Anthracene-Based Fluorophore and Its Re(I) Complexes: Investigation of Electrical Properties and Schottky Diode Behavior

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ABSTRACT: A novel fluorophore (HL) [1-(E)-(quinolin-8-ylimino)methyl]anthracen-2-ol] using a suitably designed anthrol and quinoline derivative was synthesized and well characterized. Then, two Re(I) complexes with the [fac-[Re(CO)₃]⁺] moiety were prepared with the ligand under different reaction conditions. Both the complexes [Re(L)(CO)₃] (1) and [Re(HL)(CO)₃Cl] (2) absorbed in the visible region. Steady-state fluorescence measurements and time-correlated single-photon count experiments were performed to elucidate the nature of the excited state. The ground- and excited-state geometries were theoretically investigated using density functional theory (DFT) calculations. The electrical properties of the ligand and the complexes have been explored with the help of a sandwich-structured thin-film device of an Al/sample/indium tin oxide (ITO) configuration at room temperature. The thermionic emission (TE) theory was adopted for the extraction of Schottky diode parameters such as ideality factor, barrier height, and series resistance. Further, the space-charge-limited current (SCLC) theory was employed for a better understanding of the charge transport phenomenon.

INTRODUCTION

Among the heavy-metal ions with the d⁶ configuration, rhenium(I) complexes with the non-innocent ligand-bearing fac-[Re(CO)₃]⁺ moiety are very important.¹⁻⁴ These types of Re(I) complexes were found to show sharp luminescence and their origin has been ascribed to the triplet Re(I) to ligand charge transfer (3MLCT) and/or intraligand charge transfer (ILCT).⁵ The research on rhenium has been fascinating, especially in the last decade, for its exploitation in solar energy conversion,⁹ light-emitting devices,¹⁴ trapping¹⁴ and reduction of carbon dioxide,¹⁵ and in reductive N₂ splitting.¹⁶ Rhenium complexes have found widespread applicability in the field of chemi- or electrochemiluminescence (ECL) detectors,¹⁷ luminescent metallo-drugs,¹⁸ application against bacterial infections,¹²² therapeutics,¹³ etc. thanks to their unique chemical stability, resolute visible absorption, excited-state reactivity, photoredox chemistry,¹⁴ and of course their versatile catalytic properties.²³ Zhou et al. reported for the first time the Schottky characteristics of Re on AlGaN.²⁶ Shim and co-workers²⁷ reported the negative differential resistance behavior on a phosphorene/rhenium disulfide heterojunction. Officer et al.²⁸ reported the fabrication of Re(I) complexes as organic light-emitting diode (OLED) devices. The use of the Re(I) complex in the form of a dopant in poly(vinylcarbazole) (PVK) as emissive-layer OLEDs²⁹ has been found very recently.

On the other hand, synthesis of light-sensitive fluorophoric anthraquinone derivatives has attracted researchers because of their near-visible photosorption and chemical reactivity via a quinine—methide (QM)³⁰-type intermediate. These properties prompted us to synthesize a novel chromophoric Schiff base molecule (HL) with an anthrol—quinoline fragment. First, the organic framework was thoroughly characterized by the single-crystal X-ray diffraction technique and via other routine studies viz. various spectroscopic methods. Then, Re(I) complexes of HL were utilized as Schottky barrier diode devices. The values of direct optical band gap energies of the synthesized samples [Re(L)(CO)₃] (1), [Re(HL)(CO)₃Cl] (2), and HL (3) were found to be 2.26, 2.23, and 2.39 eV, respectively, which were evaluated using Tauc’s equation.³¹⁻³³ The current—voltage characteristic curves of the materials exhibit rectifying Schottky diode behavior. Also, the I–V characteristics of the synthesized materials film showed highly influencing rectifying nature upon irradiance of light. For a better understanding of charge-transfer kinetics, effective carrier mobility of the fabricated devices is estimated with the help of a space-charge-limited current (SCLC) region.
RESULTS AND DISCUSSION

**Synthesis.** The synthesis of ligand HL [1-((E)-(quinolin-8-ylimino)methyl)anthracen-2-ol] was performed using the commercially available precursor 2-hydroxy anthraquinone (1.0 mmol). Then, it was reduced by NaBH₄ and subsequently formylated to obtain 2-hydroxyanthracene-1-carbaldehyde. Treatment of the aldehyde with quinoline-8-amine (1.0 mmol) under refluxing conditions in methanol yielded the orange-colored ligand HL. Yield: 74% Elemental Anal. Calcd for C₂₈H₁₇N₂O₄Re: C, 46.44; H, 3.57; N, 4.51. Found: C, 46.52; H, 3.45; N, 4.46. IR (KBr pellets, cm⁻¹): ν(C=O) 1739; ν(C=N) 1315. ¹H NMR CDCl₃: δ (ppm) 6.82 (1H, d, 1H, J = 14.9 Hz), 7.44 (1H, s, 1H), 8.54 (CH=O), 8.78 (s, 1H), 8.74 (dd, 1H), 8.59 (dd, 2H) 8.00 (m, 3H), 7.97 (m, 2H), 7.78 (m, 2H), 7.55 (m, 1H), 7.41 (m, 1H), 6.99 (m, 1H) ¹³C NMR DMSO-d₆: δ (ppm): 173.16, 161.15, 155.07 (CO), 150.71 (CH=N).

For the complexes, the imine proton was observed at 8.54 and 8.37 ppm.

**Crystal Structure Description.** Solid-state structures of all of the compounds were elucidated using the single-crystal X-ray diffraction technique. The crystallographic parameters are given in the Supporting Information (Table S1); selected bond lengths and angles are given in the Supporting Information (Tables S2 and S3). An apparent interruption of aromaticity, in the crystal structure of the ligand, was found in the anthracene moiety (Supporting Information, Figure S1). The C3−O1 (1.24 Å), C1−C2 (1.38 Å), and C2−C3 (1.46 Å) bond lengths suggested the partial disruption of electronic delocalization in the ring. The proton NMR peak at 6.48 ppm for the hydrogen attached to C4 in the anthracene ring confirmed the predominant presence of the keto−enamine form in solution. Careful observation of the crystal structure of the ligand revealed an almost coplanar structure with an angle of 7.84° between two planes with dihedral angles of C3−C2−C1−N1 (1.68°) and C1−N1−C26−C27 (177.47°) (Supporting Information, Table S5 and Figure S5). Structural analysis revealed that both the re-complexes crystallized in a triclinic system with a distorted octahedral geometry around the Re(I) center with the space group P1. In the complex [Re(L)(CO)₅], (1) the mono-anionic ligand (L⁻) coordinated with the metal center through phenolato oxygen, imine nitrogen, and quinoline nitrogen, where the metal center is surrounded by three carbonyl groups arranged in facial mode. For the complex [Re(HL)(CO)₃Cl] (2), the ligand coordinated to Re(I) in neutral mode with the help of two nitrogen donors keeping phenolic oxygen free and surrounded by one chlorine and three carbonyl groups in a facial manner.

The other bond angles like C18−Re1–O1 (174.4°) for complex 1 and C17−Re1–Cl1 (179.5°) for complex 2 also suggested the structure to be a distorted octahedron.

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**Scheme 1. Schematic Representation of the Synthesis of the Ligand and the Complexes**
A comparison of the distorted octahedral geometry was performed by C16–Re1–N2 bond angles of 172.6 and 175.7° for complex 1 and complex 2, respectively; dihedral angle data along with interplanar angles (Supporting Information, Table S9) for ligand and complexes strongly suggested that Re(I) facilitated the ligand to be in the nonplanar imine-ol form predominantly in both the complexes (Figure 1).

Moreover, in the case of complex 2, each discrete unit formed a pseudo-rhombohedral arrangement with four adjacent Re(I) centers having distances of 12.230 and 9.491 Å along the b-axis. Each discrete unit was stabilized by a pseudo C–H···π interaction at 3.731, 4.274, and 4.575 Å. The presence of a π···π type interaction at 5.564 Å and supramolecular interactions at distances of 3.139 and 4.119 Å further stabilized the chloro complex (Figure 2).

Analysis of Photophysical Properties. Absorption spectra of the ligand showed a band at around 350 nm and two sharp closely spaced peaks at 469 and 495 nm, respectively, in the acetonitrile–dichloromethane (DCM) mixed solvent system. Upon binding with Re(I), the band around 350 nm was red-shifted slightly; also, the other two closely separated peaks in the ligand broadened with a slight red shift in the range of 496–505 nm for both the complexes. The absorption band in the region 350 nm can reasonably be assigned to a mixture of a metal-to-ligand charge-transfer (MLCT) transition along with a little ILCT character, while the lowest-lying absorptions in the region 496–505 nm for all of the complexes had a purely ligand-centered ILCT character. The electron densities in the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) mainly reside on the ligand moiety, which was involved in the low-energy bands. The electron densities in the rest of the occupied and unoccupied orbitals, which were involved in the high-energy transition, were composed of both a ligand moiety and a metal d orbital.

In the steady-state fluorescence measurement, the ligand was found to be highly emissive, with emission maxima at 526 nm (λex = 350 nm), with a very high Stokes shift. The complexes upon excitation at around the same wavelength range were found to be low emissive than that of ligand HL. Moreover, the [Re(HL)(CO)3] complex (2), with unbound phenolic –OH, was found to be less emissive than complex (1) [Re(L)(CO)3Cl] with a decrease in the Stokes shift. Obviously, the rigidity in the crystal structure is the reason. The time-correlated single-photon count data was best fitted through a biexponential function with a long lifetime (τ). The details of all of the data are listed in Table 1 and Figures 3 and 4.

Geometry Optimization and Electronic Structure. Ground State. Theoretically, for a ligand, the keto-enamine form (here QM type) was found to be more stable in solution by an amount of energy 7.345 kcal mol⁻¹ over its imine-ol form as is evident from the potential energy scan in the S0 state (Figure 5). The dihedral angles were calculated as C3–C2–C1–N1 (0.733°) and C1–N1–C26–C27 (177.245°) for the keto-enamine form and 3.556 and 144.369° for the imine-ol form. The geometry utilized for the ground-state optimization was based on crystal structure parameters of the ligand (Supporting Information, Figure S1) and the complexes (Supporting Information, Figure S3). The optimized parameters of the ligand and the complexes were correlated mostly with the X-ray crystal structure data. The optimized bond lengths and bond angles of the complexes are given in the Supporting Information (Table S5). The isodensity plots along with the absorption transition are given in the Supporting Information (Figure S4).
Information (Figure S4). Time-dependent density functional theory (TDDFT) excited-state calculations were performed for the assignment of the experimental spectral bands. The calculated absorption energies, oscillator strengths, the main compositions, and their assignments are given in the Supporting Information (Table S6).

**Excited State.** To demonstrate the emission property of the ligand and the complexes, geometry optimizations of the ligand in excited-state (S₁) and Re(I) complexes in a low-lying excited triplet spin state (T₁) with spin density calculations were performed. Remarkable changes were observed for the ligand in the excited state, with deviation from planarity. Probably, in the excited state, the imine-ol tautomeric form was formed via the excited-state intramolecular proton transfer (ESIPT) process, which leads to high-intensity emission with a large Stokes shift. Slight destabilization of HOMO by an amount of energy 2.4133 eV and stabilization of LUMO by an amount of energy 2.415 eV in the S₁ state were the prime reasons for the large Stokes shift (176 nm) of the ligand. On coordination with metal, the conjugation involved in the ESIPT pathway was arrested, resulting in decreased emission intensity with relatively less Stokes shift.

In the case of complexes, the analysis on the lowest-lying singly occupied molecular orbitals, namely, HSOMO and LSOMO showed that the LSOMO was mainly located on the quinoline moiety for both the complexes and HSOMO was mainly located on the \(-\text{C=\text{N}}-\) group and on the anthracene moiety. In both the cases, spin density maxima were mainly localized on the functionalized center of the anthracene moiety and on the \(-\text{C=\text{N}}-\) fragment along with very little contribution of Re(I) centers. Thus, the lowest-lying T₁ excited state mainly consisted of 3ILCT and 3LLCT excited states in both the ligand and complexes.

### Table 1. Selected Photophysical Parameters of the Ligand and Complexes

| compound     | \(\lambda_{\text{max}}\) (nm) \(\varepsilon\) (M⁻¹ cm⁻¹) | \(\lambda_{\text{emi}}\) (nm) | Stokes shifts (nm) | \(\Phi_F\) | lifetime (\(\tau\)) (ns) | \(k_{\text{nr,s}}\) s⁻¹ (±5% error) | \(k_{\text{r,s}}\) s⁻¹ (±5% error) |
|--------------|---------------------------------------------------------|-----------------------------|-------------------|-----------|--------------------------|-----------------------------------|-----------------------------------|
| HL           | 350 (18584)                                             | 526                         | 176               | 0.27      | 8.15                     | 0.033                             | 0.089                             |
|              | 469 (32410)                                             |                             |                   |           |                          |                                   |                                   |
|              | 495 (33442)                                             |                             |                   |           |                          |                                   |                                   |
| [Re(HL)(CO)₃Cl] | 357 (17690)                                             | 520                         | 163               | 0.198     | 8.29                     | 0.0238                            | 0.096                             |
|              | 496 (10155)                                             |                             |                   |           |                          |                                   |                                   |
| [Re(L)(CO)₃]  | 359 (28298)                                             | 496                         | 137               | 0.257     | 8.50                     | 0.0302                            | 0.0874                            |
|              | 505 (10298)                                             |                             |                   |           |                          |                                   |                                   |

**Figure 3.** (a) Absorption spectra of the ligand and the complexes. (b) Comparative fluorescence profiles.

**Figure 4.** Excited-state decay pattern of the ligand and complexes.

**Figure 5.** Potential energy surface scan at the ground S₀ state for HL: (a) the keto-amine form and (b) the imine-ol form, obtained through calculation at the DFT/B3LYP level.
Figure 6. UV–vis absorption spectra (inset) and Tauc’s plots for (a) [Re(L)(CO)₃], (b) [Re(HL)(CO)₃Cl], and (c) HL.

Figure 7. Current–voltage (I–V) characteristic curve for (a) [Re(L)(CO)₃] (1), (b) [Re(HL)(CO)₃Cl] (2), and (c) HL (3), under dark and light conditions.
complexes. Excited-state geometry optimization of the ligand (S1) and complexes (T1) revealed that there was no significant change in geometry in the coordination sphere around the metal center, with the exception of some specific ligand pockets.

Careful observation of HSOMO, LSOMO, and the corresponding electron spin density plot revealed that the excited-state transitions were mainly ligand centered (Supporting Information, Figure S7). The details of the orbital involved and the transitions that occurred thereof for HL and the two complexes are listed in the Supporting Information (Table S8).

**Optical Characterization.** The optical properties of samples 1, 2, and 3 were studied by ultraviolet–visible (UV–vis) absorption. The absorption spectra were recorded for the deposited thin films of as-synthesized material by preparing a well dispersion in N,N-dimethylformamide (DMF) using a UV–visible spectrophotometer in the wavelength range of 350–800 nm. The absorption spectrum of the synthesized material illustrated energy absorption in the visible region at about 515–555 nm. The optical band gap of the film was determined from fundamental absorption, which corresponds to electron excitation from the valence band to the conduction band. The absorption spectra of all of the samples are shown in the insets of Figure 6c. The optical band gap energies (E_g) of the as-synthesized samples were evaluated using Tauc’s equation

$$ (ah\nu) = A(\nu - E_g)^n $$

where α is the absorption coefficient, E_g is the band gap, h is Planck’s constant, ν is the frequency of light, the exponent n is the electron transition process-dependent constant, for direct transition n = 1/2,34,35 and A is a constant that is considered as 1 for the general case.

The (ah\nu)^2 vs h\nu plot of the synthesized materials is shown in Figure 6a,b. By extrapolating the linear region of both the plot (ah\nu)^2 vs h\nu, the values of the direct optical band gap energies of the synthesized samples HL (1), Re(HL)(CO)_3Cl (2), and [Re(L)(CO)_3] (3) were evaluated as 2.26, 2.23, and
To understand the underlying mechanism of the charge transport phenomenon, electrical characterization was carried out.

Electrical Characterization. To study the electric behavior of the synthesized materials (samples [Re(L)(CO)3] (1), [Re(HL)(CO)3Cl] (2), HL (3)), a sandwich-structured thin-film device with an Al/sample/indium tin oxide (ITO) configuration was fabricated. Figure 7a–c shows the current–voltage characteristic curves of devices (samples 1, 2, and 3) under dark and light conditions (irradiance ~1000 Wm⁻²). The inset of Figure 7 shows the logarithmic presentation of current as a function of voltage. Evidently, the current–voltage characteristic curve in Figure 7 showed that the devices based on samples 1, 2, and 3 exhibited nonlinear rectifying behavior, like the Schottky diode behavior. Also, the I–V characteristics of the synthesized sample film showed a highly influencing rectifying nature upon irradiance of light. The characteristic curves under light showed larger current, which illustrated the photoresponse of the devices. Hence, we have computed the photosensitivity of all devices (samples 1, 2, and 3) and the values are 1.38, 1.13, and 0.90, respectively. The photosensitivity (Pₛ) of the diode was defined as the ratio of photocurrent (where Iᵣk = I₁ − I₀, I₀ is the current under light) to the dark current (I₀) [35,36]

\[ Pₛ = \frac{I₁ - I₀}{I₀} \]

To understand the underlying mechanism of the charge transport phenomenon, the I–V characteristic curves were analyzed with the help of the thermionic emission (TE) theory of a Schottky diode. In this regard, we started I–V curves analyzing quantitatively by considering the following standard equations[8]

\[ I = I₀ \exp\left[\frac{qV}{kT}\right] \left(1 - \exp\left[\frac{-qV}{kT}\right]\right) \]

where \( I₀ \) is the saturation current derived from the straight-line intercept of \( \ln(I) \) at \( V = 0 \) and is given by

\[ I₀ = A*A*T² \exp\left(-\frac{q\varphi_b}{kT}\right) \]

where \( q \) is the electronic charge, \( k \) is the Boltzmann constant, \( T \) is the temperature in kelvin, \( V \) is the forward bias voltage, \( A \) is the effective diode area, \( \eta \) is the ideality factor, and \( A* \) is the effective Richardson constant. The effective diode area was estimated to be \( 7.065 \times 10^{-6} \) m² and the effective Richardson constant was considered as \( 1.20 \times 10^{6} \) A K⁻² m⁻² for all of the devices. At low bias, linearity in current was observed, which is consistent with eq 2, while the deviation from linearity at higher bias voltages occurred due to the change in diode series resistance. From Cheung, the forward bias I–V characteristics in terms of series resistance can be expressed as [39,40]

\[ I = I₀ \exp\left[\frac{q(V - IRₛ)}{\eta kT}\right] \]

where the IRₛ term is the voltage drop across series resistance of the device. In this circumstance, the values of the series resistance can be determined from the following functions using eq 4.41

\[ \frac{dV}{d \ln (J)} = \left(\frac{\eta kT}{q}\right) + RₛA \]

(5)\n
\[ H(J) = RₛA + \eta \varphi_b \]

(6)\n
and \( H(J) \) can be represented as

\[ H(J) = V - \left(\frac{\eta kT}{q}\right) \ln\left(\frac{I}{A*+T²}\right) \]

(7)\n
The series resistance \( Rₛ \) and ideality factor \( \eta \) for all devices under dark and light conditions were determined from the slope and intercept of \( dV/d \ln (J) vs J \) plot (Figure 6). The potential barrier heights for all devices were evaluated from the y-axis intercept of the \( H(J) vs J \) curve (Figure 8). The slope of this plot also furnished a second determination of the series resistance. The obtained values of the ideality factor, barrier height, and series resistance are listed in Table 2.

The values of the ideality factor \( \eta \) under the dark condition deviated from ideal behavior and this difference was due to the presence of inhomogeneities of Schottky barrier height, high probability of electron and hole recombination in the depletion region, existence of interface states, and series resistance.42,43 However, the value of the ideality factor approached unity under the illumination of light. Series resistance \( Rₛ \) of all of the compounds in both cases decreased after soaking light, which signifies its applicability in the field of optoelectronic devices.

The charge transport mechanism through the metal–semiconductor (MS) junction was further analyzed by employing the space-charge-limited current (SCLC) theory. In this regard, we diagrammed the logarithm current vs voltage (I–V) curves under dark and photoillumination conditions (Supporting Information, Figure S6) for three devices. Figure S6 clearly demonstrated two regions with different slopes, indicating different conduction mechanisms. The current conduction mechanism was governed by the power law \( I \propto V^{m} \),[44] where \( m \) is the slope of the I vs V curve. At low bias
voltage (region I), the sample exhibited ohmic behavior, i.e., the current was directly proportional to the applied bias voltage \( I \propto V \). The \( I-V \) characteristics in this region could be attributed to the thermionic emission of current and the occurrence of the series resistance effect. Region II corresponded to the higher-ordered magnitude of slope and exhibited variation of current with the square of forward bias voltage \( I \propto V^2 \). In this region, the current was governed by space charge, designated as space-charge-limited current (SCLC). The trap distribution was the key factor in this type of charge transport mechanism.

In region 2, the slope is close to 2, which reveals a shallow trap-filled SCLC-dominant charge transport mechanism. From this region, the effective mobility and transit time are evaluated. To gain better insight into the charge transport properties, effective carrier mobilities of the three devices fabricated were estimated from an \( I \) vs \( V^2 \) plot (Supporting Information, Figure S8) for the SCLC region, by evaluating the slope with the help of the Mott–Gurney space-charge-limited current (SCLC) equation

\[
I = \frac{9\mu_{eff} \varepsilon_0 \varepsilon_r A}{8d} \left( \frac{V^2}{d^5} \right)
\]

where \( I \) is the current, \( \mu_{eff} \) is the effective carrier mobility, \( V \) is the applied bias voltage, \( d \) is the thickness, \( \varepsilon_0 \) is the permittivity of free space, and \( \varepsilon_r \) is the dielectric constant. The value of the dielectric constant of the material was measured from a capacitance vs frequency plot (\( C \)–\( f \)) (Figure 9) using the following equation:

\[
\varepsilon_r = \frac{Cd}{\varepsilon_0 A}
\]

where \( C \) is the capacitance (at saturation), \( d \) is the thickness, \( \varepsilon_0 \) is the permittivity of free space, and \( A \) is the area \( (7.065 \times 10^{-8} \text{ m}^2) \). The dielectric constant values are measured from the frequency vs capacitance plot. The values of dielectric constants are 3.21, 1.72, and 1.08 for \([\text{Re}(L)(CO)_3]\), \([\text{Re}(HL)(CO)_3\text{Cl}]\), and \( HL \), respectively.

Mobility and transit time were the prime factors used to determine the device performance. Transit time \( \tau \) was defined as the time required by a carrier to travel from the anode to the cathode. It can be expressed as the summation of the average total time spent by each electron as a free carrier plus the total time spent in the trap. The transit time \( \tau \) of the charge carrier was deduced from the slope of the \( I \) vs \( V \) plot in region II (Supporting Information, Figure S9) with the help of the following equation:

\[
\tau = \frac{9\varepsilon_0 \varepsilon_r A}{8d} \left( \frac{V}{I} \right)
\]

The effective mobilities of the carriers under the dark condition were calculated to be \( 1.28 \times 10^{-6}, 1.19 \times 10^{-6}, \) and \( 0.93 \times 10^{-6} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1} \) for compounds 1, 2, and 3, respectively. After irradiation of light, the values of effective carrier mobility \( (\mu_{eff}) \) improved to \( 2.73 \times 10^{-6}, 2.51 \times 10^{-6}, \) and \( 1.39 \times 10^{-6} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1} \) for these compounds, respectively. Longer transit time under the dark condition led to higher trapping probabilities but after illumination of light, the situation was reverse due to the higher carrier mobility.

The values of the effective carrier mobility and the transit time of samples 1, 2, and 3 are tabulated in the Supporting Information (Table S8).

### Impedance Analysis

An impedance spectroscopy (IS) study was carried out over a wide frequency range (40 Hz to 10 MHz) at room temperature with the help of a computer-controlled Agilent 4294A precision impedance analyzer. Figure 10 shows the Nyquist plot for our fabricated devices with the three compounds. The higher-frequency semicircular arc
depicted the bulk contribution and the intermediate- or low-frequency semicircular arc represented the grain-boundary or electrode-specimen effect. The intercept of the semicircle on real axis $Z'$ gives the value of the charge-transfer resistance ($R_{CT}$) of the sample. The lower resistance implied better possibility of charge transfer among the others. Additionally, it has been seen that impedance analysis one to one correlates with the study of the current–voltage characteristics.

**CONCLUSIONS**

In summary, we have explored a photosensitive Schottky diode of a novel fluorophoric Schiff base ligand with the quinimethide (QM)-type fragment and its Re(I) complexes. The $I$–$V$ characteristic curves of all of the synthesized materials exhibited the sign of Schottky nature under both dark and light conditions. The thermionic emission (TE) theory was utilized for the extraction of the ideality factor and barrier height from dc $I$–$V$ measurements (under dark and light conditions). The charge transport properties through the metal–semiconductor junction were well explained by employing the SCLC theory, which showed that the effective carrier mobility of the complexes increased ∼43% in the light condition with respect to the dark condition in comparison to the ligand along with reduced transit time after light soaking. Complexes exhibited better electrical properties under dark as well as light conditions, which is suitable for optoelectronic applications. To the best of our knowledge, this is the first report of Re(I) complexes as photosensitive Schottky diodes.

**EXPERIMENTAL SECTION**

**Materials and Methods.** Rhenium pentacarbonylchloride (98%) and 2-hydroxyanthraquinone were purchased from Aldrich Chemical Co. All of the chemicals and solvents were of analytically pure grade and were used without further purification. Infrared spectra were recorded on a PerkinElmer 1120-00A FT-IR spectrometer with the samples prepared as KBr pellets. $^1$H NMR spectra were recorded on a Bruker FT 400 MHz instrument. For NMR spectra, DMSO-$d_6$ was used as the solvent using tetramethylsilane (TMS) as an internal standard. UV–vis experiments were performed on a PerkinElmer Lambda 25 spectrophotometer and the fluorescence experiment was performed using a Horiba FluoroMax-4 fluorescence spectrometer and a cuvette of 10 mm path length. Elemental analysis (C, H, and N) was performed on a PerkinElmer 2400 series II analyser. The quantum yields of the ligand and the complexes $[\text{Re(L)}(\text{CO})_3]$ and $[\text{Re(HL)}(\text{CO})_3\text{Cl}]$ were determined in a freeze-pump-thaw-degassed solution of the same by a relative method using quinine sulfate as the standard ($\Phi_{\text{rel}} = 0.54$ (at 298 K) in 0.1 M H$_2$SO$_4$, at $\lambda_{\text{ex}} = 350$ nm). A time-correlated single-photon counting (TCSPC) measurement was carried out for the luminescence decay of complexes $[\text{Re(L)}(\text{CO})_3]$ and $[\text{Re(HL)}(\text{CO})_3\text{Cl}]$ and ligand HL in methanol. For the TCSPC measurement, photexcitation was performed using a picosecond diode laser (IBH Nanoled-07) in an IBH Fluorocube apparatus. The fluorescence decay data were collected on a Hamamatsu MCP photomultiplier (R3809) and were analyzed using IBH DAS6 software.

**Computational Details.** The geometrical structure of the singlet ground state ($S_0$) and the lowest-lying triplet excited state ($T_1$) were optimized using the density functional theory (DFT) method at the RB3LYP and UB3LYP levels of theory. The geometries of the monovalent Re(I) complexes were fully optimized in the solution phase by imposing the center of symmetry constraint. The absorption and photoluminescence spectral properties of the Re(I) complexes, based on the ground- and excited-state geometry-optimized structures, were computed using the time-dependent density functional theory (TD-DFT) approach in an acetonitrile solution with the help of a conductor-like polarizable continuum model (CPCM). In the calculation, the quasi-relativistic pseudopotentials of Re atoms proposed by Hay and Wadt with 14 valence electrons (outer-core [[5s$^2$5p$^2$]] electrons and the (5d$^6$) valence electrons) were employed, and a “double-$\xi$” quality basis set LANL2DZ was adopted as the basis set for Re atoms. The 6-31G basis set was used for the C, H, N, and O atoms for the optimization of both the ground state and the lowest-lying triplet excited-state geometries. All of the calculations were performed using the Gaussian 09W software package.

**Crystallographic Studies.** Single crystals of $[\text{Re(L)}(\text{CO})_3]_2$ and $[\text{Re(HL)}(\text{CO})_3\text{Cl}]$ complexes were grown by slow diffusion of hexane in a dichloromethane solution at 20 °C. Data were collected on a Bruker SMART CCD diffractometer using a Mo Kα monochromator ($\lambda = 0.71073$). Structure solution was carried out using the Shelx-97 PC version program. Full-matrix least-square refinements on $F^2$ were performed using the SHELXL-2014 program. All of the non-hydrogen atoms were refined anisotropically using the full-matrix least-squares method. Hydrogen atoms were included for structure factor calculations after placing them at calculated positions. The atomic coordinates and isotropic thermal parameters of $[\text{Re(L)}(\text{CO})_3]_2$ and $[\text{Re(HL)}(\text{CO})_3\text{Cl}]$ are given in the Supporting Information (Table S1).

**Fabrication of the Schottky Device.** To fabricate the Schottky devices of samples 1, 2, and 3, at first, an indium tin oxide (ITO)-coated glass substrate was cleaned using 2-propanol, distilled water, and acetone sequentially and repeatedly by an ultrasonication bath. For deposition of the film, the dispersed solutions of samples 1, 2, and 3 were prepared individually in an N,N-dimethylformamide (DMF) medium by the ultrasonication technique until a homogeneous solution was obtained. The dispersed solution was spin-coated on the ITO-coated glass (at 800 rpm for 1 min) to produce a thin film with the help of an SCU 2700 spin-coating unit and dried under vacuum conditions. A metal (Al) was deposited onto the thin film with the help of a shadow mask by the thermal evaporation technique to construct a metal–semiconductor junction with the help of a 12A4D HINDHIVAC vacuum coating unit under a pressure of 10$^{-6}$ Torr. The
thickness of the film was measured (∼900 nm) with the help of a surface profiler. The effective diode area was maintained at 7.065 × 10⁻⁶ m².

The current–voltage (I–V) characteristics of the devices were recorded under dark and light (AM 1.5 radiation) conditions with the help of a Keithley 2635B source meter interfaced with a PC by applying bias voltage in the range of −2 V to +2 V. All of the measurements were performed at room temperature.

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Notes

The authors declare no competing financial interest.

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