1. Introduction

Fossil fuels such as petroleum, coal, and natural gas play the foremost role in satisfying energy needs and are being rapidly exhausted. Using fossil fuels inevitably emits toxic greenhouse gases that are very injurious to the environment.\[1\] Solar energy has been appraised as the supreme alternative sustainable energy source for fossil fuels. Dye-sensitized solar cells (DSSCs) and dye-sensitized photoelectrochemical cells (DSPECs) are the major focus of solar energy harvesting. Semiconductor-based DSSCs and DSPECs have attracted great attention due to their low cost, simple fabrication, and high solar energy conversion potential. Dye-sensitized semiconductor materials have been considered a powerful practical method in the conversion of solar energy to chemical energy in recent years.\[2\] Among the various semiconductor materials used, TiO\textsubscript{2} is a common and extremely effective material in the field of photoelectrocatalysis. TiO\textsubscript{2} is nontoxic, highly stable, cost-effective, and has good photocatalytic performance.\[3\] But conventional TiO\textsubscript{2} suffers from problems such as low quantum efficiency, a wide bandgap, and a high recombination rate. These eventually restrict its capability in possible applications. However, Fujishima and Honda in 1972 conducted a pioneering experiment of photoelectrocatalytic water splitting using a TiO\textsubscript{2} photoelectrode under UV light.\[4\] Latterly, molecular hydrogen can be produced from the water-splitting process using dye-sensitized photoelectrochemical cells, in which a photosensitizer is attached to a mesoporous TiO\textsubscript{2} semiconductor that drives the half-cell reactions of conversion of water to \(\text{O}_2\) and \(\text{H}_2.\)[5–9] In this context, photoelectrochemical hydrogen production from photoactive cathodes based on dye-sensitized TiO\textsubscript{2} semiconductors is of great interest. TiO\textsubscript{2}-based photocathodes were acquired by loading of nanostructured TiO\textsubscript{2} films with dyes and seemed to enhance the photoelectrochemical activity in aqueous media. In such photocathodes, the dye plays a critical role in the gathering of sunlight and the initiation of electron-transfer processes. Ruthenium(II) dyes are good candidates for photosensitizers, which tender long-lived excited states and charge-separated states due to metal-to-ligand charge transfer processes. Ruthenium(II) complex dyes are supposed to improve the light absorption and charge injection into the conduction band of TiO\textsubscript{2}.\[10–14\] The light absorption of ruthenium(II) dyes can be tuned by varying the ligands. Their good photophysical properties have increased the interest toward the use of coumarins as ligands and their corresponding Ru(II) complex dyes are supposed to improve the light absorption and charge injection into the conduction band of TiO\textsubscript{2}.\[15\] In this study, we focused on the design and synthesis of a new coumarin-based ruthenium(II) dye with tunable photophysical and redox properties. The sensitizer was loaded on TiO\textsubscript{2} films and the photoelectrodes were tested as photocurrent...
generators for water-splitting reactions and dye-sensitized solar cells. The structure of the quinoline-coupled coumarin-based ruthenium(II) sensitizer (RQC) is shown in Figure 1.

2. Results and Discussion

2.1. Photophysical Properties

Coumarins are known to be the best photoluminescence materials for their strong absorption and fluorescence emission properties. The UV–vis absorption and emission spectra of the Quinoline-coupled coumarin (QC) ligand in acetonitrile (Figure S11, Supporting Information) shows a strong absorption band at 333 nm that can be assigned to $\pi \rightarrow \pi^*$ transition from a filled orbital localized on the quinoline phenoxide ring toward an antibonding molecular orbital localized on the pyridyl ring.[16] The two narrow sharp peaks at 207 and 242 nm correspond to $\pi \rightarrow \pi^*$ transition of the coumarin ring. The photoluminescence spectrum for this ligand showed the most intense peak at 442 nm. The UV–vis absorption and emission spectra of the RQC sensitizer in acetonitrile is shown in Figure 2. The complex shows intense metal $d \rightarrow$ ligand $\pi^*$ charge transfer (MLCT) transition at 494 nm. The strong absorptions at about 208, 244, and 344 nm were assigned to the $\pi \rightarrow \pi^*$ electronic transition for the QC ligand. The band at 304 nm is assigned as intraligand $\pi \rightarrow \pi^*$ charge transfer transitions of dicarboxy bipyridine ligands. On excitation at the MLCT band, RQC shows a sharp peak at 542 nm.

2.2. Electrochemical Properties

Cyclic voltammetry of the RQC complex was conducted with a three-electrode configuration in deoxygenated acetonitrile using 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte. The potentials were measured using a Ag/AgCl reference electrode with a swipe rate of 100 mV s$^{-1}$. The cyclic voltammogram of RQC (Figure 3) showed a reversible wave at $+0.484$ V, which was assigned to the Ru(II)/Ru(III) couple. Multiple peaks are observed at $-0.141$, $-0.298$, $-0.014$, and $-0.649$ V due to ligand reductions. To use the RQC dye as a sensitizer in DSSCs and DSPECs, it is essential to ensure its energy levels are appropriate for efficient electron injection and dye regeneration. The highest occupied molecular orbital (HOMO), lowest occupied molecular orbital (LUMO), and energy gap ($E_g$) values were calculated from the cyclic voltammogram using the following equations[11]

\[
\text{HOMO} = -(E_{\text{onset}}^{\text{ox}} + 4.40) \text{ eV} \quad (1)
\]

\[
\text{LUMO} = -(E_{\text{onset}}^{\text{red}} + 4.40) \text{ eV} \quad (2)
\]

\[
E_g = \text{HOMO} - \text{LUMO} \quad (3)
\]

Table 1 shows that the HOMO energy level of RQC ($-5.117$ eV) is sufficiently lower than that of the $I^-/I_{3^-}$ redox
couple, ensuring efficient electron transfer from the electrolyte for efficient dye regeneration. Also, the LUMO energy level of the dye (–3.597 eV) indicated that it is suitable for electron injection into the conduction band of TiO₂.

### 2.3. Quantum Chemical Methods

Quantum chemical methods were used to model the electronic structure of the ground state and excited state of RQC. All the calculations were conducted using the B3LYP method in the 6–311++G(d,p) basis set. The optimized structure of the ruthenium complex is shown in Figure S12, Supporting Information, as a ball-and-stick model. The geometry optimization yields a nonplanar structure.[17]

#### 2.3.1. Electronic Properties

The HOMO and LUMO are collectively called frontier molecular orbitals (FMOs). The HOMO, LUMO, and their energy gap (Eₙ) are very useful parameters in quantum chemistry. The HOMO and LUMO are the main orbitals taking part in chemical reactions. The energy of the HOMO is directly related to the ionization potential (IP) and the LUMO energy is directly related to the electron affinity (EA). Also, the frontier orbital gap, the energy gap between the HOMO and LUMO, represents the stability of structures and helps to characterize some significant issues, including the kinetic stability as well as chemical reactivity of the molecule.[18,19] Chemical hardness is allied with the stability and reactivity of a chemical system. The larger the HOMO–LUMO energy gap, the harder, more stable, and less reactive is the molecule. The smaller the HOMO–LUMO energy gap, the softer, less stable, and more reactive is the molecule. The value of the LUMO–HOMO energy gap reflects the chemical activity of the molecule.[20]

To evaluate the energetic behavior of RQC, the HOMO and LUMO energies were calculated by the B3LYP method in the 6–311++G(d,p) basis set. Figure 4 shows the FMOs’ shape. The density of the HOMO is circulated around the ruthenium atom (Ru), quinoline ring, O and N atoms in hydroxyquinoline, 2,2’-bipyridyl carbon atoms, and carboxylic acid groups. The LUMO is localized on the ruthenium atom, coumarin ring, quinoline ring, azomethine group, and 2,2’-bipyridyl carbon atoms. The ground-state orbital is occupied on the nitrogen of quinoline, C═O of the carboxylic acid group with weak association, and on the ruthenium atom and all bipyridyl carbon atoms with weak involvement. The excited-state orbital is engaged on the quinoline ring and the bipyridine rings through a weak donation and on the ruthenium atom, coumarin ring, and azomethine group with a great role. Theoretical calculations showed that the ground-state energy of RQC was −4.236 eV, excited-state energy was −2.928 eV, and bandgap was 1.307 eV. This small bandgap confirms that the complex RQC has huge reactivity in addition to great polarizability.[21,22] The HOMO, LUMO, and bandgap values calculated from the density functional theory (DFT) calculations were compared with electrochemical calculations (Table 1). A small discrepancy was observed in electrochemical parameters due to solvent effect.

#### 2.4. Thermal Analysis

Thermogravimetric and differential thermal studies were used to examine the thermal stability of RQC and the recorded thermogram is shown in Figure 5. The TG curve illustrated the absence of any detectable weight loss up to 247 °C and the material decomposed immediately after melting. The decomposition

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**Table 1.** Electrochemical and DFT calculations of HOMO–LUMO and energy gap values.

| Dye  | Electrochemical parameters | Theoretical parameters |
|------|---------------------------|------------------------|
|      | EₜHOMO [eV] | EₜLUMO [eV] | Eₙ [eV] | EₜHOMO [eV] | EₜLUMO [eV] | Eₙ [eV] |
| RQC  | −5.117       | −3.597       | 1.52    | −4.236       | −2.928       | 1.307    |

---

**Figure 4.** Atomic orbital compositions of the frontier molecular orbital of RQC.

**Figure 5.** Thermogravimetric analysis (TGA)-DTA curves of RQC complex.
takes place gradually in the high temperature in a single stage into volatile gaseous products such as CO₂ or NH₃. The residue that remains after the decomposition may be a stable carbon compound. The differential thermal analysis (DTA) curve indicated the same changes shown by the TG curve. The sharp endothermic dip at 247 °C indicates the melting point of the material. The sharpness of this endothermic peak shows the good degree of crystallinity and purity of the material. This is further confirmed by a melting point apparatus.

2.5. Photoelectrochemical Water-Splitting Studies

A three-electrode photoelectrochemical cell was constructed with the photoanode FTO/TiO₂/RQC as the working electrode, Ag/AgCl as the pseudoreference electrode, and Pt wire as the cathode under visible light illumination for water splitting. Linear sweep voltammetry (LSV) under dark and light illumination was performed on the RQC-sensitized photoanodes to assess the best applied potential to be used in the photoelectrochemical studies.\(^\text{[23]}\) Figure S13, Supporting Information, shows the linear sweep voltammograms recorded under dark and light illumination at pH 7 in the presence of a sacrificial electron donor, 10 mM triethanolamine (TEOA). From the light/dark ratio, the best applied potential to use in further measurements was decided to be +0.78 V versus relative hydrogen electrode (RHE). The photoelectrochemical water splitting efficiency (\(\eta\)) of the photoanode can be calculated by\(^{[24]}\)

\[
\eta = \left( \frac{J_p \text{(mA cm}^{-2}) \times (1.23 - V_{\text{app}}) \text{(V)}}{I_0 \text{(mW cm}^{-2})} \right) \times 100
\]

where \(J_p\) is the photocurrent density, \(V_{\text{app}}\) is the applied potential versus RHE, \(I_0\) is the intensity of the light source in milliwatt per squared centimeter, and 1.23 V versus RHE is the standard cell

Figure 6. Light-controlled photocurrent measurements in the three-electrode cell a) at different pH with 10 mM TEOA as the sacrificial electron donor, b) at pH 6 with 10 mM solution of different sacrificial electron donors, and c) at pH 6 with different concentrations of TEOA as the sacrificial electron donor (applied external bias: 0.78 V (vs RHE)).
potential for water splitting. The PEC efficiency ($\eta$) is directly depends on the photocurrent density; thus a high value of photocurrent density shows a higher PEC efficiency. PEC activity is appreciably influenced by some key features, such as the pH of the medium and the type and concentration of the sacrificial electron donor.\[25\]

2.5.1. Effect of pH

Light-controlled chronoamperometric titrations were conducted at different pH values in the presence of 10 mM TEOA as the sacrificial electron donor. As shown in Figure 6a, the photocurrent density was influenced by the pH of the medium. When the pH of the solution was 3, a photocurrent density of 7.05 mA cm$^{-2}$ ($\eta = 3.17\%$) was found after 10 s light irradiation. On increasing the pH of the solution up to 6, photocurrent density also increased and the highest photocurrent density of 9.8 mA cm$^{-2}$ ($\eta = 4.41\%$) was obtained at pH 6. Further increasing the pH decreases the photocurrent densities: 9.0 mA cm$^{-2}$ ($\eta = 4.05\%$) and 8.33 mA cm$^{-2}$ ($\eta = 3.74\%$) were obtained at pH 7 and 8, respectively. Lower and higher pH of the medium leads to a significant decrease in photocurrent densities because the sacrificial electron donor TEOA undergoes protonation at lower pH and the H$^+$ concentration of the solution is too low at higher pH. In both conditions, the electron-donating ability of TEOA decreases.\[25,26\] The water-splitting process in natural photosynthesis usually occurs at neutral condition (pH ≈ 7) and from these results the pH 6 was selected for further studies.

2.5.2. Effect of Sacrificial Electron Donor

The instant recombination of photoinduced electron–hole pairs in the electrode limits the efficiency of water splitting and the addition of reagents as sacrificial electron donors to the electrolyte promotes the regeneration and photocatalytic activity of the photocatalyst. The type of sacrificial electron donor used in PEC studies also influences the photocurrent density. The effect of 10 mM solutions of TEOA, ethylene diamine tetra acetic acid (EDTA), ascorbic acid, and triethylamine (TEA) as electron donors in the electrolyte was investigated by light-controlled chronoamperometry at pH 6 (Figure 6b). The photocurrent densities of 9.8 mA cm$^{-2}$ ($\eta = 4.41\%$), 8.82 mA cm$^{-2}$ ($\eta = 3.96\%$), 7.35 mA cm$^{-2}$ ($\eta = 3.30\%$), and 6.66 mA cm$^{-2}$ ($\eta = 2.99\%$) were obtained for TEOA, EDTA, ascorbic acid, and TEA, respectively. This is due to the different electron-donating potentials of the electron donors. Among them, TEOA shows a higher efficiency, which may be due to the facile adsorption of TEOA on the TiO$_2$ surface and the regeneration of the RQC dye.\[25,26\]

2.5.3. Effect of Concentration of Sacrificial Electron Donor

On the basis of the previous discussion, TEOA was used as the sacrificial electron donor in this work and the effect of various concentrations of TEOA (10, 20, 30, 40, and 50 mM) in the electrolyte was investigated by light-controlled chronoamperometry at pH 6, as shown in Figure 6c. The photocurrent densities of 9.8 mA cm$^{-2}$ ($\eta = 4.41\%$), 10.29 mA cm$^{-2}$ ($\eta = 4.63\%$), 11.07 mA cm$^{-2}$ ($\eta = 4.98\%$), 10.78 mA cm$^{-2}$ ($\eta = 4.85\%$), and 9.5 mA cm$^{-2}$ ($\eta = 4.27\%$) were obtained for 10, 20, 30, 40, and 50 mM concentrations of TEOA, respectively. Increasing the concentration of TEOA increases the photocurrent density up to 30 mM and further increase of the concentration of TEOA decreases the photocurrent density. This is due to the amount of TEOA adsorbed on TiO$_2$ increasing and this competitive adsorption between RQC and TEOA decreases the PEC efficiency.\[25,26\]

2.5.4. PEC Water-Splitting Efficiency

The PEC water-splitting efficiency of dye-sensitized TiO$_2$ photoanodes were consequently investigated in the presence of 30 mM TEOA as the sacrificial electron donor at pH 6 phosphate buffer electrolyte solution in the same three-electrode configuration. Light-controlled chronoamperometry (CA) measurements were conducted under chopped-irradiation conditions with 30 s intervals (30 s light on/30 s light off) with constant light illumination with an applied potential 0.78 V versus RHE, as shown in Figure 7. The results indicated that an initial photocurrent density of 11.07 mA cm$^{-2}$ and a final photocurrent density of 9.66 mA cm$^{-2}$ were found at light irradiation and current density dropping to zero when the incident light was turned off. Under these conditions, the maximum PEC water-splitting efficiency ($\eta$) of 4.98 % was obtained. Upon light illumination at pH 6, the RQC-based photoanode showed good reproducibility and steady photocurrent responses.\[27–29\]

2.6. Photoinduced Electron Transfer Reactions

Photoinduced electron transfer reactions and charge separation are of considerable interest in the realm of solar energy conversion schemes. To investigate the electron transfer interaction between RQC and TiO$_2$ nanoparticles (NPs), the absorption spectra of RQC in water were recorded with varied amounts of TiO$_2$ nanoparticle suspension. A known amount of TiO$_2$ nanoparticle
suspension in water was added to a $1 \times 10^{-5}$ mol L$^{-1}$ solution of RQC and Figure 8a shows the absorption spectral changes of RQC with the existence of an increasing concentration of the TiO$_2$ nanoparticle suspension. It is noted that the intensity of the MLCT band of RQC increases constantly by means of remarkable bathochromic shift after the addition of the TiO$_2$ nanoparticle suspension. This evinces a complex formation between RQC and the TiO$_2$ nanoparticle suspension. The ground-state association constant ($K_a$) was calculated using the Benesi and Hildebrand equation

$$\frac{1}{A - A_0} = \frac{1}{A_c - A_0} + \frac{1}{(A_c - A_0)K_a[TiO_2 \text{ NPs}]}$$  \hspace{1cm} (5)$$

where $A_0$ and $A$ are the absorbance intensities of RQC in the absence and presence of diverse concentrations of TiO$_2$ nanoparticle suspension, respectively, $A_c$ is the absorbance of the ground-state RQC$^-$ TiO$_2$ nanoparticle suspension complex, and [TiO$_2$ NPs] is the concentration of TiO$_2$ nanoparticle suspension. Plotting of $1/(A - A_0)$ versus $1/[TiO_2 \text{ NPs}]$ is shown in Figure 8b. The association constant ($K_a$) was estimated to be $3.12 \times 10^3$ L mol$^{-1}$. The changes in absorption intensity and wavelength of RQC confirmed that static quenching was dominant in the interaction process, as dynamic quenching only affected the excited state of the fluorophore.

The excited-state interactions were investigated by fluorescence titrations of RQC with the TiO$_2$ nanoparticle suspension in water. Decreasing of the fluorescence intensity (quenching) was observed with the successive additions of the TiO$_2$ nanoparticle suspension to the RQC solution (Figure 9a). This quenching process revealed the transfer of

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**Figure 8.** a) Absorption spectral changes of RQC ($1 \times 10^{-5}$ mol L$^{-1}$) with incremental addition of TiO$_2$ nanoparticle concentrations. b) Double reciprocal plot of $1/(A - A_0)$ versus $1/[TiO_2 \text{ NPs}]$.

**Figure 9.** a) Change in the emission intensity of RQC ($1 \times 10^{-5}$ mol L$^{-1}$) on incremental addition of TiO$_2$ nanoparticles when excited at 495 nm. b) S–V plot of quenching of RQC by TiO$_2$ nanoparticles.
an electron from the excited-state RQC to the conduction band of the TiO$_2$ nanoparticles. Fluorescence quenching can ensue via different mechanisms, usually classified as dynamic quenching or static quenching. To confirm the quenching mechanism, the quenching data were analyzed using the Stern–Volmer (S–V) equation

$$F_0/F = 1 + K_{SV}[TiO_2\text{NPs}]$$  \hspace{1cm} (6)

where $F_0$ and $F$ correspond to the fluorescence intensities in the absence and presence of the quencher, respectively, $K_{SV}$ is the S–V quenching constant, and [TiO$_2$ NPs] is the concentration of the TiO$_2$ nanoparticle suspension. The S–V quenching constant $K_{SV}$ was calculated from the S–V plot (Figure 9b) and was found to be $1.54 \times 10^4$ L mol$^{-1}$. The decrease in fluorescence intensity and the calculated $K_{SV}$ value were attributed to the efficient transfer of an electron from the excited state RQC to the conduction band of the TiO$_2$ nanoparticles.

The sacrificial electron donor TEOA was used to regenerate the RQC dye by donating an electron to the dye. So, it is necessary to explore the electron transfer reactions between the RQC dye and TEOA. The addition of various concentrations of TEOA brought about no considerable changes in the absorption spectra; in contrast, fluorescence quenching occurred in the excited state with a slight bathochromic shift (Figure 10a). A combined fluorescence quenching and bathochromic effect confirms the excited-state electron transfer between RQC and TEOA. The quenching data were analyzed using the S–V equation and the S–V quenching constant, $K_{SV}$, was calculated from the S–V plot (Figure 10b) and was found to be $3.9 \times 10^3$ L mol$^{-1}$.$^{[30,31]}$

### 2.7. Dye-Sensitized Solar Cells

A 21 nm sized TiO$_2$ (P25) nanoparticle film was printed on the cleaned FTO glass plate by the doctor blade method and this photoanode film was sintered at 450 °C for 30 min. Afterward, the TiO$_2$ photoanode film was immersed in methanol solvent, which contained 0.3 mM RQC dye for 24 h. The counter electrode was obtained by spreading a drop of 0.02 mM H$_2$PtCl$_6$ solution. An RQC-based DSSC device was fabricated by clipping the two electrodes and the internal space was filled with an I$_1$I$_3^-$ electrolyte. The photoelectrochemical measurements were performed using a Photo Emission Tech-SS50AAA-EM solar simulator (300 W xenon lamp with an AM 1.5G filter with the incident light intensity 100 mW cm$^{-2}$) coupled with a CHI6005E electrochemical workstation at room temperature. In our previous works, we have fabricated Ru(II)-sensitized DSSCs and to enhance the efficiency the DSSCs were cosensitized by coumarin-based dyes. After cosensitization, the efficiencies of DSSCs were significantly enhanced. In this work, a new Ru(II) complex was coupled with coumarin moiety and the power conversion efficiency was explored by J–V characterization and impedance analysis.

![Figure 10. a) Change in the emission intensity of RQC (1 x 10$^{-5}$ mol L$^{-1}$) on incremental addition of TEOA when excited at 495 nm. b) S–V plot of quenching of RQC by TEOA.](image-url)

![Figure 11. J–V curve of DSSC device fabricated with RQC using standard AM 1.5G illumination.](image-url)
2.7.1. J–V Characterization

The photocurrent–voltage (J–V) characterization of the DSSC device fabricated with RQC using standard AM 1.5G illumination is revealed in Figure 11. The solar-to-power conversion efficiency of the device can be evaluated by the equation

\[
\eta = \frac{J_{sc} \times V_{oc} \times FF}{I_0} \times 100
\]  

where \(\eta\) is the power conversion efficiency, \(V_{oc}\) is the open-circuit voltage, \(J_{sc}\) is the short circuit current, FF is the fill factor, and \(I_0\) is the intensity of illuminated light (100 mW cm\(^{-2}\)). The RQC-based DSSC furnished a \(J_{sc}\) of 11.4 mA cm\(^{-2}\), \(V_{oc}\) of 0.69 V, FF of 0.53, and power conversion efficiency (\(\eta\)) of 4.16 %. The coumarin-based quinoline ligand acts as a light-harvesting antenna and increases the power conversion efficiency of the Ru(II) DSSC.

2.7.2. Electrochemical Impedance Analysis

To examine the interfacial charge recombination dynamics in the DSSC device, impedance analysis was conducted in a frequency range of 0.1–100 kHz. Figure 12a is the Nyquist plot, which shows one small semicircle at the longer frequencies and one big semicircle at the shorter frequencies, which were ascribed to the charge transfer at the counter electrode/electrolyte interface and the charge transfer at the photoanode/electrolyte interface, respectively. The experimental Nyquist data were fitted by the equivalent circuit \(R_s[(C_1R_1)(C_2R_2)]\). The smaller resistance values \(R_1\) (64.43 \(\Omega\)), \(R_2\) (222.6 \(\Omega\)), and \(R_s\) (27.86 \(\Omega\)) result in the higher power conversion efficiency (\(\eta = 4.16 \%\)) of the device.

In a Bode’s plot (Figure 12b), the middle frequency of the peak is directly related to the electron lifetime in conduction band of TiO\(_2\) (\(\tau_{CB}\)). Under open-circuit conditions, the efficiency increases by the electron lifetime, i.e., higher \(\tau_{CB}\) favorable for charge accretion on the TiO\(_2\) conduction band, and this increases the electron density and \(V_{oc}\) values. From the midfrequency value, the \(\tau_{CB}\) of the fabricated device was found as 5.1 ms.
3. Conclusion

In summary, we have successfully assembled both dye-sensitized photoelectrochemical cells and dye-sensitized solar cells using a new coumarin-based ruthenium(II) photosensitizer on the nanostructured TiO₂ as the photoanode. In DSPECs a maximum photocurrent density of 11.07 mA cm⁻² was found under light illumination at pH 6 in the presence of 30 mM TEOA as the sacrificial electron donor. Under these conditions, a maximum PEC water splitting efficiency (η) of 4.98 % was obtained. During visible light illumination with an applied potential (+0.78 V vs RHE), bubbles of oxygen and hydrogen evolved from the anode and cathode, respectively, which were observed by the naked eye. In the DSSC, a maximum power conversion efficiency (η) of 4.16 % was achieved. The idea of fabrication of DSPEC and DSSC devices using a single photosensitizer makes a big step forward toward artificial photosynthesis and encourages further research in reduction of carbon dioxide.

4. Experimental Section

Materials: Chemicals for syntheses and photoelectrochemical measurements were purchased with high purity and used as such without any further purification. 4-Chloro-3-formyl coumarin (97%), 5-amino-8-hydroxy quinoline (95%), titanium(IV) chloride (≥97%), TiO₂ nanoparticles of size 21 nm (≥95.5%), 4-tert-butylypyridine (98%), dimethylpropyl imidazolium iodide (99.0%), and FTO glass sheets (50 mm × 50 mm × 2.2 mm) were purchased from Sigma Aldrich. RuCl₃.3H₂O was received from Himedia Chemicals Pvt. Ltd. Sodium dihydrogen phosphate, disodium hydrogen phosphate, NaOH, KCl, and H₃PtCl₆.6H₂O were received from Merck. TEA, triethylamine, EDTA, and ascorbic acid were purchased from Sd Fine Chemicals Ltd.

Characterization Techniques: ¹H-NMR spectra of the coumarin-based hydroxyquinoline ligand and its ruthenium(II) complex were recorded from a Bruker 400 MHz NMR spectrometer using CDCI₃ and DMSO as solvents, respectively. ESI mass spectra were recorded on a THERMO FINNIGAN LCQ Advantage max ion trap mass spectrometer. Acetonitrile: water (90:10) was used as the mobile phase and the flow rate was 250 μL min⁻¹. Elemental analyses (CHN) were done using a Perkin-Elmer elemental analyzer. Fourier transform-infrared (FT-IR) spectra were recorded using a JASCO FT/IR-410 spectrometer in the range 4000–400 cm⁻¹ using KBr pellets. The photoelectrodes were analyzed with X-ray diffraction using a Panalytical X’pert Powder X’celerator Diffractometer in the 2θ range 10°–80° and a scanning electron microscope (SEM) using Hitachi H-7100 with a copper grid. Photophysical properties of the ligand, complex, and quenching studies were performed with a Perkin Elmer Lambda 25 UV-vis spectrophotometer and JASCO FP-8500 spectrofluorometer, respectively. Electrochemical properties of the complex (10⁻³ M in acetonitrile solution) were studied by a CHI660E electrochemical workstation containing a platinum working electrode (2 mm diameter), a platinum wire counter electrode, a nonaqueous Ag/AgCl reference electrode, and 0.1 M tetrabutylammonium perchlorate supporting electrolyte. The sample solutions were deoxygenated by purging purified nitrogen gas (99.9%) for 30 min prior to each measurement. Quantum chemical calculations (DFT) were done by the Gaussian 09 software package at the B3LYP/6-311++G(d,p), level. FMO levels (HOMO and LUMO), energy gap, and geometry optimization were obtained with the Gaussian 09 program package. Visual depictions of the HOMO and LUMO were accomplished via Gaussian view. EIS analyses were conducted in an open circuit potential (OCP) at room temperature over a frequency range of 0.1–100 kHz. The impedance data were collected using ZSimpWin software. The photoelectrochemical measurements (both DSPECs and DSSCs) were performed using a Photo Emission Tech-SS50AAA-EM solar simulator (300 W xenon lamp with an AM 1.5G filter with the incident light intensity 100 mW cm⁻²) coupled with a CHI660E5 electrochemical workstation at room temperature. The pH was measured using a bench pH meter (Eutech Instruments).

Synthesis of [Ru(dcbpy)₂(QC)]⁺ Complex (RQC): An ethanol solution (10 mL) of 4-chloro-3-formyl coumarin (1 mmol) was added dropwise to a solution of 5-amino-8-hydroxy quinoline (1 mmol) in ethanol. The reaction mixture was refluxed at about 80–90 °C for 8 h. The volume of the solution was reduced to half of the initial volume under reduced pressure. The yellow precipitate formed was collected by vacuum filtration, washed with ethanol, and dried in room temperature. The purity of the synthesized ligand was checked by TLC and recrystallized from ethanol (Scheme S1, Supporting Information). Yield was 82%.

Synthesis of [Ru(dcbpy)₂(QC)]⁺Cl⁻ Complex (RQC): The QC ligand (1 mmol) was added to a solution of [Ru(dcbpy)₂Cl₂] (1 mmol) in 50 mL of DMF. The mixture was refluxed under a nitrogen atmosphere for 28 h. After refluxing, the dark-color solution turned into reddish brown. The reaction mixture was allowed to cool to room temperature and filtered through a sintered glass crucible. The solvent DMF was evaporated completely on a rotatory evaporator under vacuum. The resulting solid product was washed with acetone and diethyl ether (Scheme 1). Purity of the complex was confirmed by UV–vis absorption and emission spectroscopy. λmax(abs) = 494 nm and λmax(emi) = 542 nm. Yield was 92%.

Preparation of Photoelectrodes: The FTO glass substrates for the photoanodes were first cleaned in a bath of detergent solution, pure distilled water, acetone, and 2-propanol for 15 min each using an ultrasonic cleaner. Then, a transparent and mesoporous titanium layer was deposited by treating with 0.2 M TiCl₄ aqueous solution at 70 °C. The TiO₂ paste was spread on the FTO plates by the doctor-blade technique and were gradually heated at 150 °C for 10 min and annealed at 450 °C for 30 min. After sintering, the photoanodes were dipped in a 0.3 mm methanol solution of RQC overnight to adsorb the dye effectively. The unadsorbed and loosely adsorbed dye molecules were removed by washing with excess of methanol. The active area of the fabricated device was 1 cm² for DSPECs and 0.25 cm² for DSSCs. The amount of RQC dye adsorbed was calculated from the UV–vis absorption spectra of the solution before and after the adsorption process.

Amount of dye adsorbed (mol g⁻¹) = \[ \frac{A_{\text{before}} - A_{\text{after}}}{A_{\text{before}}} \times \frac{C(\text{mol L}^{-1}) \times 25 \times 10^{-3}(\text{L})}{W \times 10^{-3}(\text{g})} \] (8)

where Abefore and Aafter are the absorbance of the solution before and after the adsorption process, respectively, C is the initial concentration of the solution, and W is the weight of TiO₂ nanoparticles in milligrams.[23] The amount of RQC loaded was 1.39 μmol for DSPECs and 0.35 μmol for DSSCs.

For the preparation of DSSC counter electrodes, the same FTO plates were used after the cleaning procedure. After drying out in air, they were coated with activated platinum by spin coating of 0.02 M H₂PtCl₆.6H₂O solution. Then, the plates were heated at 500 °C for 30 min. The photoanodes and the counter electrodes were clipped together with conducting surfaces facing inward. Finally, the iodide/triiodide electrolyte consisting of 0.6 M dimethylpropyl imidazolium iodide, 0.05 M I₂, 0.1 M LiI, and 0.4 M tert-butylpyridine in acetonitrile was injected into the crevice between the electrodes.

Photoelectrochemical Water Splitting Experiments: PEC water splitting measurements were conducted using a conventional three-electrode system in a one-compartment glass reactor. As-prepared dye-sensitized TiO₂ slides (1 cm² geometrical surface area) were studied as working electrode, a Pt wire was used as counter electrode, and a Ag/AgCl(ref) reference electrode were used. The electrolyte was phosphate buffer and 0.1 M potassium chloride with a pH of 6. All potentials were measured versus the Ag/AgCl reference electrode and converted to RHE using the Nernst equation.

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During PEC water splitting experiments, the cell was degassed with nitrogen gas for 30 min prior to each measurement. During chronogrammetry measurements chopped-light illumination was applied with 30 s intervals (30 s light on/30 s light off) with constant light illumination.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

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