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Chemical and Physical Stability of Carbon Quantum Dots Synthesized from *Mahonia aquifolium*

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Carbon quantum dots (CQDs) are among the most popular carbon-based nanomaterials of recent years due to their low toxicity, eco-friendly nature as opposed to chemically derived carbon nanomaterials, high biocompatibility, easy water solubility, short synthesis time, low cost, and tunable fluorescence properties. In this study, quantum dots were synthesized by the hydrothermal method using Yellow Paint Bush (*Mahonia aquifolium*) and citric acid as carbon sources. The synthesized CQDs were characterized by using Fourier-transform infrared spectroscopy (FT-IR), photoluminescence spectroscopy (PL), UV–Vis spectroscopy, X-Ray diffraction (XRD), and thermal analysis (TG/DTA/DTG). Stability of carbon quantum dots (on the 1st, 5th, 10th, 15th, 20th and 30th days) were investigated in the refrigerator, at room conditions, in the dark, and moreover in the UV cabinet at 365 nm wavelength (between 0 and 30 minutes and 1-7 hours) and pH (pH=5-12) dependent emission properties.

1. Introduction

Carbon quantum dots (CQDs) are the most popular carbon-based nanomaterials which have been broadly studied due to their unparalleled optical properties, low-cost production, and plenty of raw materials to synthesize them. The stability of the optical properties of CQDs is in significant aspect that has received attention [1]. Synthesis methods of CQDs in the literature include; Laser ablation [2], carbonization [3], and electrochemical oxidation [4] in the top-down approach; and microwave [5], hydrotehermal [6], solvothermal [7], and pyrolysis [8] the bottom-up approach respectively.

Many studies have been done on *Mahonia aquifolium* in the literature. Çoklar and Akbulut investigated the antioxidant activity of Mahonia aquifolium fruits. The results showed that the antioxidant activity of anthocyanins was all but twice that of non-anthocyanin phenolic fractions [9]. Jatrorrhizine extracted from *Mahonia aquifolium* was the most potent towards many fungal species [10]. In the tumor microenvironment (TME), *Mahonia* extracts have been reported not to cause secondary effects when administered systemically alone or in combination with standard antitumor drugs [11]. *Mahonia aquifolium* have been shown to have anticancer potential. Damjanović, A. and et al. suggest that nontoxic M. aquifolium extracts enhanced the activity of Dox against lung cancer cells. Accordingly, it is predicted that it can be applied at low doses in vivo, reducing its toxic effects in normal tissues [12]. Palmatine and jatrorrhizine were an isoquinoline alkaloid present in *Mahonia aquifolium*. Palmatine is effective against bacterial, viral, and fungal infections [13].

The CA-EDA-carbon dots (C-E-CDs) were prepared using a one-step pyrolysis method. CDs exhibit excellent optical properties and purity without further purification [14]. On account of their pronounced pH-responsive behavior attribute to pH-induced aggregation of CDs result in an obvious fluorescence quenching, the obtained CDs have in great potential as pH sensor [15].

CQDs are very dispersible in water furthermore exhibit a longtime stability without any recognizable precipitation at room temperature [16]. Prathap et al. (2023); invesgated the effect of pH on the fluorescent intensity of the CDs. The florescence intensity of CDs depends on the pH of the solution. Decreasing pH increased the fluorescence intensity. At the same time, increasing the pH values decreased the fluorescence intensity. This study shows that at low pH values, CDs most likely exist as isolated species in the aqueous solution [17].

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Synthesis methods and chemical and physical properties of CQDs have been investigated by the scientists. Carbon dots are nanoparticles consisting of carbon with a diameter of less than 10 nm. The specific structure and size of CQDs suggest that their physical, electrical, chemical and optical properties are modifiable. In addition to this, they possess properties such as low toxicity, chemical stability, high water solubility, photoluminescence, photostability, high quantum yield, and environmental friendliness. The stability of carbon quantum dots is of great importance because it is one of the biggest factors in the spread of its usage areas [18].

CDs can show distinctly unique luminescent properties and has stability through injection of different solvents [19]. Elango et al. (2022), waste shrimp shells were used for sustainable synthesis of CQDs by hydrothermal method. Moreover, the prepared S-CQDs have good fluorescence stability and biocompatible spherical structures. The storage stability of S-CQDs was examined by keeping the sample at room temperature for 30 days with small fluctuations in PL density, and they reported that no sample precipitation was observed, indicating long shelf life [20].

The nitrogen-doped CDs have a great optical stability in a wide pH range of 1.89–11.82; the fluorescence emission intensity of CDs is substantially unchanged. The CDs can make a stable fluorescence emission in both strong acidic solution and strong basic solution. The important optical stability of CDs in a wide pH range is because the heteroatom N on the surface of CDs mostly exists in the form of imidazolium nitrogen, which is in a saturated coordination state and does not undergo movement of electrons [21].

In the present work, carbon quantum dots were synthesized from Yellow Paint Bush (*Mahonia aquifolium*) using citric acid. The chemical and physical stability of the synthesized carbon quantum dots were examined under different conditions; at the refrigerator temperature, dark environment, room temperature and UV-Vis illumination at 365 nm, and different pH ranges.

2. Results and Discussion

Thermal behaviours of the synthesized CQDs was evaluated with TG/DTA/DTG analysis. The TGA of the synthesized CQDs were recorded in temperature 800 °C under nitrogen flow (Figure 1). The structure was stable up to 180°C without any loss of water. After that, the degradation was observed with two endothermic steps.

Firstly, the substituents such as, hydroxyl, carboxyl, esther, amine, amide and ether groups were degradated from 180 to 330 °C with a 25% weight loss. Secondly, carbonic backbone structure was decomposed up to 800 °C with a 65 % weight loss. Totally, organic structure of CQDs was degraded approximately with a 90% weight loss (Figure 1). The residue was oxide form of inorganic compounds in CQDs [22, 23].

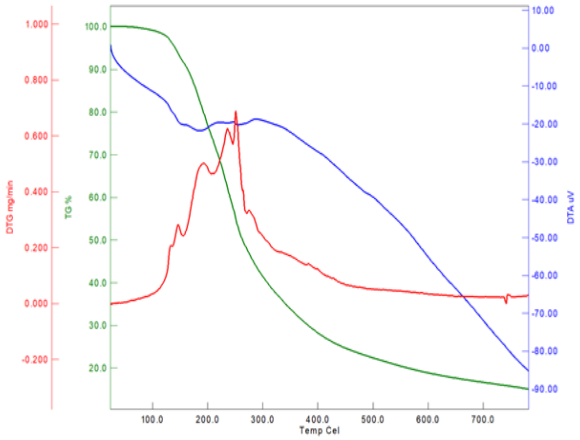

Figure 1. TG/DTA/DTG Curves of CQDs.

Additionally, the synthesized CQDs were characterized with FT-IR in the range of 450-4000 cm^{-1} (Figure 2.). The strong peak at around 3437 cm^{-1} corresponds to O–H and N–H stretching vibrations; the absorption peaks at 2915 and 2951 cm^{1} were associated with aromatic and aliphatic C–H stretching; and the absorption peak at 1671 cm^{-1} was related to C=O stretching from carboxylic, estheric and amidic groups. C-N and C-O stretches and Aromatic C=C stretches also observed around 1630 cm^{-1}. C-N and C-O stretchings in amine, esther, alcohola and ether groups were observed at about 1030 cm^{-1} as a strong band. O-H bendings from carboxylic and alcoholic groups were recorded around 1405 cm^{-1} [5,6,11-24].

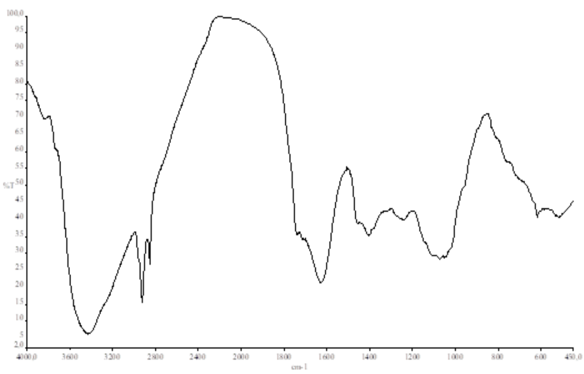

Figure 2. FT-IR spectrum CQDs.

The crystal structures of CQDs were examined by XRD analysis (Figure 3). A distinct broad diffraction peak was observed at 23.35°, showing the characteristic structure of nano-sized CQDs

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materials in XRD spectrum. This diffraction peak indicates that CQDs are of amorphous structure.

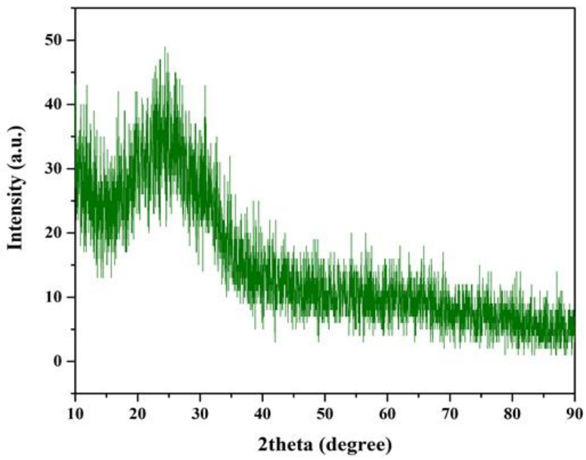

Figure 3. X-Ray diffraction pattern.

The size distribution and morphology of the resulting carbon quantum dots were characterized by TEM (Figure 4). The average particle diameter size of CQDs calculated by considering 41 particles average sized as 66.19 nm with a 16.88 nm standard deviation (Figure 4).

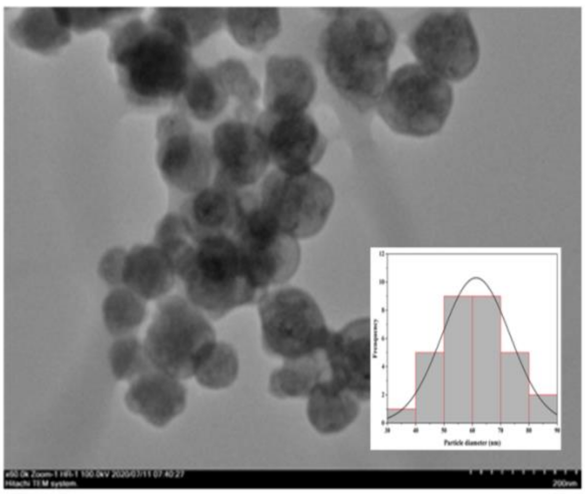
Figure 4. TEM image of CQDs and Particle diameter.

In order to evaluate the optical properties of the synthesized CQDs, UV–Vis spectra were recorded. The absorption spectrum showed two peaks at 250 and 325 nm corresponding to π-π* and n-π* transitions respectively. Besides, the synthesized CQDs were fluoresced blue light under 365 nm (Figure 5) [25].

The optical properties of the synthesized CQDs were examined using PL. Moreover, according to the excitation-emission scanning spectrum (Fig.6), CQDs were observed to be excited at 340 nm and intensity at 84 nm.

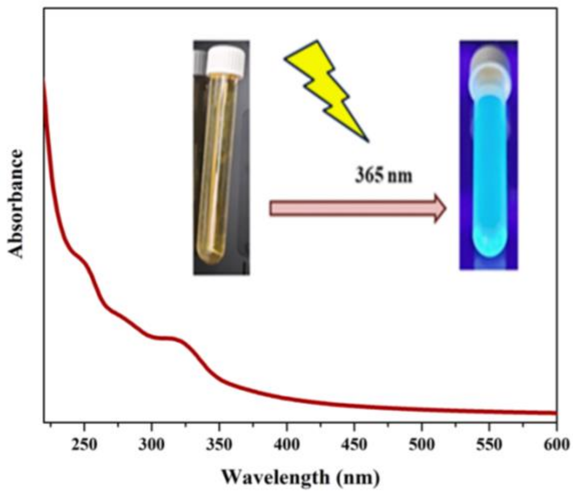

Figure 5. UV–Vis spectrum of CQDs.

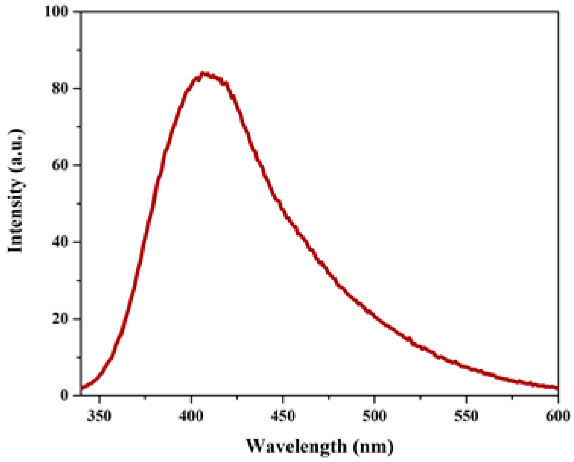

Figure 6. PL spectrum of CQDs.

The stability of water-dispersed CQDs was investigated at refrigerator temperature (Figure 7). Measurements were taken for stability on different days between 0 and 30 days under refrigerator conditions. The synthesized CQDs exhibit good stability because they decreased by only 4.8% and 5.7% on the 10th and 15th days, respectively, while no significant change was observed on the other days. [16].

The stability of water-dispersed CQDs was investigated in dark environment (Figure 8). Measurements were taken for stability on different days between 0 and 30 days dark environment conditions. The synthesized CQDs exhibit good stability because decreased by only 4.8% on the 5th day, while no significant change was observed on the other days [16].

The stability of water-dispersed CQDs was investigated at room temperature (Figure 9). Measurements were taken for stability on different days between 0 and 30 days at room temperature. The synthesized CQDs exhibit good stability

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because they decreased by only approximately 7.4% and 4.8% on the 5th and 15th days, respectively, while no significant change was observed on the other days. Stabilization study is compatible with the studies of Yan et al. [15, 16, 20].

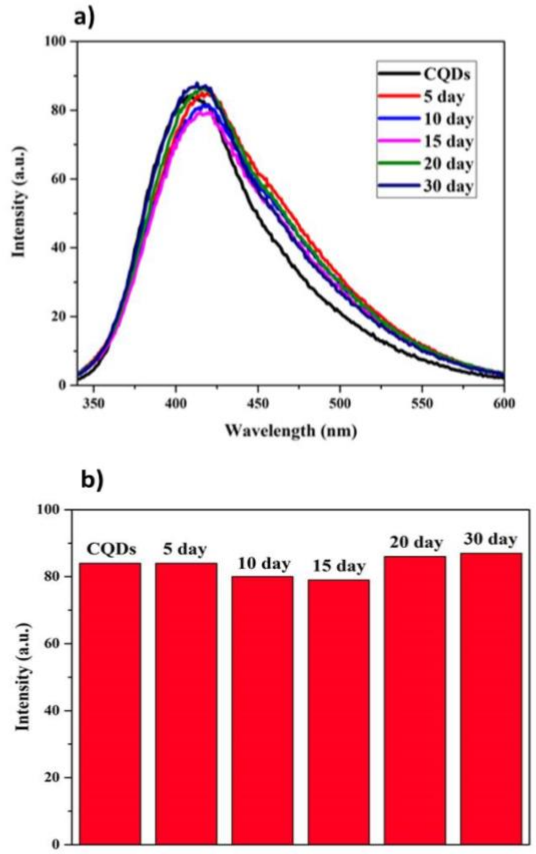

Figure 7. Stability in refrigerator a) PL and b) histogram.

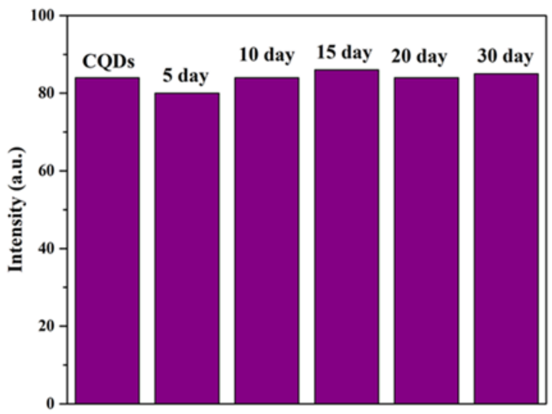

Figure 8. Stability in dark environment a) PL and b) histogram.

The stability of water-dispersed CQDs was investigated at 365 nm under UV illumination (Figure 10). For stability, analysis was performed for 0.30 min to 1-7 h. The synthesized CQDs exhibit good stability, with an increase of approximately 5% in the first 30 min., 7.1% increase for 1 h, 3% increase for 3 h, 8.1% decrease for 5 h, and 4.7% increase for 7 h [26]. According to the literature, it showed very good stability.

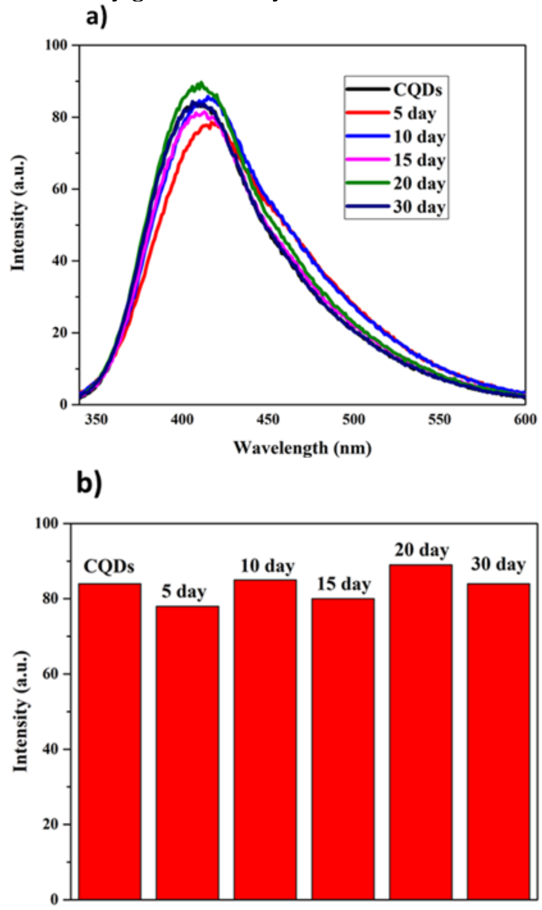

Figure 9. Room temperature stability a) PL and b) histogram.

The stability of water-dispersed CQDs was investigated in dependent on pH (Figure 11). For stability analysis, pH=5-12 range was taken as basis. An approximately 8.3 % intensity decrease in the photoluminescence spectra of the synthesized CQDs was observed from pH=5 to 12. It can be said that the substituents on the surface of CQDs chemically are inert in the range of pH: 6-12. Finally, it can be used in mediums having the wide range pH values providing the effective applications in different hard conditions as a stable material [15-17, 27].

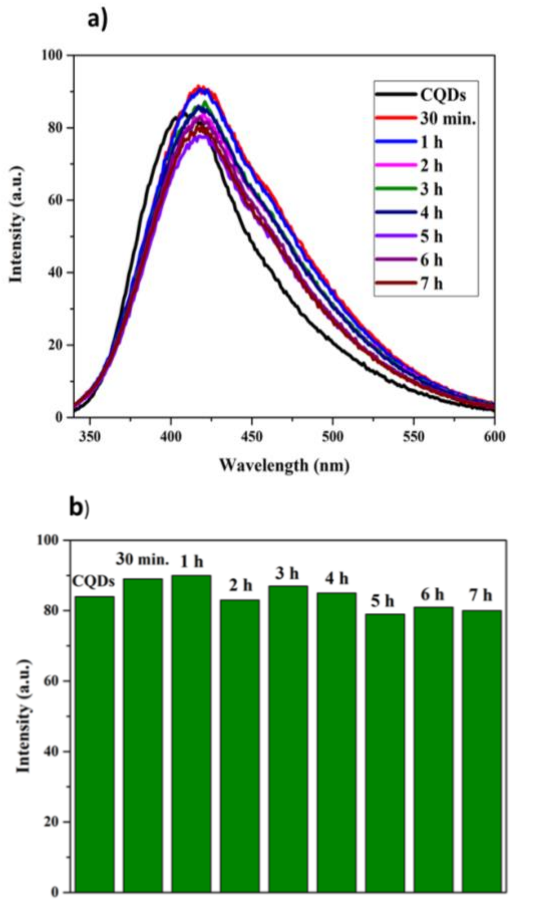

Figure 10. Stability under UV illumination (a) PL and (b) histogram.

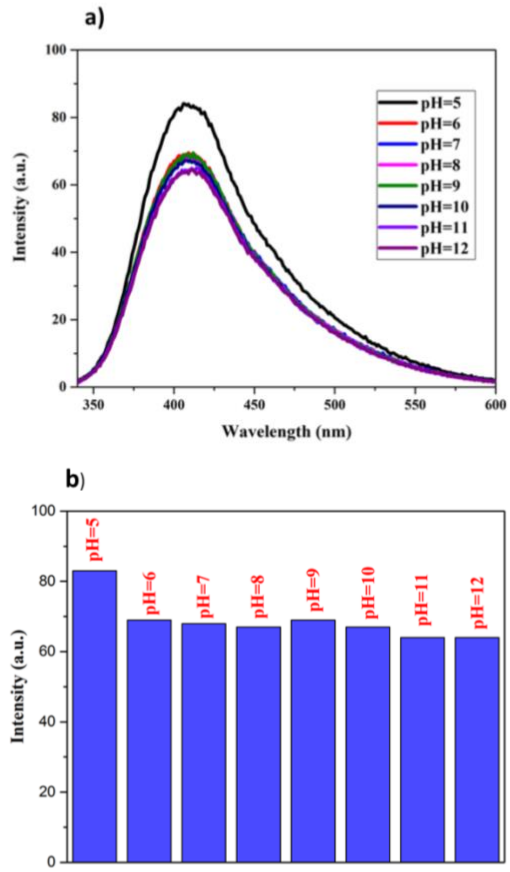

Figure 11. pH dependent stability (a) PL and (b) histogram.

3. Conclusion

In conclusion, carbon quantum dots were synthesized using Yellow Paint Bush (*Mahonia aquifolium*) and citric acid. The hydrothermal method, which is quite economical and easy, reaction temperature, completed in a short time, was used for the synthesis process. The synthesized CQDs were characterized with crystal structure by XRD, infrared spectroscopies (FT-IR), photoluminescence (PL) and UV-Vis techniques. The stability behaviors of the synthesized carbon quantum dots under different conditions were analyzed. Shortly; the synhtesized carbon quantum dots are very stable in all the conditions.

Antimicrobial, antifungal and anticancer properties of the extract and CQDs of *Mahonia aquifolium* have been reported in many studies in the literature. In addition, the extracted samples and CQDs of *Mahonia aquifolium* can be used for long-term use and applicability in biological applications. In our study, it was synthesized with a different method and applied and obtained theremarkable results under different conditions in the stabilization studies.

Method

On March 17, 2023, Yellow Paint Bush (Mahonia aquifolium) flowers were collected from Kahramanmaraş Sütçü İmam University (KSÜ) Avşar campus, washed with plenty of ultrapure water and dried under room conditions for approximately three weeks. 1 g *Mahonia aquifolium* leaves were dissolved, 1 g of citric acid was added to 50 ml pure water and to ultra-sonicated for 30 min. The prepared solution was heated at 185°C for 12 h in a teflon line stainless steel autoclave. After heat treatment solution cooled down to room temperature. The obtained solution was centrifuged at 14.000 rpm for 15 min. For later use, it was dried in the oven at 40°C after centrifugation and stored in the refrigerator at +4 C. To prepare carbon quantum dot solution, 0.025 g of CQDs was weighed and then dissolved in 100 ml of ultrapure water. pH of the samples was prepared by dissolving carbon quantum dot in NaOH solutions adjusted by 0.1 M stock solutions.

The fluorescence intensity of the carbon quantum dot was measured at each pH (5-6) value. Sodium hydroxide and citric acid were obtained from Sigma-Aldrich, Merck. The X-Ray diffraction (XRD) pattern of the samples was recorded with a Philips X'Pert PRO XRD with Cu Kα radiation (λ =0.154056 nm, tuned at 40 kV and 30 mA). FT-IR spectra were obtained with Perkin-Elmer Spectrum 400 system attached ATR apparatus in the range 4000–400 cm^{-1}. UV-Vis absorption spectra were performed by using Shimadzu-1800 UV-Visible spectrometer. Photoluminescence (PL) spectra were collected on a Varian Cary Eclipse spectrometer.

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Authors' contributions:

B.T. edited the study, interpreted the analysis results and wrote the article. A.B.S. and S.U. helped with the synthesis studies and conducted research.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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