined by exciting the sample at 400 nm with the use of fac-Ir(ppy)₃ (fac-tris(2-phenylpyridine) iridium) as the standard ($\Phi = 0.86$) in CH₂Cl₂ solution [43].

2.2 Computational details

The ground-state and the lowest-lying triplet excited-state geometries were optimized by density functional theory (DFT) with Becke's LYP (B3LYP) exchange-correlation functional and the unrestricted B3LYP (UB3LYP) approach, respectively. On the basis of ground- and excited-state optimization, the time-dependent DFT (TDDFT) approach associated with the polarized continuum model (PCM) in dichloromethane (CH₂Cl₂) media was carried out to obtain the vertical excitation energies of singlet (S_n) and triplet (T_n) states. The calculation was performed using the Gaussian 03 suite of programs [44]. The LANL2DZ basis set was used to treat the iridium atom, whereas the 6-31G* basis set was used to treat all other atoms. The contours of the highest occupied molecular orbitals and lowest unoccupied molecular orbits (HOMOs and LUMOs) were plotted.

2.3 Materials

All starting materials and reagents, unless otherwise specified, were purchased from commercial suppliers and used without further purification. All solvents were purified before use.

2.4 Synthesis

2-(4-Bromophenyl)quinoline (Brpq), 2-(4-(dimesitylboryl)phenyl)-quinoline (Bpq), and 2-(quinolin-2-yl)quinoxaline (quqo) were prepared according to the literature procedures, [34, 42] and the synthetic route is shown in Scheme 1.

Synthesis of complex 1

Complex 1 was synthesized through a standard two-step procedure according to the literature method. A mixture of 2-ethoxyethanol and water (3:1, v/v) was added to a flask containing $IrCl_3 \cdot 3H_2O$ (1 mmol) and Bpq (2.5 mmol). The mixture was refluxed for 24 h. After cooling, the orange solid precipitate was filtered to give crude cyclometalated Ir(III) chloro-bridged dimer. The solution of cyclometalated Ir(III) chloro-bridged dimer (0.079 mmol) and quqo (0.158 mmol) in CH₂Cl₂/MeOH [30 mL, 2:1 (v/v)] was heated to reflux. After 4 h, the black solution was cooled down to room temperature and then a 10-fold excess of potassium hexafluorophosphate was added. The suspension was stirred for 2 h and then was filtered to remove insoluble inorganic salts. The solution was evaporated to dryness under reduced pressure. It was chromatographed by using CH₂Cl₂/acetone (50:1) to afford black solid in a 70% yield. ¹H NMR (400 MHz, CDCl₃): $\delta = 9.41$ (s, 1H), 8.58 (d, J = 8.6 Hz, 1H), 8.16 (d, J = 8.6 Hz, 2H), 7.85–7.94 (m, 3H), 7.43–7.75 (m, 10H), 7.24-7.36 (m, 4H), 7.14-7.17 (m, 2H), 6.93-7.03(m, 2H), 6.98 (t, J = 7.9 Hz, 1H), 6.68 (t, J = 7.9 Hz, 1H), 6.60 (s, 4H), 6.48 (s, 4H), 6.35 (s, 1H), 6.21 (s, 1H), 2.30 (s, 6H), 2.19 (s, 6H), 1.61–1.66 (m, 24H); ¹³C NMR (101 MHz, CDCl₃): δ = 169.30, 168.84, 156.92, 153.61, 148.41, 147.78, 147.39, 147.27, 147.12, 146.55, 146.29, 144.77, 144.19, 141.85, 140.74, 140.35, 140.26, 140.22, 139.68, 139.59, 139.18, 138.36, 138.33, 132.41, 131.81, 131.45, 131.17, 130.84, 130.67, 130.58, 130.10, 129.32, 129.22, 128.83, 128.00, 127.85, 127.60, 127.55, 127.41, 127.31, 127.05, 126.02, 125.57, 124.91, 123.92, 120.95, 117.10, 116.54, 23.10, 23.05, 21.43, 21.34; MS (ESI-MS) [m/z]: 1354.25 $(1-PF_6)^+$; Anal calcd (%) for $C_{83}H_{73}N_5F_6B_2PIr$: C 66.49, H 4.91, N 4.67. Found: C 66.15, H 4.92, N 4.69.

3 Results and discussion

3.1 Synthesis and characterization of complex 1

Scheme 1 shows the synthetic route of complex **1**. The N^AN ligand quqo and cyclometalated C^AN ligand Bpq were prepared according to the literature procedures [34, 42]. The dinuclear cyclometalated Ir(III) chloro-bridged precursor $[Ir(Bpq)_2Cl]_2$ with Bpq as cyclometalated ligand was synthesized using the same method as that reported by Nonoyama [45]. The cationic Ir(III) complex was then routinely synthesized with a high yield of 70% by reacting cyclometalated Ir(III) chloro-bridged precursor with ligand quqo, and the synthetic route is shown in Scheme 1. The structure of

complex **1** was characterized by ¹H NMR spectroscopy, ¹³C NMR spectroscopy, elemental analysis, and ESI-MS spectrometry.

3.2 Photophysical properties of complex 1

The UV-vis absorption spectrum of complex 1 was investigated and is shown in Figure 1. The complex displayed intense absorption bands below 400 nm, moderately intense absorption bands in the range of 400-525 nm, and weak absorption bands above 525 nm. The absorption bands at λ < 400 nm related to the singlet ligand-centered π - π * transitions from Bpg and gugo ligands. According to the previous study, both ligand-to-ligand charge transfer (LLCT) and metal-to-ligand charge transfer (MLCT) transitions may contribute to the visible-region absorption bands. Therefore, we believe that the moderately intense absorptions at ca. 400-525 nm and weak absorptions above 525 nm may receive contributions from singlet and triplet LLCT and MLCT for complex 1. Interestingly, low-energy absorption bands around 610 nm were observed evidently, providing the possibility of detection using long-wavelength excitation

To better understand the absorption properties of 1, DFT and TDDFT calculations for this complex were performed employing the Gaussian-03 package. The ground-state and the lowest-lying triplet excited-state geometries were optimized by DFT with B3LYP exchange-correlation functional and UB3LYP approach, respectively. On the basis of ground- and excited-state optimization, TDDFT approach associated with the PCM in CH₂Cl₂ media was carried out to obtain the vertical excitation energies of singlet (S_n) and triplet (T_n) states. From the calculated results, no obvious bond length differences between the lowest singlet state and the lowest triplet state are observed for 1, and the frontier molecular orbital compositions of excited-state are similar to those of ground state. The frontier molecular orbital compositions and energy levels are given in Table 1 and Table 2. According to the calculated oscillator strength and energy level, the weak absorption band at 610 nm originates



Figure 1 Absorption and PL spectra ($\lambda_{ex} = 450$ nm) of 1 (20 μ M) in CH₂Cl₂ solution.

Table 1Calculated energy levels of the singlet states and lowest tripletstate for complex 1

State	Excitation	$E_{\rm cal}^{a)} ({\rm eV})$	$\lambda_{cal}^{a)}(nm)$	$F^{b)}$
S_1	HOMO→LUMO (70%)	1.97	630	0.0020
S_2	HOMO→LUMO (57%) HOMO-9→LUMO (30%)	2.50	497	0.0035
S_3	HOMO-2→LUMO (46%) HOMO-10→LUMO (47%)	2.58	481	0.0004
S_4	HOMO→LUMO+1 (65%) HOMO-1→LUMO (14%)	2.61	475	0.0568
S_5	HOMO→LUMO+1 (19%) HOMO-1→LUMO (59%)	2.61	474	0.0050
S_6	HOMO-2→LUMO (47%) HOMO-10→LUMO (43%)	2.64	470	0.0011
S_7	HOMO→LUMO+2 (67%)	2.68	463	0.0074
S_8	HOMO-2→LUMO (47%) HOMO-10→LUMO (43%)	2.73	454	0.0008
S_9	HOMO-5→LUMO (57%) HOMO-4→LUMO (34%)	2.74	453	0.0009
\mathbf{S}_{10}	HOMO-6→LUMO (55%) HOMO-5→LUMO (33%)	2.75	451	0.0054
T_1	HOMO→LUMO (70%)	1.46	849	-

a) E_{cal} : calculated energy, λ_{cal} : calculated wavelength; b) f: calculated oscillator strength.

from S₁ state, namely HOMO \rightarrow LUMO (70%) transitions. From the corresponding molecular orbital distributions (shown in Table 2), we can see that the HOMO distribution primarily resides on the Mes₂B fragments of ligand Bpq and the LUMO distribution is dominated by N^N ligand quqo. So, this band can be mainly assigned to the LLCT transition from the Mes₂B group on C^N ligands to the N^N ligand quqo. The extended conjugation length of N^N ligand, which decreases the LUMO energy level, is responsible for the long-wavelength absorption. The moderately intense absorption band at 450 nm can be attributed to S₄ state from HOMO-LUMO+1 (65%) and HOMO-1-LUMO (14%) transitions according to the calculated oscillator strength and energy level. This band can be assigned to a mixture of the intraligand charge transfer (ILCT) transition from Mes₂B group to 2-phenylquinoline moiety on C^N ligands and LLCT transition from Mes₂B group to N^N ligand quqo.

The photoluminescence (PL) spectrum of complex 1 in CH₂Cl₂ solution was measured. From Figure 1, we can see that complex 1 showed NIR emission around 680 nm. The observed emission lifetime of 1 in air-balanced CH₂Cl₂ solution is 0.2 µs, indicating the phosphorescent nature of the emission. At room temperature in CH₂Cl₂ solution, upon excitation at different wavelength of 379, 450 and 613 nm respectively, complex 1 showed the similar NIR phosphorescence. So, there is no dependence of emission band of complex 1 on excitation wavelength. With fac-Ir(ppy)₃ as the standard, we measured the room-temperature phosphorescent quantum yields (Φ) of complex **1** in CH₂Cl₂ solution. Complex 1 shows quantum efficiency of 0.02. Furthermore, the excitation spectrum of complex 1 monitored at 680 nm was investigated. As shown from the excitation spectrum (see Figure 2), we can see that the major excitation peak is located at 613 nm, further demonstrating the possibility of detection using long-wavelength excitation. And such long



Figure 2 The emission ($\lambda_{ex} = 610 \text{ nm}$) and excitation spectra ($\lambda_{em} = 680 \text{ nm}$) of complex **1** in CH₂Cl₂ solution.

excitation wavelength is beneficial for the detection in the complex system. In order to clarify the origin of emission at 680 nm, the energy of triplet states was calculated. The calculated maximum emission band (T_1 state) of **1** is centered at 849 nm, which exhibits a red-shift of 169 nm compared to the experimental value (680 nm), and can be assigned to

 Table 2
 Calculated molecular orbits of complex 1

the HOMO→LUMO transition. The discrepancies between the calculated values and experimental data may be attributed to DFT method, which generally gives a smaller HOMO-LUMO gap for molecules and thus generates smaller excitation energies, especially for larger conjugated systems and charge-transfer complexes in excited states [46, 47]. According to the HOMO and LUMO distributions shown in Table 2, we can conclude that the NIR emission of complex 1 can be assigned to the LLCT transition from Mes₂B groups to N^N ligand quqo.

One of the challenges in the design of luminescent probes, particularly those aimed at complex system detection and practical application, is to shift the excitation wavelength from UV region to long-wavelength range because many background fluorescence cannot be excited by long wavelength light and long wavelength excitation requires cheaper optical cells and optics. Herein, we chose blue-emitting ligand Bpq as fluorescent noise to demonstrate the advantage of long excitation and emission wavelengths of complex 1 applied in detection. We mixed Bpq and complex 1 together in CH_2Cl_2 solution and then measured its emission spectra excited at UV wavelength of 360



nm and visible light of 610 nm, respectively. The emission spectra are shown in Figure 3. From Figure 3, we can see that the solution showed strong blue emission at 425 nm from Bpq and very weak emission at 680 nm from complex 1 when excited at 360 nm. This indicated that the target phosphorescent signal at 680 nm was contaminated by the fluorescent noise of Bpq. In order to purify the signal, long-wavelength excitation of 610 nm was applied. From Figure 3 we can see that the sample effectively eliminates the fluorescent noise, and thus gives the clean phosphorescent signal at 680 nm. Hence, the reduced background emission interference and improved signal-to-noise ratio were realized for complex 1 utilizing the long wavelength excitation.

3.3 Optical responses of complex 1 to F

In view of specific interaction between F^- and boron center, the response of complex 1 to F^- was investigated through UV-vis absorption and emission spectra. Figure 4 shows the variation in the absorption spectra of complex 1 upon the addition of F^- . The absorbance peaks at 365 and 613 nm decreased gradually. The variation in the PL spectra with 613 nm as excitation wavelength is shown in Figure 5. Upon addition of F^- to the CH₂Cl₂ solution of complex 1, the NIR phosphorescent emission intensity around 680 nm decreased gradually, and completely quenched eventually. Hence, complex 1 realizes the ON-OFF-type NIR phosphorescent detection for F^- .

As shown by emission titration curves in Figure 6, after the addition of approximately 2 equivalents of F^- , the emission intensity ratio of I/I_0 at 680 nm reaches the saturated point. Considering that there are two boron centers in one complex molecule, it is possible for complex 1 to form a 1:2 complex with 2 equivalent of F^- because the two Mes₂B groups are electronically separated in the ground state and spatially distant from each other. The stability constants for the binding of one and two F^- to complex 1 (H) in CH₂Cl₂ solution were determined from the emission titration data.



Figure 3 The emission spectra of mixed free ligand Bpq (blue emission) and complex 1 in CH₂Cl₂ solution with different excitation wavelengths.



Figure 4 Change in the UV-vis absorption spectra of complex 1 (20 μ M) in a CH₂Cl₂ solution with various amounts of F⁻.



Figure 5 Change in the emission spectra of complex 1 (20 μ M) in CH₂Cl₂ solution with various amounts of F⁻ ($\lambda_{ex} = 613$ nm).



Figure 6 Phosphorescent titration profile (dot) and its fitting curve (solid line) of emission intensity at 680 nm versus the equivalent of F^- of i complex **1** in CH₂Cl₂ solution (20 μ M).

Fitting the emission changes at wavelengths of 680 nm according to ref. [48], the binding constants (K_1 and K_2) of complex **1** to F⁻ were determined to be 2.64×10^6 and 2.12×10^4 M⁻¹, respectively (see Figure 6), which are similar to the values reported previously for boryl-based fluorescent and phosphorescent receptors [11, 34].

To better understand the sensing mechanism of complex 1 to F^- , the lowest-lying triplet excited-state geometry was



Table 3 Calculated molecular orbits of 1-2F-

optimized by DFT with UB3LYP approach. On the basis of excited-state optimization, TDDFT approach associated with the PCM in CH₂Cl₂ media was carried out to obtain the vertical excitation energies of triplet (T_n) states. The HOMO and LUMO distributions are shown in Table 3. According to the calculation results, the T_1 state for the adduct 1-2F⁻ originates from HOMO→LUMO (70%) transition. The HOMO distribution primarily resides on the Mes₂B-F⁻ fragments, and the LUMO distribution resides on the N^N ligand (quqo). Maybe the binding of boron center with F⁻ blocks the charge transfer from Mes₂B groups to N^N ligand responsible for the emission in free 1 and changes the excited-state property of complex, quenching its emission.

3.4 Selectivity

The binding studies of probe **1** were extended to other anions in order to investigate the selectivity. As shown in Figure 7 from the absorption spectra, only the addition of $F^$ results in prominent change of A/A_0 at 367 nm, whereas the addition of other anions (Cl⁻, Br⁻, ClO⁻₄, NO⁻₃, H₂PO⁻₄, CH₃COO⁻) causes little changes. From the emission spectra (see Figure 8), the addition of most other anions caused little changes, and only I⁻ showed some change in emission spectra. Therefore, probe **1** displayed a high selectivity in sensing F⁻. Similarly, achieving high selectivity for the an-



Figure 7 UV-vis spectral response of complex **1** (20 μ M) in the presence of various anions (4 equiv) in CH₂Cl₂ solution. Bars represent the ratio of absorbances at $\lambda = 367$ nm (A/A_0). Black and red represent A/A_0 before and after the addition of anions, respectively. Blue bar represents A/A_0 after addition of F⁻ to the solution of complex **1** containing other anions. 1 F⁻; 2 Cl⁻; 3 Br⁻; 4 l⁻; 5 NO₃; 6 H₂PO₄; 7 CH₃COO⁻; 8 ClO₄.



Figure 8 Emission response of probe **1** (20 μ M) in the presence of various anions (4 equiv) in CH₂Cl₂ solutions. Bars represent the ratio of emission intensity at $\lambda = 680$ nm (*III*₀). Black and red represent *III*₀ before and after the addition of anions, respectively. Blue bar represents *III*₀ after addition of F⁻ to the solution of complex **1** containing other anions. 1 F⁻; 2 Cl⁻; 3 Br⁻; 4 l⁻; 5 NO⁻; 6 H₂PO⁻; 7 CH₃COO⁻; 8 ClO⁻.

alyte of interest over a complex background of potentially competing species is a challenge in probe development. Thus, the competition experiment was also carried out by adding F^- to the solutions of complex **1** in the presence of other anions. As shown in Figures 7 and 8, whether in the absence or presence of other anions, obvious spectral changes were observed for complex **1** upon addition of F^- , indicating that the sensing of F^- by complex **1** is hardly affected by other anions.

4 Conclusions

In summary, we designed and synthesized a novel NIRemitting cationic Ir(III) complex with C^N ligands containing dimesitylboryl groups and extended N^N ligand. Upon photoexcitation, the complex shows NIR phosphorescent emission around 680 nm. Interestingly, the complex can be excited with long wavelength around 610 nm, which can reduce the background emission interference and improve the signal-to-noise ratio. Through the selective binding between boron centers and F⁻, an ON-OFF-type NIR phosphorescent probe was realized. Considering the advantages of near-infrared and phosphorescent signals in sensing, we wish that the results reported herein will be helpful for the further design of excellent near-infrared phosphorescent probes based on heavy-metal complexes.

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