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Synthesis and Spectroscopic Characterization of Novel Fluorescent quinolinyl hydrazone for Latent Fingerprint and Anticounterfeiting Applications

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Abstract

The fluorescent quinolinyl hydrazone (**QH**) development for latent fingerprint and anticounterfeiting detection under UV illumination has not yet been adequately researched. In this sense, this work presents the fabrication and characterization of **QH** for latent fingerprint and security ink applications. The fluorescence properties of **QH** were studied in different surrounding mediums (Powder, PVB, silica, and DMF). **QH** exhibited intensive greenish-blue luminescence with spectacular visual emission under unharmful UVA excitation. Based on the highly luminescent character of **QH**, latent print details, including their characteristic three levels, have been identified from various forensic substrates (non-porous, semi-porous, and porous). **QH** has, moreover, been used to develop luminescent ink for anti-counterfeiting applications.

Keywords: Fluorescent; Latent fingerprint; Quinolinone; Luminescence; Anticounterfeiting.

1. Introduction

The friction ridge skin on hands leaves impressions known as fingerprints when they contact with an object's surface. Since the late 19th century, when friction ridge skin patterns were found to be both unique and invariant, fingerprints have been considered among the most significant pieces of evidence that may be used for individual identification [1,2]. Most of the time, external and sebaceous secretions from friction ridge skin were transfer to an item to generate fingerprints. These secretions are called latent fingerprints (LFPs) since they are seldom visible and require development techniques to visualize. Traditionally, powdering fingerprints, fuming cyanoacrylate, powder suspensions, and vacuum metal deposition are used to create LFPs on such objects. Since the early 20th century, the most often employed technique in crime scene analysis has been straightforward and reasonably priced fingerprint powdering. One of the main reasons is that it works incredibly well for fixed things that are difficult to return to forensic labs. Because of this, forensic investigators have been unrelenting in their hunt for novel, effective materials, such as fingerprint powders, which are progressively drawing attention from the fields of chemistry and materials science. Also, the development of LFPs is known to be successful when the contrast between the fingerprint area and background area is increased to a level where image sensors can detect it. Regarding fingerprint powdering, the principle is primarily implemented by exploiting the stickiness of fingerprint residues, which can draw fingerprint powder with distinct qualities (such as optical properties) in contrast to the background area. However, the real situation is much more intricate as three crucial factors must be considered. There are three layers of morphological features: the general pattern that shows the flow of papillary ridges, substantial ridge path variations (also called minutiae), and intrinsic or innate ridge forms. The interactions between powder particles and background area and fingerprint residues are determined by several factors, including surface functional groups, surface charge characteristics, particle shape, size distribution, and surface functional groups. These factors collectively determine how well a powder visualizes these features. The second requirement is that a fingerprint powder must contrast with the surrounding region; this is mostly related to the optical characteristics of object surfaces and fingerprint powders [3].

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In recent times, counterfeiting has affected every aspect of society, including government offices, industry, and the medical and financial sectors. Therefore, it is thought that the security of all these industries is a serious issue. This is because counterfeiting may pose risks to the safety of people's health, the economy, and society. The commercial and industrial sectors, as well as central banks, employ a variety of anti-counterfeiting techniques. Simple markers, holograms, security inks, etc. are examples of these techniques. A technique called visible photoluminescent security ink works by making the ink glow when exposed to UV light. In this field, numerous studies have been made about highly toxic, widely luminous, and costly nanoparticles that are soluble in hazardous media, like gold, CdS, and CdSe. Additionally, certain kinds of security inks that glow are unstable [4]. So, the researchers focus their attention on biocompatible materials with distinct optical, photoluminescent properties.

Quinolines are employed in drug design and discovery among the heterocyclic derivatives with nitrogen atoms because of their diverse biological actions [5, 6]. Quinolines have been shown to exhibit a variety of biological activities, including antitubercular, anti-HIV, anticancer, antimalarial, antihypertensive, anti-inflammatory and analgesic, antibacterial, anti-HIV, anti-cardiovascular activities, and inhibition of tyrosine kinase [7-10]. Nowadays, medications with quinoline backbones in their structures include ofloxacin, norfloxacin, ciprofloxacin, and sparfloxacin, all of which have been licensed for use in the treatment of different bacterial illnesses [5, 11]. Most studies concentrate on how quinoline derivatives affect biology. Thus, a new frontier in the field of forensic science and anti-counterfeiting is opened in this work by the distinct optical, photoluminescent, and bioactive features of materials based on quinolinone as activators.

Experimental:

2.1. Materials and Instrumentation

The synthesis needed extremely pure and high-grade analytical reagent components and solvents. Glacial acetic acid, dimethyl formamide (DMF), phosphorous oxychloride, Polyvinyl butyral (PVB), tetraethyl orthosilicate (TEOS), and hydrazine hydrate were acquired from Sigma-Aldrich and utilized exactly as supplied.

The Micro-analytical Central Laboratory at Cairo University used the Vario EL Element Analyzer to determine the proportion of hydrogen and carbon. The produced QH's melting point temperature was determined using a Stuart melting point device. Using KBr discs, a Nicolet 6700 FT-IR spectrometer captured the examined QH's FT-IR spectrum, which ranges 4000-400 cm-1. The fluorescence spectrum data and lifetime were detected using a Perkin Elmer LS55 luminescence spectrometer (USA). DMSO-d6 was used as a solvent while recording 1H-NMR (300 MHz) (75 MHz) spectra on Mercury 300BB or Gemini 300BB spectrometers (δ). Using a Shimadzu GC-2010 gas chromatography equipment mass spectrometer, mass spectra (70 eV) were acquired. Digital camera (Sony 80) was also used.

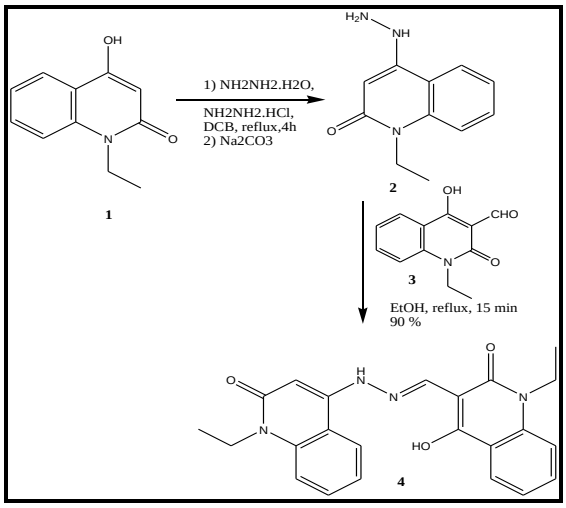
2.2. Synthesis of 1-Ethyl-3-[(1-ethyl-2-oxo-1,2-dihydroquinolin-4-yl)hydrazonomethyl]4-hydroxyquinolin-2(1H)-one (4) (QH)

A mixture of hydrazine compound 2 (2.03 g, 1 mmol) and aldehyde 3 (2.17 g, 1 mmol) in ethanol was refluxed for 15 min. The reaction mixture was cooled to room temperature and the precipitated solid was collected by filtration and dried to give **compound 4** in yield (3.62 g, 90%). IR (KBr, cm-1): νmax, 3211 (NH), 3416-2800 (OH), 3082 (C–Harom), 2983 (C–H_{aliph}), 1625 (C=O), 1603, 1579, 1446, 1352, 1249, 1139 and 751. ^{1}H NMR (300 MHz, DMSO-d6), δ: 1.19 (m, 6H, NCH_2CH_3), 4.26 (m, 4H, NCH_2CH_3), 5.90 (s, 1H, 3-H), 7.28-8.10 (m, 8H, two quinolinone ring), 8.96 (s, 1H, N=CH), 11.03 (s, 1H, NH disappeared by D_2O), 13.40 (s, 1H, OH disappeared by D_2O). MS, m/z (Ir%):403(28.14) (M^{+1}), 402 (100)(M^{+}), 385(74.23), 373(23.71), 356(17.58), 328(7.75), 252(18.25), 225(4.19), 215(62.98), 214(20.38), 189(17.33), 188(52.87), 187(51.31), 173(14.65), 146(12.37), 132(22.23), 120(16.80), 104(15.38), 77(30.66) Anal. Calcd. for $C_{23}H_{22}N_4O_3$(402.45): C, 68.64; H, 5.51; and N, 13.92 %. Found C, 68.62; H, 5.50; and N, 13.90 %.

2.3. Preparation of QH dispersed into amorphous silica

QH dispersed into a silica matrix was prepared with acid-catalyzed sol-gel process. In detail, TEOS was added to methanol and water solution in a molar ratio of 1.0: 10: 4.0, respectively in the presence of hydrochloric acid. The solution stirring at room temperature for 2 h. Then the appropriate amount of **QH** was dissolved in DMF to prepare a 10^{-3} M stock solution. 0.1 ml from **QH** was vigorously stirred with 10 mol of silica sol for 30 min at room temperature. The transparent sol was aged for 24 h

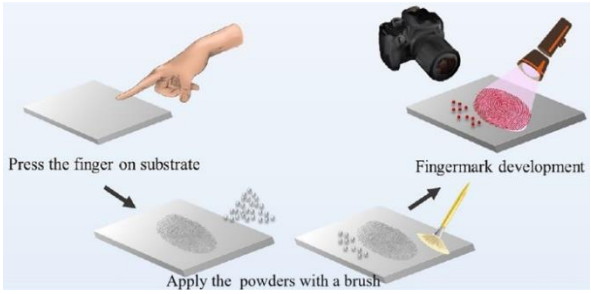
till the gel formed. The gel was dried at 80 ^{o}C for 6 h. The obtained powder was grounded and annealed at different temperatures (110, 240, 300, and 450 ^{o}C).



Scheme 1. Schematic representation of the synthesis of **QH**

2.4. Latent fingerprint detection

A healthy person's completely cleaned and laundered hands were used to collect LFPs, which were then carefully wiped and pressed on non-porous, semi-porous, and porous surfaces. LFPs were seen using highly PL intensity **QH**. The prepared sample was softly colored with a gentle brushing motion over the surfaces [4]. After that, a UVA light (4 W, 365 nm) was used to illuminate the substance and a digital camera was used to take pictures of the fingerprints (Scheme 2).



Scheme 2. The visualization of the latent fingerprint scheme

2.5. Anti-counterfeiting detection

The 10% wt of PVB was dissolved in absolute ethanol by ultrasonication technique for 30. An appropriate amount of **QH** was dissolved in a small amount of DMF and then mixed vigorously in an ultrasonic bath for 30 min with 10 ml of PVB solution to obtain a homogeneous luminous security ink. The resultant mixture was applied as a security ink in different surfaces.

Results and Discussion

3.1. Characterization of 1-Ethyl-3-[(1-ethyl-2-oxo-1,2-dihydroquinolin-4-yl)hydrazonomethyl]4-hydroxy-quinolin-2(1H)-one (4) (QH)

Quninolinyl hydrazine 2 was obtained by treating 4-hydroxy-1-ethylquinolin-2(1H)-one (1) with a mixture of hydrazine hydrate and hydrazine dihydrochloride. This method is a one-step greener, efficient, and facile route [**12**]. Condensation reaction of compound 2 with 3-formyl-4-hydroxyquinolinone 3 led to formation of 1-ethyl-3-[(1-ethyl-2-oxo-1,2-dihydroquinolin-4-yl)hydrazonomethyl]4-hydroxy-quinolin-2(1H)-one (**QH**) (**4**). The structure of the hydrazone compound **4** was inferred from its correct elemental analysis as well as ^{1}H NMR and IR spectra. The IR spectrum of **4** displayed characteristic absorption bands at ν 3211 (NH), and 3416-2800 (OH) cm $^{-1}$. ^{1}H NMR spectrum clearly showed the disappearance of both the amino which appeared in compound 2 at δ 4 ppm and formyl functions which appeared in compound 3 at δ 10 ppm. Moreover, the appearance of two specific singlet signals at δ 5.90 for the proton at position 3 in hydrazone compound **4** and 8.96 for the proton of N=CH in compound **4** results from the condensation of hydrazine compound 2 with formyl compound 3 as shown in **Fig. 1**. Also, another two singlet signals are exchangeable on the addition of D_2O at δ 11.03 and 13.40 due to the proton of NH and OH, respectively (**Fig. 2**). In respect to a mass spectrum (**Fig. 3**) refers to the molecular ion peak at 402 as the base peak.

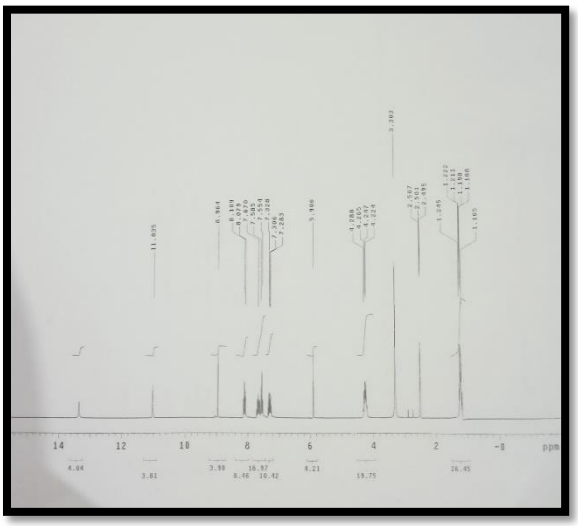


Fig. 1. ^{1}H NMR for compound 4 in DMSO.

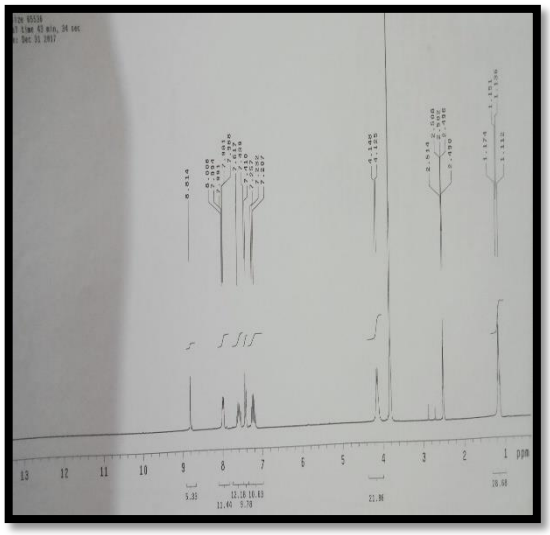


Fig. 2. ^{1}H NMR for compound 4 in DMSO and D_2O.

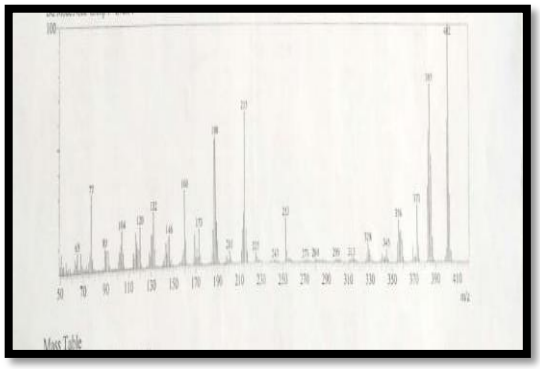


Fig. 3. Mass spectrum for compound 4

3.2. Photoluminescence properties

The fluorescence properties of **QH** were studied in the different surrounding mediums (Powder, PVB, silica, and DMF). Fig. 4 shows the fluorescence excitation and emission spectra of **QH** in a powder and dispersed in PVB, silica, and DMF. The **QH** emits a greenish-blue color which is visualized under UVA illumination. Both maximum excitation and emission spectra of **QH** as a solid powder, dispersed into PVB and silica showed a significant red shift in comparison with **QH** in DMF. The emission maximum of **QH** takes the following order in redshift PVB (493 nm) ~ Silica (491 nm) > Solid powder (473 nm) > DMF (433 nm). Dispersion of **QH** in rigid hosts such as PVB and silica induces the formation of planar form from **QH** than in the case of solid and DMF solution. The presence of the hydroxyl group in **QH** leads to the formation of intermolecular hydrogen bonding, in addition to the intermolecular hydrogen bonding interaction between the C—O and –NH groups. This leads to adopting a more coplanar **QH** form and increases π-π overlap, especially in PVB and silica hosts [13]. Moreover, the effect of annealing temperature on the fluorescence excitation and emission of **QH** dispersed into silica were also studied (Fig. 5). **QH** dispersed into silica shows strong excitation and emission with a maximum at 404 nm and 491 nm, respectively, when annealed at 110^{o}C. This emission band is related to π-π* transition in **QH**. The excitation and emission intensity of **QH** shows a significant decrease with slight blue shift as the annealing temperature reaches to 240^{o}C due to decay of **QH**. At 300^{o}C, the old emission and excitation bands were completely disappeared and a new strong excitation and emission bands with maximum at 372 nm and 437 nm were observed. Appearance of new band in excitation spectra means formation of new luminous compound. This new band is related to transformation of **QH** to carbon dots confined into silica host. This carbon dots characterized with blue emission color. It was reported that dispersion of carbon source such as **QH** into silica followed by annealing treatment is a universal method for production of CD/SiO_2 [14]. This carbon dot emission band was start to thermally bleaching at higher annealing temperature (450^{o}C) (Fig. 5).

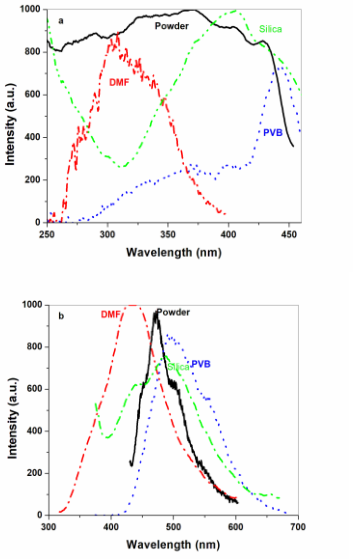


Fig. 4. The excitation (a) and emission (b) spectra of **QH** in as solid powder, dispersed into PVB, silica, and DMF.

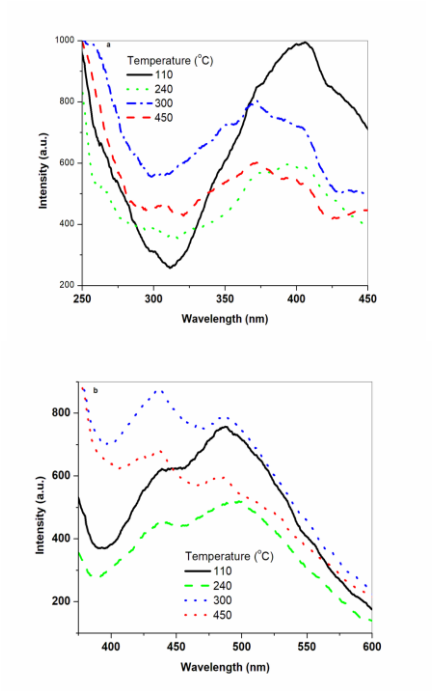


Fig. 5. The excitation (a) and emission (b) spectra of **QH** dispersed into silica at different annealing temperatures.

4. Applications

4.1. Fingerprint detection character.

Under biocompatible UVA light, the greenish blue **QH** was tested as a latent fingerprint sensor on a variety of surfaces, including smooth, fluorescent, non-penetrative, or non-porous (CD), semi-porous (yellow and black paper), and porous (fabric wool). Latent print images with no autofluorescence background, great contrast, sharpness, and clarity that were stained with **QH** from different previous surfaces are shown in Fig. 6. Because of the strong binding affinity between the free functional carbonyl groups of **QH** and the functional groups (carbonyl, phenolic) of latent secretions, the fluorescent marker **QH** has been successfully used as a fingerprint labeling agent. Consequently, fingermark ridges and fluorescent marker **QH** have a strong adhesive force.

Fig. 7 shows the classification of the fingerprint ridge pattern at different levels (1-3) under UVA illumination. Level 1 minutiae display the Arch. Level 2 minutiae were noted to have bifurcation, ridge end, and pores. Level 3 minutiae had line width, path deviation, and dots [(15) 24, (16) 28]. Furthermore, it was noted that in normal light, the latent print features (levels 1-3) remained uncleared (Fig. 6).

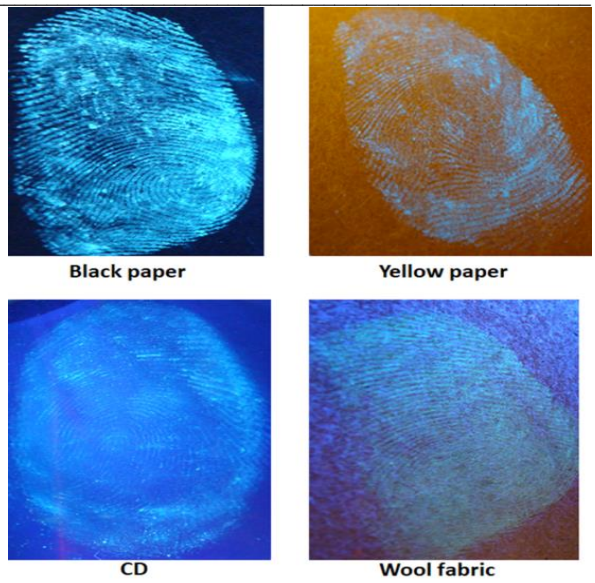


Fig. 6. Digital photographs of FPs of different nonporous surfaces such as (a) black paper (b) black paper, (c) CD and (d) wool fabric developed by of **QH** fluorescent sensor under UVA illumination.

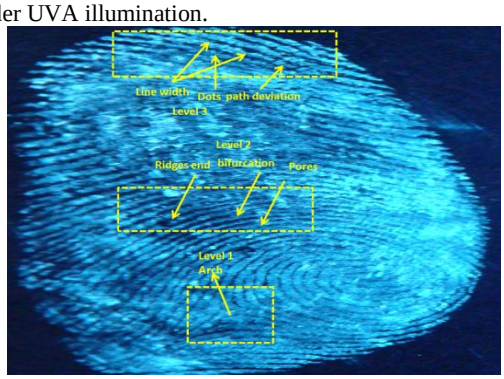


Fig. 7. Various latent fingerprint ridge characteristics on black paper developed using QH fluorescent sensor under UVA illumination

4.2 Anti-counterfeiting application

PVA has been combined with the new **QH** fluorescent material to create a highly transparent solution. Under both normal and UVA nm illumination, this fluorescent substance has been employed as dip pen writing ink (Fig. 8). Under typical lighting conditions, the writing inks made from prepared fluorescent material (QH) were found to be unclear indifferent materials. Under UVA lighting, images of pure and strong greenish blue color have emerged on surfaces such as writing multi colored card, drug cover, black paper and medical tube. The facts above supports the use of prepared samples as anti-counterfeiting tools even more.

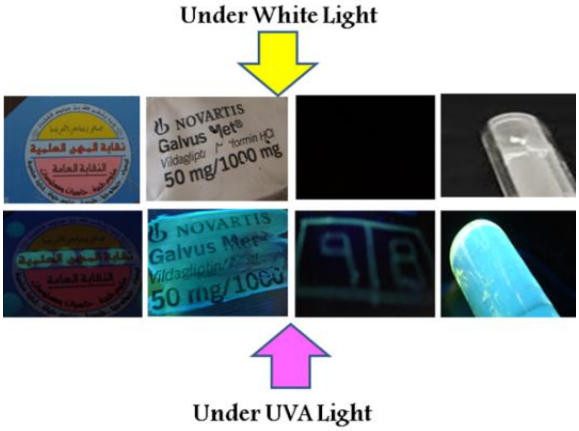


Fig. 8. Anti-counterfeiting labels plated with **QH** fluorescent security ink under white light and 365 nm UVA light.

5. Conclusions

The fluorescent quinolinyl hydrazone (QH) has been fabricated for latent fingerprint and anticounterfeiting applications. QH was characterized by various techniques via elemental analysis, FT-IR, 1H-NMR, and mass spectra. The photoluminescence of QH was measured in different media. QH shows greenish blue luminescent under unharmful UVA excitation. A rigid matrix such as PVA and silica stabilizes the coplanar form. Based on the highly luminescent character of QH, latent print details, including their characteristic three levels, have been identified from various forensic substrates (non-porous, semi-porous, and porous). Moreover, luminous ink for anti-counterfeiting applications has been developed using QH.

6. Conflicts of interest

- The authors declare that they have no conflict of interest.
- This work was not funded from any sources
- all authors at the faculty of education-Ain Shams University are agree to submit this work for journal of photoluminescence research.
- Authors whose names appear on the submission have contributed sufficiently to the scientific work and therefore share collective responsibility and accountability for the results.

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