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Photoluminescence Measurement of Triplet Sensitizer-Emitter Solution Using a Customized 3D-Printed Sample Holder

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ABSTRACT

This study explores the photoluminescence (PL) measurement of triplet sensitizer-emitter (TSE) solutions using a custom 3D-printed sample holder, within the context of triplet-triplet annihilation based molecular photon upconversion (TTA-UC) systems targeting the Vis-to-UV spectral region. TTA-UC converts low-energy visible photons to higher-energy ultraviolet (UV) photons, holding promise for solar energy harvesting and photonics applications. Two TSE couples, 4CzIPN/TP and 4CzIPN/QP, were investigated, and their upconverted fluorescence spectra showed peaks at 344 nm and 354 nm / 370 nm, respectively, confirming efficient upconversion capabilities. The 3D-printed sample holder facilitated reproducible PL measurements, enabling the calculation of quantum yields (Φ_{UC}). The 4CzIPN/TP and 4CzIPN/QP couples exhibited low quantum yields (0.028% and 0.043%, respectively), suggesting the need for improved deoxygenation methods to enhance the triplet-triplet annihilation process and overall quantum efficiency. Despite modest yields, successful UV upconverted fluorescence observation underscores the feasibility of the Vis-to-UV TTA-UC system. This study provides insights into TTA-UC optimization and demonstrates the utility of the 3D-printed sample holder for affordable and precise PL measurements, paving the way for future advancements in photonics and solar energy applications.

Keywords: *Photoluminescence, 3D-printing, sensitizer-emitter, triplet-triplet annihilation based molecular photon upconversion (TTA-UC), upconversion system, Vis-to-UV*

1. INTRODUCTION

Harnessing solar energy effectively necessitates the utilization of advanced materials, such as solar cells, dye-sensitized solar cells (DSSC),[1]–[4] and specialized light-absorbing materials,[5] which can efficiently convert sunlight into usable energy. The TTA-UC systems, with their capability to upconvert low-energy photons, complement these materials by enhancing their overall light absorption and conversion efficiencies.The study of triplet-triplet annihilation based molecular photon upconversion (TTA-UC) has emerged as a promising approach for efficiently converting low-energy photons into higher-energy ones [6], [7]. TTA-UC systems typically involve a triplet sensitizer that absorbs low-energy photons and transfers the energy to an annihilator, resulting in the emission of upconverted fluorescence. Accurate measurement of the upconverted fluorescence intensity is crucial for understanding the quantum efficiency of these systems and optimizing their performance for various applications. In this regard, photoluminescence (PL) measurements play a significant role, providing valuable insights into the behavior of triplet sensitizer-emitter (TSE) solutions.

The field of photoluminescence research, particularly in measuring triplet sensitizer-emitter solutions, is often hampered by the complexities associated with traditional sample holders. Typically constructed from sophisticated and expensive metal construction setups, these holders necessitate intricate configurations involving multiple optical cables and precise lens alignments, making the measurement process labor-intensive and prone to errors. To streamline this procedure and minimize the steps involved in accurate measurement, our research introduces a solution: a 3D-printed sample holder designed to mount directly onto the opening of a light detector. This sample holder makes sure the TSE solution and notch filter are always in the same place. It also keeps a constant distance between the light source and the light detector. It reduces chances of different measurement outcomes and makes the results more dependable.

The present study focuses on the PL measurement of TSE solutions containing 4CzIPN coupled with TP and 4CzIPN coupled with QP under varying excitation intensities. The TTA-UC mechanism of the couple of 4CzIPN (sensitizer) and TP/QP (annihilator) along with their chemical structures are shown in Figure 1. The TTA-UC quantum yields of these couples are calculated and analyzed, providing valuable information on the efficiency of upconverted fluorescence generation. The investigation of Vis-to-UV TTA-UC systems [7]–[11] holds significant importance in harnessing wasted spectrum within the visible region and efficiently utilizing it for solar energy applications and other photonics-related fields [12],[13]. The results obtained from this study can pave the way for optimizing TTA-UC systems and fostering their potential integration into diverse technological applications.

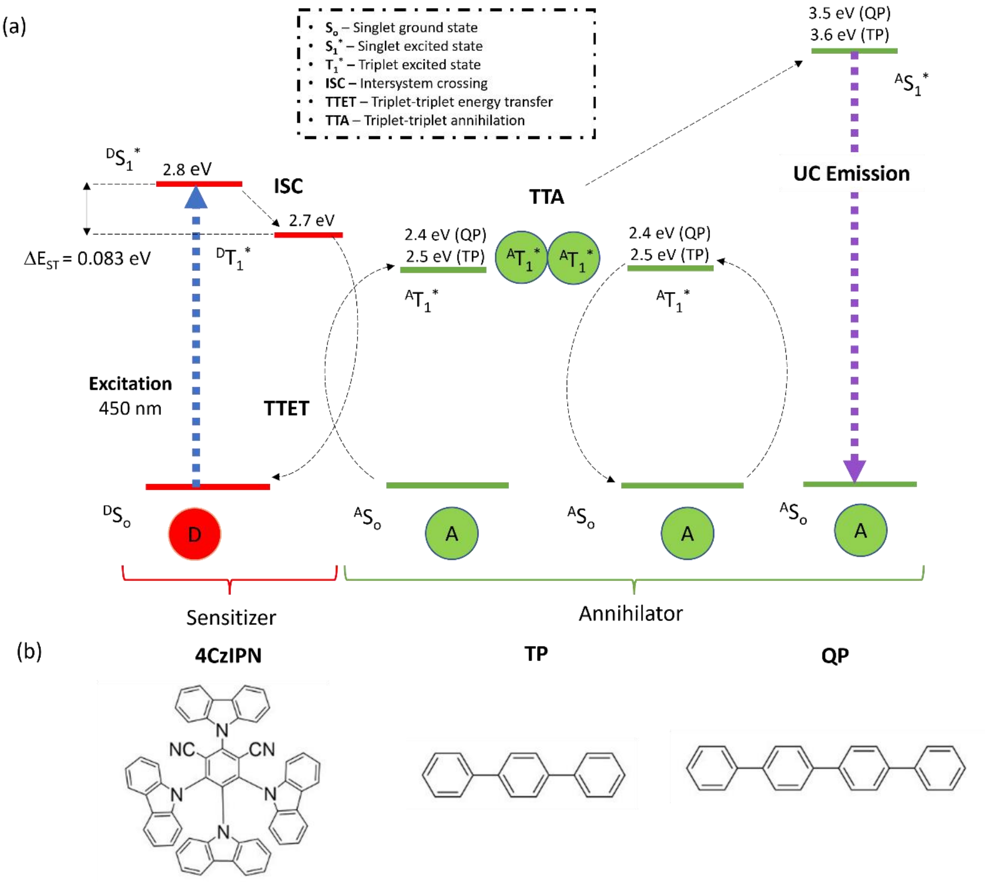

Figure 1. (a) Jablonski diagram for the TTA-UC mechanism of the couple of 4CzIPN (sensitizer) and TP/QP (annihilator), along with their respective energy levels. (b) The chemical structures of 4CzIPN, TP, and QP.

2. EXPERIMENTAL SECTION

2.1. Triplet Sensitizer-Emitter Materials

In this study, carbazolyl dicyanobenezene (4CzIPN) was used as sensitizer while p-quarterphenyl (QP) and p-terphenyl (TP) were used as the emitter, dissolved in benzene. 4CzIPN (≥ 99.0 %) was purchased from Ossila, while QP (≥ 98.0 %) and TP (≥ 99.0 %) were purchased from TCI. Benzene solvent (≥ 99.9 %) was purchased from Sigma-Aldrich. The material was used as received without any further purification. The triplet sensitizer-emitter solution was purging in a quartz cuvette through N_2 bubbling cycles (10 ml/min) to prevent quenching of the triplet states by molecular oxygen. The bubbling setup was illustrated in Figure 2.

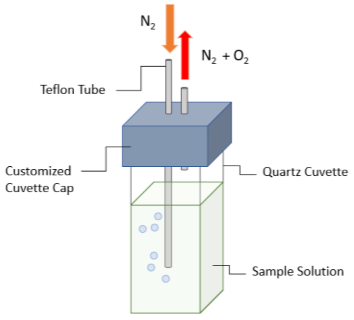

Figure 2. Schematic diagram of the N_2 bubbling setup for a 3 ml sample solution in a quartz cuvette with a dimension of 12.5 mm × 12.5 mm × 45.0 mm.

2.2. Measurement and Analysis

The measurement of upconverted fluorescence intensity of the TSE solution was conducted using a Photoluminescence (PL) machine (IHR 550, Horiba). The PL measurement covered a wavelength range from 300 nm to 500 nm. The machine was configured with an average scan rate of 3 times, an exposure time of 2 seconds, and a front entrance slit width of 0.2 mm.

In Figure 3(a), the optical system setup for photoluminescence intensity measurement is depicted. 1.5 ml sensitizer mixed with 1.5 ml annihilator was transferred into a quartz cuvette (Scioutlet, 45 mm × 12 mm × 12 mm). An excitation light of 450 nm was provided by a 450 nm LED light source (Chanzon, 50 W 450 nm LED, FWHM = 15 nm). The cuvette sample was irradiated with the LED light, and the resulting upconverted fluorescence passed through a notch filter (Pixelteq, 2 mm thickness × 20 mm diameter) before reaching the spectrophotometer. The notch filter permitted $\lambda \leq 400$ nm, effectively filtering out the incident light (λ = 450 nm), with a transmittance of approximately 82.4% at $\lambda \sim 350$ nm,

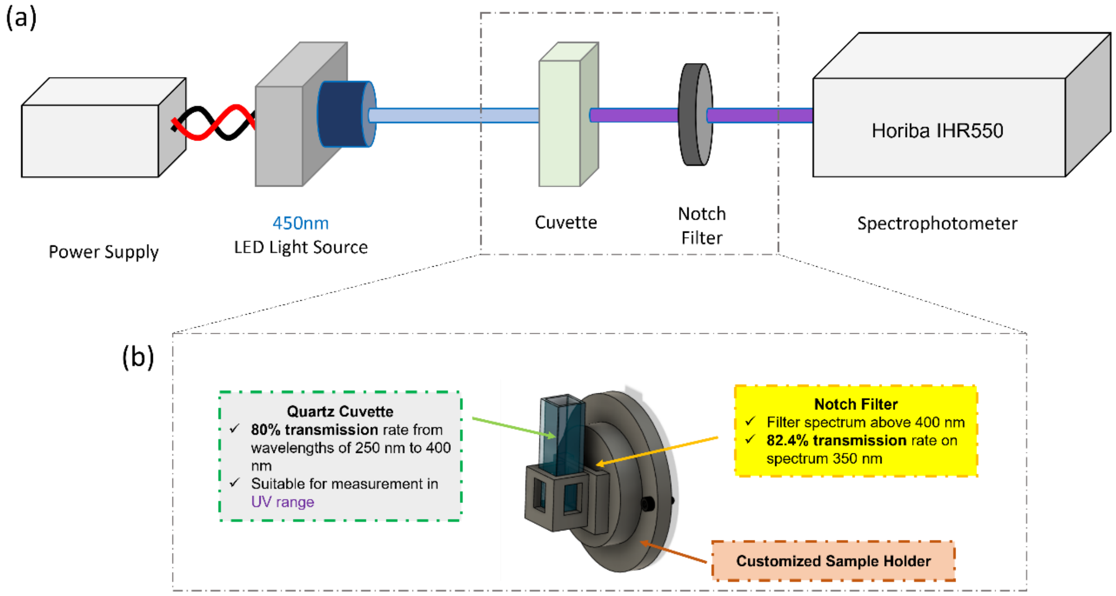

Figure 3. Schematic diagram of the (a) photoluminescence intensity measurement, and (b) customized sample holder with the designed slot to locate the cuvette and notch filter.

To ensure experimental reproducibility, a customized sample holder was used to fix the distance between the light source and the light detector, as well as the position of the tested sample. This holder accommodated the cuvette sample and notch filter in a consistent and precise manner. The customized sample holder was designed using the software Autodesk Fusion 360 and manufactured using 3D printing technology.

Figure 3(b) illustrated the appearance of the customized sample holder, along with the tranmittance data of the quartz cuvette and notch filter. The customized sample holder was mounted on the inlet of the spectrophotometer. The indicident light was irradiated perpendicularly to avoid interference with the emitted fluorescene of the sample. This setup allowed for consistent and reliable measurements throughout the PL measurement.

The quantum efficiency of the TSE solution was calculated based on Equation (1) [14]:

$$\Phi_{UC} = \Phi_{std}\left(\frac{A_{std}}{A_{UC}}\right)\left(\frac{I_{UC}}{I_{std}}\right) \tag{1}$$

where Φ represents the quantum yield, A represents the absorbance at 450 nm, and I represents the integrated photoluminescence spectral profile (Coumarin 6: 475 nm to 535 nm, 4CzIPN/QP: 340 nm to 400 nm, and 4CzIPN/TP: 325 nm to 385 nm). The spectrum coverage used to obtain the integrated photoluminescence spectral profile was set at 60 nm. The subscripts UC and std indicates the parameters of the upconversion and standard systems. Coumarin 6 in benzene (Φ_{std} = 88.2 %) with a concentration of 50 µM is used as the standard system to obtain the A_{std} and I_{std}.

2.3. Properties of the Customized Sample Holder

The dimensions of the customized sample holder were shown in Figure **4**. This sample holder was specifically intended for employment with the Horiba IHR 550 PL spectrometer. However, its dimensions could be adjusted to adapt a different spectrometer inlet requirement. Flexibility was offered in adjusting the dimensions for accommodating the cuvette and filter holding positions, as well as configuring the spacing between individual components.

The chosen material for 3D printing was resin, selected for its capability to create exceptionally precise structures, minimizing error deviation to a mere ± 0.05 mm. To eliminate any potential light absorption or reflection, a matte black resin was employed, with a polished smooth surface. Additionally, the 3D-printed custom holder presented an economical alternative for PL measurements. By bypassing the necessity for optical tables, breadboards, optical mounts, and motion control stages, this approach substantially minimized costs.

3. RESULT AND DISCUSSION

3.1. N_2 Bubbling Time Dependence

To enhance the upconverted fluorescence intensity of the TSE solution, a deoxygenation process was implemented before conducting the PL measurement. This process involved bubbling nitrogen (N_2) through the solution at a flow rate of 10 ml/min. The PL intensity of the TSE solution, containing the 50 µM for 4CzIPN mixed with 25 mM for TP in benzene solvent, are depicted in Figure 5. The measured PL intensity exhibited a gradual increase with the duration of N_2 bubbling, reaching its peak value of 585.7 Counts after 30 minutes of bubbling.

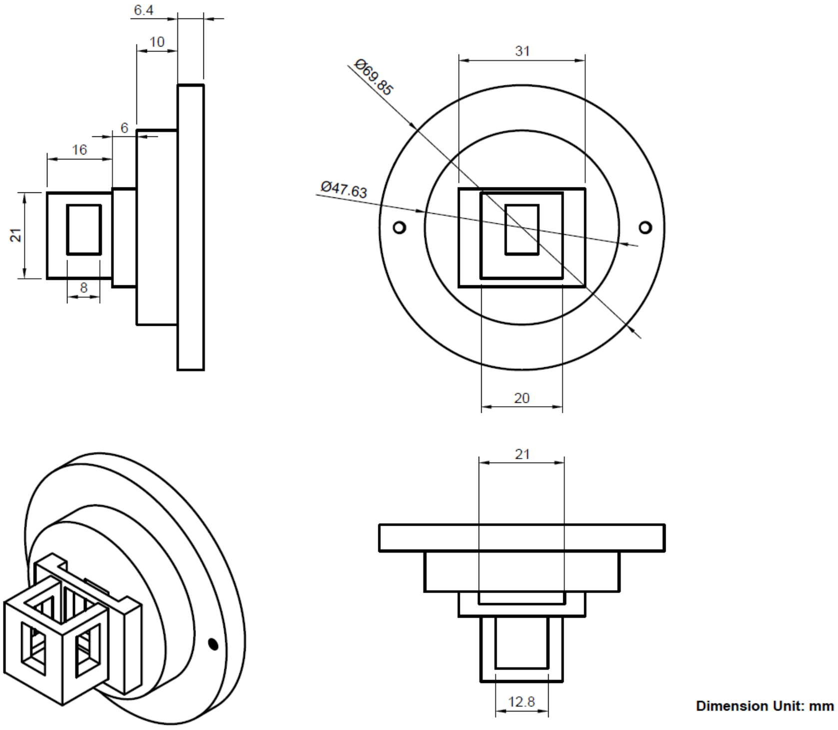

Figure 4. Schematic drawing of the customized sample holder with dimensions in millimeters (mm).

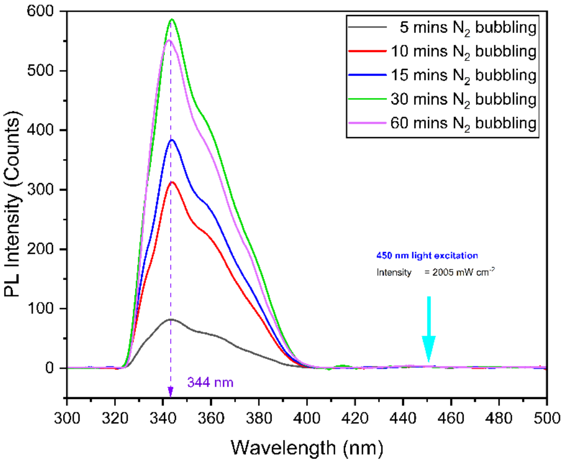

Figure 5. PL spectrum of a solution containing 50 µM 4CzIPN coupled with 25 mM TP after various durations of N_2 bubbling (5, 10, 15, 30, and 60 minutes). The peak upconverted fluorescence, observed under 450 nm light excitation with an intensity of 2005 mW cm^{-2}, occurred at 344 nm.

For samples with N_2 bubbling times less than 30 minutes, the PL intensity was lower, indicating that the deoxygenation was not sufficient. This remaining oxygen could induce triplet quenching issue in the TSE solution, leading to reduced PL intensity. On the other hand, the PL intensity did not show any further improvement after a longer N_2 bubbling time (60 minutes), suggesting that the deoxygenation process was already completed. However, a small reduction in intensity may have occurred due to the evaporation of benzene (low boiling point, *i.e.* 80°C) during the extended N_2 bubbling time. Therefore, the optimum N_2 bubbling time was determined to be 30 minutes, which could minimize the wastage of material usage and the experimental time. The N_2 bubbling time dependence of 4CzIPN/QP couple was not carried out since the TTA-UC mechanism was expected to be the same.

3.2. N_2 Bubbling Time Dependence

The PL profile of 4CzIPN mixed TP under 450 nm spectrum excitation intensity of 1850 mW cm^{-2} was shown in Figure 6(a). The excitation intensity dependence was analyzed under different excitation intensities of 450 nm spectrum irradiation, ranging from 230.70 mW cm^{-2} to 1849.97 mW cm^{-2}. The PL peaks of upconverted fluorescence (344 nm) for the TSE solution, comprising 4CzIPN/TP were plotted against the excitation intensity in Figure 6(b). As shown in Figure 6(b, inset), the double logarithm graph (log-log plot) revealed the quadratic relationship between the upconverted fluorescence intensity and the excitation intensity. This behaviour is consistent with the biphotonic TTA-UC mechanism, where two lower-energy photons are absorbed and upconverted into one higher-energy photon, occuring under low-intensity excitation [15]–[17]. The quadratic dependence arises from the intrinsic decay of annihilator triplets, known as pseudo-first-order decay. However, under a higher-intensity excitation TTA becomes the dominant decay channel, surpassing the pseudo-first-order decay, and the TTA-UC intensity becomes linearly dependent on the excitation intensity [18], [19].

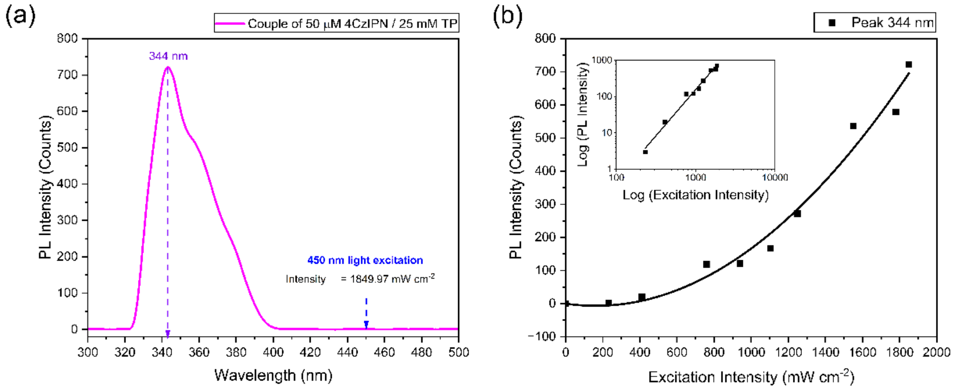

Figure 6. (a) The PL profile of 4CzIPN mixed with TP under the 450 nm light at 1850 mW cm^{-2} intensity. (b) The upconverted fluorescence peak intensity at 344 nm against the excitation intensity of 450 nm. Inset: A double logarithm plot with a slope value of 2.5.

The PL profile of 4CzIPN:QP (50 µM: 300 µM) under 450 nm excitation at 2098 mW cm^{-2} intensity was shown in Figure 7(a). The excitation intensity dependence was analyzed under different excitation intensities of 450 nm spectrum irradiation, ranging from 192.25 mW cm^{-2} to 2098.08 mW cm^{-2}. The PL peaks of upconverted fluorescence (354 nm and 370 nm) for the TSE solution, comprising 4CzIPN/QP were plotted against the excitation intensity in Figure 7(b). The PL profile of the 4CzIPN/QP couple showed similar characteristic to the 4CzIPN/TP couple.

In Figure 6, the upconverted fluorescence peak of the 4CzIPN/TP couple was observed at 344 nm, while Figure 7 showed that the 4CzIPN/QP couple exhibited upconverted fluorescence peaks at 354 nm and 370 nm.. Furthermore, the anti-Stokes shift (ΔE_{UC}) values for the 4CzIPN/TP and 4CzIPN/QP couples were 0.85 eV and 0.75 eV, respectively (*i.e.* the energy difference between the excitation light (450 nm) and the upconverted emission). The detected upconverted fluorescence peaks were consistent with previous reports. [14], [19]

3.3. Upconversion Quantum Yield

The UC quantum yield (Φ_{UC}) of the TSE solution was calculated with Equation (1). Figure 8 shows that the maximum Φ_{UC} obtained for the couple of 4CzIPN/TP and 4CzIPN/QP is 0.028 % and 0.043 %, respectively. To achieve a higher quantum yield, a high rate of TTA-UC process is essential, which highlights the significance of effective deoxygenation in the TSE solution. As compared with the previous study[14], the Φ_{UC} value for the couple of 4CzIPN/TP and 4CzIPN/QP were 1.4 % and 2.0%, respectively. In that study, the deoxygenation method was using freeze-pump-thaw degassing method. In this present study, since the deoxygenation process of the samples was performed through a simple N_2 bubbling setup, it was suspected that the oxygen removal in the TSE solution was not sufficient, and hence induced the triplet quenching issue. Furthermore, the sample preparation and PL measurements were conducted in an ambient atmosphere, which could have contributed to the observed low quantum yield efficiency.

Despite the low quantum yield obtained, the upconversion characteristics of the TS solution in the UV region were still observable. This successfully demonstrated the application of the customized 3D-printed sample holder in the PL measurement of the upconversion system.

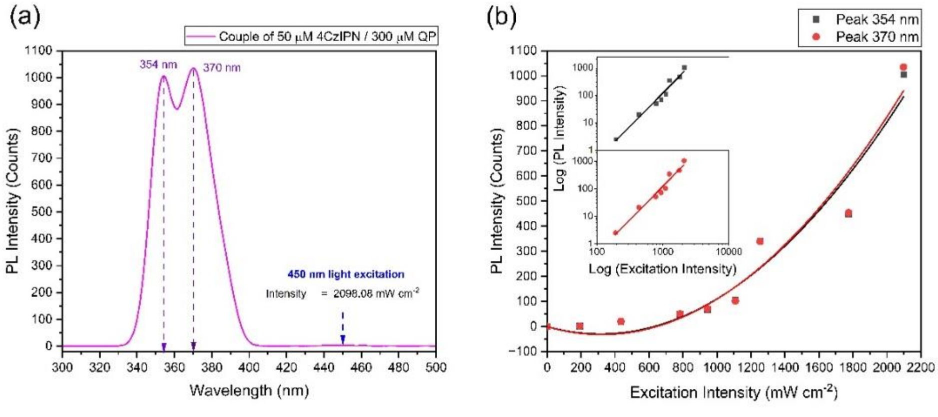

Figure 7. (a) The PL profile of 4CzIPN mixed with QP under the 450 nm light excitation at 2098 mW cm^{-2} intensity. (b) The plotted graphs of 354 nm (filled grey square) and 370 nm (filled red dots) upconverted fluorescence peak intensity against the excitation intensity of 450 nm. Inset: A double logarithm plot of the filled grey square and filled red dots with the same slope value of 2.4.

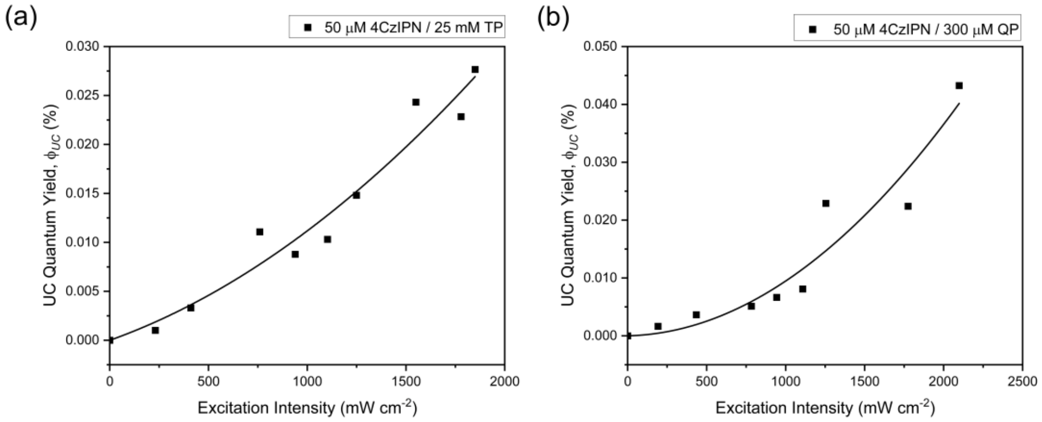

Figure 8. The quantum yield against the 450 nm excitation for (a) 4CzIPN mixed with TP and (b) 4CzIPN mixed with QP.

4. CONCLUSION

In conclusion, using a special 3D-printed sample holder has helped in getting precise and consistent PL measurements of TSE solutions, especially for TTA-UC systems. The application was looked at the 4CzIPN/TP and 4CzIPN/QP pairs for the photoluminescence data. The data showed upconverted fluorescence in the UV region. Since the measured PL result is consistent with the previous result, this led to trustworthy measurements utilizing the 3D printed setup. It means the setup itself does not transmit additional spectrum of light after irradiation. Also, using this holder can replace more expensive equipment usually needed for PL tests. This gives a cost-friendly option for PL test setups.

SUPPORTING INFORMATION

Link to 3D CAD file: https://grabcad.com/library/3d-printed-customized-sample-holder-for-pl-measurement-1.

ACKNOWLEDGMENTS

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