Flexible and Transparent Electrodes of Cu$_{2-x}$Se with Charge Transport via Direct Tunneling Effect

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In this paper, it is demonstrated that copper selenide (Cu$_{2-x}$Se) films onto polyester sheets may serve as transparent electrodes in inorganic–organic hybrid light emission devices (IOHLED), as possible replacement to indium tin oxide or fluorine-doped tin oxide. The Cu$_{2-x}$Se film synthesized via bath chemical deposition is electrically stable with a sheet resistance of 148 $\Omega$ cm$^{-1}$ and optical bandgap of 2.3 eV. IOHLED are made with poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) as an organic layer for hole transport and poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) as electroluminescent semiconductor. The IOHLED emits in the visible range owing to the simultaneous emission from Cu$_{2-x}$Se and MEH-PPV layers. The enhanced performance is explained by analyzing the charge transport mechanisms at the inorganic–organic interface, which for Cu$_{2-x}$Se/PEDOT:PSS changes from Fowler-Nordheim to direct tunneling regardless of the device temperature (90–370 K). The onset voltage is 75% smaller than in the absence of the PEDOT:PSS layer due to a 27 meV decrease in the potential barrier, and the direct tunneling becomes more relevant to device performance than the sheet resistance of the Cu$_{2-x}$Se layer. Upon adding transparency, mechanical flexibility, and covering large areas, the ultrathin Cu$_{2-x}$Se films on polyester substrates permit new designs for electro-optical devices with inorganic–organic heterojunctions.

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1. Introduction
New generations of organic semiconducting devices have driven the search to replace the well-established indium-doped tin oxide (ITO) and fluorine-doped tin oxide (FTO) electrodes. The requirements for alternative materials include a high electrical conductivity and possibility to prepare thin, transparent and flexible films with large areas at low cost. ITO is used as anode in organic light-emitting diodes (OLEDs) due to its transparency in the visible region and high conductivity ($>10^5$ S cm$^{-1}$). However, the high Schottky barrier on ITO (or FTO) interfaces makes it difficult to inject charge carriers into the active semiconducting layer, especially because of its work function of $\approx$4.4 eV.$^{[13]}$ This problem can be mitigated by treating its surface to alter the working function or by inserting intermediate layers to change electron mobility and promote a better balance between the injected charge carriers.$^{[4]}$ Another possibility is to employ chalcogenide metals such as copper selenide that can exist in different compositions, namely stoichiometric Cu$_2$Se, Cu$_3$Se$_2$, Cu$_5$Se$_3$, and Cu$_8$Se$_3$ and non-stoichiometric Cu$_{2-x}$Se.$^{[5-9]}$ The latter is a p-type semiconductor with an energy gap of $\approx$2.3 eV and work function of 4.17 eV, therefore promising as a hole-injecting electrode for OLEDs.$^{[7,9]}$ Films of Cu$_{2-x}$Se can be prepared with vacuum evaporation,$^{[12,13]}$ cation-anion combination,$^{[14-16]}$ cation-anion combination in hot coordinating solvents,$^{[17-19]}$ element combination in the solid state,$^{[20]}$ galvanic synthesis,$^{[21]}$ chemical reduction from CuSe,$^{[22]}$ electrochemical methods,$^{[23]}$ and chemical bath deposition.$^{[24-26]}$

We demonstrate here that Cu$_{2-x}$Se films can function as electrodes for organic electronics. The films were synthesized from copper deposited from the vapor phase followed by chemical bath deposition. With polyester as substrate, the resulting films are flexible, thin and transparent. For comparison, devices with an FTO electrode are also discussed. Poly-[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) was used in a light-emitting inorganic–organic hybrid diode (IOHLED). The effectiveness of Cu$_{2-x}$Se as electrode was demonstrated in a comparison with a device containing an intermediate layer of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) between the inorganic and the organic semiconductor. The devices in this work were designed also to...
investigate the energy barrier for charge carriers (hole) on the Cu₂₋ₓSe/MEH-PPV and Cu₂₋ₓSe/PEDOT:PSS/MEH-PPV interfaces.

2. Results and Discussion

2.1. Gap Energy and Surface Morphology of Cu₂₋ₓSe Films

The optical and morphological properties of Cu₂₋ₓSe films deposited onto polyester sheets were compared with the conventional FTO electrodes. To analyze the absorption coefficient (α) and optical energy gap (E_g) of Cu₂₋ₓSe films, we followed the methodology by Tauc applied to amorphous semiconductor materials,[27–29] using Equation (1) for the allowed direct transition[4,10,30]

\[ \alpha h\nu = A_0 (h\nu - E_g)^{1/2} \] (1)

where \( A_0 \) is a proportionality constant and \( h\nu \) is the incident photon energy.[28] Figure 1 shows the transmittance spectrum of the polyester/Cu₂₋ₓSe film at room temperature. The transmittance spectrum and Tauc plot of the glass/FTO film are shown in Figure S1 in the Supporting Information, for comparison. The inset shows the Tauc plot, from which the bandgap can be calculated using Equation (1). From the extrapolation of the linear region of \((\alpha h\nu)^2\) versus \(h\nu\) we estimated an optical gap energy \(E_g\) for FTO and Cu₂₋ₓSe as 3.4 and 2.3 eV, respectively, consistent with the literature.[14, 9–11,24,31–34] The bandgap for Cu₂₋ₓSe is suitable for organic optoelectronic devices.

Figure 2 shows the AFM images (5.0 μm x 5.0 μm) in the tapping mode for polyester, polyester/Cu, and polyester/Cu₂₋ₓSe films. The image of the glass/FTO substrate is shown in Figure S2 in the Supporting Information. Both polyester and polyester/Cu are more homogeneous and smoother than polyester/Cu₂₋ₓSe and glass/FTO surfaces. The Cu₂₋ₓSe film is uniform and covers the entire substrate, similar to what is observed for FTO. The thickness of the copper and FTO films was obtained from the AFM measurements (see Supporting Information). The thickness of the Cu₂₋ₓSe film was estimated assuming a parabolic growth with coefficients taken from reference 39. The thickness and mean square roughness (σ_RMS), skewness (σ_SK), and kurtosis (σ_KU) parameters for each image in Figure 3 are given in Table 1.[35] The values σ_RMS, σ_SK, and σ_KU are similar for polyester and polyester/Cu, which suggests that the copper layer is conformable to the polyester substrate. The parameters for copper selenide were close to those for FTO. In fact, both surfaces are similar qualitatively (see Figure 2 and Figure S2 (Supporting Information)).

The copper surface changes due to a reaction with the selenous sulphate ion forming copper selenide. The thickness of the initial layer increases with the agglomerates originating from nucleation of multiple clusters. The σ_KU parameter suggests that the peaks on the film surface are sharper than for an FTO film. This can be an advantage to reduce kurtosis (sharpness of the peaks) on the electrodes, an effect that decreases the performance of electronic devices in the electrode/semiconductor region. The parameter σ_SK indicates that the Cu₂₋ₓSe surface has more peaks than valleys.

The height distribution function \( p(h) \), where \( h \) is the height along the surface, has a Gaussian profile for FTO and Cu₂₋ₓSe.
films, with the profile for Cu$_{2-x}$Se film being 35% narrower. The height profile of copper resembles that of polyester. Overall, we may consider all samples as having a random distribution of heights. The increase in mean quadratic roughness for Cu$_{2-x}$Se indicates a larger height dispersion on the film surface. The histograms of area distribution for the cross section of polyester/Cu$_{2-x}$Se and Glass/FTO are given in Figure S3 (Supporting Information), with circular clusters for Cu$_{2-x}$Se and rectangular clusters for FTO. The average areas of the grain section are 38713 and 20715 nm$^2$ for Cu$_2$Se (average radius of 160 nm) and FTO (length of 312 nm and width of 123 nm), respectively. These data are consistent with the lowest $\sigma_{\text{RMS}}$ for Cu$_{2-x}$Se and reflect the large difference in morphology between FTO and Cu$_{2-x}$Se surfaces. Table S11 in the Supporting Information presents the parameters $h_c$ (center) and $\Delta h$ (width) of the Gaussian fitting of $p(h)$ for the images in Figure 2 and Figure S3 (Supporting Information). The self-correlation image between heights in Figure S4 (Supporting Information) shows the characteristic curves after the 60th scan. The results in Figure 3 represent a demonstration that efficient IOHLEDs may be obtained with Cu$_{2-x}$Se in the transparent electrode and a PEDOT:PSS layer for hole injection. Furthermore, one infers that it is also possible to fabricate a hybrid LED without a PEDOT:PSS layer for hole injection. The electrical device stability was verified with 120 consecutive scans polarizing directly the IOHLEDs devices (Figure S9 in the Supporting Information). No change was observed in the $I$ versus $V$ curves after the 60th scan.

### Table 1. Thickness, mean quadratic roughness, skewness and kurtosis of Glass/FTO, polyester, polyester/Cu, and polyester/Cu$_{2-x}$Se.

| Sample            | Thickness [nm] | $\sigma_{\text{RMS}}$ [nm] | $\sigma_k$ | $\sigma_{\text{Ku}}$ |
|-------------------|----------------|----------------------------|------------|---------------------|
| Glass/FTO         | 350 ± 4        | 17.2                       | 0.2        | 2.8                 |
| Polyester         | –              | 2.0                        | 1.0        | 9.0                 |
| polyester/Cu     | 43 ± 5         | 2.5                        | 0.8        | 6.8                 |
| Polyester/Cu$_{2-x}$Se | 140        | 11.3                       | 0.4        | 3.5                 |

We used the four-point methodology to determine the sheet resistance ($R_s$) and electrical resistivity ($\rho$) of FTO, Cu and Cu$_{2-x}$Se.$^{[36,37]}$ The details of layout and parameters are given in the Supporting Information. A constant electric current of 1 mA was used. The results for FTO agree with the data provided by the manufacturer with $R_s$ of 14.6 $\Omega$ sq$^{-1}$.$^{[32]}$ While the average of $R_s$ for copper selenide is 148.8 $\Omega$ sq$^{-1}$, compatible with applications in electronic devices.$^{[38,39]}$ In subsidiary experiments with 100 repeated bending cycles (0–170$^\circ$), we obtained an average value of 148 ± 5 $\Omega$ sq$^{-1}$ for $R_s$ of Cu$_{2-x}$Se films, according to the results in Figure S8 in the Supporting Information. Figure 3 shows the characteristic curves of $I$ versus $F$ (electric field) of IOHLEDs at room temperature. The threshold voltages differ in the potential range studied with significant carrier injection in the device with PEDOT:PSS (5 MV m$^{-1}$). This should lower the potential barrier at the junction compared to the IOHLED without the PEDOT:PSS layer (21.7 MV m$^{-1}$). The magnitude of the electric current in these devices is as expected from the literature.$^{[35,36]}$ Note that for conventional OLEDs, for example FTO/PSS:MEH-PPV/Al, the threshold voltage is ~80 MV m$^{-1}$. Hence, despite the increased sheet resistance of the Cu$_{2-x}$Se layer in comparison with conventional electrodes, the decrease in the energy barrier at the inorganic–organic semiconductor junction can be significantly more effective in the charge transport along the IOHLED layers. The electrical device stability was verified with 120 consecutive scans polarizing directly the IOHLEDs devices (Figure S9 in the Supporting Information). No change was observed in the $I$ versus $V$ curves after the 60th scan.

Three main charge transport mechanisms are involved on the interfaces of these devices. The first includes the Schottky barrier (BS) formed at the interface between a metal and a semiconductor owing to the difference in work functions. The second mechanism is the Fowler-Nordheim (FN) process, which manifests itself at low temperatures and high electric fields. The third is direct tunneling (DT), significant at small electric fields because carrier injection depends exponentially on the difference in carriers energy and potential energy at the semiconductors interface.$^{[40]}$ In the devices studied here, the Schottky barrier (BS) is formed on the electrode/polymer interface (MEH-PPV/Al) due to the difference between the energy levels, increasing contact resistance and being rectified with the application of a polarization voltage. The injection of charge carriers into organic films occurs through tunneling and
thermionic emission mechanisms. The equations for direct tunnelling (DT) and Fowler-Nordheim (FN) are, respectively[7,41–43]

\[ \ln\left( \frac{I}{F^2} \right) = \ln\left( \frac{1}{\pi} \right) - \frac{2\sqrt{2m_{\text{eff}}\phi}}{h} \]

\[ \ln\left( \frac{I}{F^2} \right) = -\frac{4\sqrt{2m_{\text{eff}}\phi}}{3e}\]

where \( I \) is the electric current, \( F \) is the electric field, \( \phi \) is the height of the barrier, \( m_{\text{eff}} \) is the effective mass of the holes injected into the polymer layer, \( e \) is the electron charge, \( h \) is the Planck’s constant, and the thickness of the thin barrier is 1 nm. Note that DT occurs when the applied bias voltage is less than the average barrier height and FN occurs if the bias voltage exceeds that barrier. FN tunnelling is a consequence of reducing the width of the barrier.

Electrical measurements were performed at various temperatures to examine the competition between thermionic emission and charge transport via tunneling, and the \( I \) versus \( V \) curves are shown in Figure S9 in the Supporting Information. The device without PEDOT:PSS had a distinctive characteristic curve at higher temperatures, with an increased electric current. However, the characteristic curve had its shape altered slightly with the temperature for the PEDOT:PSS device. The change in electrical current with increasing temperature is due to the thermal activation of charge carriers, with the results for the device without PEDOT:PSS being in accordance with the literature.[44] Figure 4 shows the tunneling plot for both devices from 90 to 370 K. Different charge injection behaviors through the inorganic-organic semiconductor interfacial barrier are identified. FN and DT tuning occur in the device without PEDOT:PSS and DT occurs only in the device with PEDOT:PSS. A detailed analysis of the \( \text{Cu}_2\text{Se}/\text{MEH-PPV} \) interface shows a non-linear increase in the region of lower polarization, which reveals an FN to DT transition. In contrast, the \( \text{Cu}_2\text{Se}/\text{PEDOT:PSS}/\text{MEH-PPV} \) device shows increasing curves over the polarization interval, which indicates a dominating DT mechanism. When a lower polarization is applied to the \( \text{Cu}_2\text{Se}/\text{MEH-PPV} \) contact in Figure 4a, carriers have to overcome a wide barrier (rectangular barrier) and charge transport takes place via DT. This result indicates that the DT effect is more important than the sheet resistance of the CuSe layer, i.e., the relevant physical parameter is the decrease in the potential energy barrier at the inorganic/organic interface. For such a decrease allows for considerable carrier injection in the device when the electrode is a p-type inorganic semiconductor.

At a higher polarization, the energy barrier reduces, becoming thin and approximately triangular, increasing the probability of FN tunneling. Therefore, there is a change in transport mechanism from DT at the smallest polarization (or larger \( 1/F \)) to FN at the highest polarization (smallest \( 1/F \)). The intersection occurs at 0.026 m MV\(^{-1}\) at an ambient temperature of 290 K and at 0.07 m MV\(^{-1}\) for the higher temperatures of 330 and 370 K. The crossing point is known as the transition voltage \( (V_{\text{tran}}) \). Figure S10 in the Supporting Information shows details of the transition of the two regimes for the polyester/\( \text{Cu}_2\text{Se}/\text{MEH-PPV}/\text{Al} \) device.

Two factors compete to determine how the tunneling plot changes with temperature in Figure 4, which can be detected at lower polarizations. The first relates to the vibrational levels of the polymer, which become more accessible with increasing temperatures (charge carriers have more energy to jump over barriers on the interfaces). The second is the aforementioned vacancy defects (traps) in \( \text{Cu}_2\text{Se} \), where the charge carriers are susceptible to being trapped. In the device without PEDOT:PSS in Figure 4a the access to the vibrational levels of the polymer increases with temperature, while trapping due to \( \text{Cu}_2\text{Se} \) defects decreases. In the device with PEDOT:PSS in Figure 4b, the two processes occur equally, one compensating the other. Therefore, the values of electric current for this sample vary little with temperature as shown in Figure S9d in the Supporting Information. At low temperatures, we observed only DT in the device without PEDOT:PSS. With less thermal energy, the charge carriers are less likely to overcome the energy barrier on the interface. Therefore, the low temperature mechanism is tunneling. The transition from DT to FN occurred only at temperatures 290, 330, and 370 K. We do not rule out the mechanism via hopping because the crossing point between the two tunneling processes varies. This transition occurs at lower voltages at higher temperatures (330 and 370 K). We estimate the barrier height, \( \phi \), at 27 meV based on the FN tunneling equation. We assume the linear dependence in the higher field interval (\( \approx 30 \text{ V m}^{-1} \)) and the effective mass of the

**Figure 4.** Tunneling plots (Equations (2 and 3)) for IOHLED samples at various temperatures, from 90 to 370 K: a) without PEDOT:PSS and b) with PEDOT:PSS. The insets show a zoom in the high field region and dashed lines indicate the transition from DT to FN mechanisms.
hence yielding a significant decrease in the energy barrier. The energy levels of Cu$_2$-XSe and MEH-PPV in the PEDOT:PSS device are consistent with that in the IOHLED Cu$_2$-XSe/MEH-PPV/Al there is an interface region creating a small barrier, originated in the interstitial defects of Cu$_2$-XSe. In the Cu$_2$-XSe/PEDOT:PSS junction, the residual charges of the organic layer should passivate the surface of the inorganic semiconductor.

2.3. Electroluminescence of the IOHLEDs

Electroluminescence is observed only with the device without PEDOT:PSS after the stability test (after 120 scans), as shown in Figure S9 in the Supporting Information. Probably, the hole injection through the PEDOT:PSS layer is higher than the electron injection provided by aluminum, resulting in the imbalance of electron-hole pairs required in the active layer for light emission. Figure 6 shows the normalized photoluminescence spectra of MEH-PPV, polyester/Cu$_2$-XSe and polyester/Cu$_2$-XSe/MEH-PPV films excited at 405 nm at room temperature. It is worth noting that the presence of PEDOT:PSS does not change the emission spectrum (not shown) of polyester/PEDOT:PSS/Cu$_2$-XSe/MEH-PPV film. The optical absorption spectra of these films are shown in Figure S11 in the Supporting Information. Two characteristic peaks of the MEH-PPV polymer represent the emission of zero phonon at 588 nm (transition 0–0) and the first phonon replica at 632 nm (transition 0–1), and there is an emission band of the Cu$_2$-XSe at 504 nm. The emission spectrum of the polyester/Cu$_2$-XSe/MEH-PPV sample shows the overlap of both emission bands of Cu$_2$-XSe and of MEH-PPV semiconductors. The electroluminescence spectrum (15 V at room temperature) is also shown in Figure 6 for the device without PEDOT:PSS. We identified two peaks from the emission of Cu$_2$-XSe at 504 nm and zero phonon emission from MEH-PPV at 578 nm. The third peak at 637 nm represents the first phonon replica of MEH-PPV. The line intensity at 637 nm increased substantially for the electroluminescence spectrum probably due to the self-absorbing effect of the light transmitted through the Cu$_2$-XSe layer. This can be controlled if we change the thickness of each active layer, thus introducing another parameter to adjust the spectral emission center of the device.

An important feature to be highlighted is the wide emission spectrum for the IOHLED upon combining emitting inorganic and organic semiconductors, with the inorganic one also serving as a hole transporting layer. Since this latter layer of Cu$_2$-XSe is transparent and flexible, it may replace ITO or FTO. Table 2 lists transparent oxides, graphene, carbon nanotubes, composites, and conducting polymers used in p-type hole injecting electrodes. Useful characteristics of the electrodes are: transparency above 60% in the visible region (~500 nm), sheet resistance ~100 Ω sq$^{-1}$, mechanical flexibility, even when synthesized with different techniques. Also in Table 2 is a comparison of physical properties of Cu$_2$-XSe and other electrode materials, with chemical bath deposition being the technique that permits large area applications.

3. Conclusions

Copper selenide is stable and can be used as a hole injector electrode in IOHLEDs devices in the form of thin transparent...
Table 2. Comparison of electrodes for OLED applications.

| Electrode                  | Properties                                      |
|----------------------------|-------------------------------------------------|
| Cu$_{2-x}$Se$_{x}$[46–50] | Optical bandgap = 2.3 eV                        |
|                            | Sheet resistance = 148 Ω sq$^{-1}$               |
|                            | Transmittance = 50–60%                          |
|                            | $d_{\mathrm{Se}}$ = 11.3 nm                      |
|                            | Flexibility: yes                                |
|                            | Synthesis: Chemical Bath Deposition (CBD)       |
| Transparent conductive oxides: ITO, FTO, ZnO, InZnO, ZTO, TiO$_2$, MoO$_3$[51–53] | Optical bandgap = 3.5 eV                        |
|                            | Sheet resistance = 20–36 Ω sq$^{-1}$             |
|                            | Transmittance = 95%                             |
|                            | $d_{\mathrm{Se}}$ = 17.2 nm                      |
|                            | Flexibility: no (rigid glass substrate)         |
|                            | Synthesis: radiofrequency (RF) sputtering       |
| Graphene[54]               | Optical bandgap = 4.7 eV                        |
|                            | Sheet resistance = 43 Ω sq$^{-1}$                |
|                            | Transmittance > 97.7%                           |
|                            | Flexible: yes                                    |
|                            | Synthesis: Chemical Vapor Deposition (CVD) on Cu foil |
| Graphene/MoO$_3$[55]       | Optical bandgap = 2.8 eV                        |
|                            | Sheet resistance = 100–200 Ω sq$^{-1}$          |
|                            | Transmittance = 90%                             |
|                            | Flexibility: yes                                |
|                            | Synthesis: low-pressure CVD                      |
| Graphene/TiO$_2$[54–56]    | Optical bandgap = 2.4 eV                        |
|                            | Sheet resistance = 93 Ω sq$^{-1}$                |
|                            | Transmittance = 90%                             |
|                            | Flexibility: no (rigid glass substrate)         |
|                            | Synthesis: DC pulsed (500 W) or RF (120 W)      |
|                            | sputtering process on single-layer graphene on a Cu foil and subsequent wet-transfer process to a target substrate |
| Graphene/Ag nanowire[57,58] | Optical bandgap = 4.9 eV                        |
|                            | Sheet resistance = 26.4 Ω sq$^{-1}$              |
|                            | Transmittance = 91.5%                           |
|                            | $d_{\mathrm{Se}}$ = 6.4 nm                       |
|                            | Flexibility: no (rigid glass substrate)         |
|                            | Synthesis: CVD                                  |
| Carbon Nanotubes (CNT)[59] | Optical bandgap = 4.1 eV                        |
|                            | Sheet resistance = 100 Ω sq$^{-1}$               |
|                            | Transmittance = 90%                             |
|                            | Flexibility: no (rigid glass substrate)         |
|                            | Synthesis: micro-contact printing CNT films with polydimethylsiloxane (PDMS) stamp |
| Single-Wall Carbon Nanotube (SWNT)[60] | Optical bandgap = 4.7 eV                        |
|                            | Sheet resistance = 60 Ω sq$^{-1}$                |
|                            | Transmittance = 45%                             |
|                            | Flexibility: no                                 |
|                            | Synthesis: pulsed laser vaporization technique  |
| SWNT/PEDOT[61]             | Optical bandgap = 1.6 eV                        |
|                            | Sheet resistance = 160 Ω sq$^{-1}$               |
|                            | Transmittance = 86%                             |
|                            | Flexibility: yes                                |
|                            | Synthesis: in situ polymerization of PEDOT on polyethylene naphthalene (PEN)/SWNT |
| Polyethylene               | Optical bandgap = 2.5 eV                        |
| Terphenyl/hexyl/pryaniline:camphor sulfonic acid (PET)/PANI:CSA[62] | Sheet resistance = 100 Ω sq$^{-1}$               |

Flexible films. The following characteristics were determined for 140 nm thick films: bandgap energy of 2.3 eV, edge of the absorption band close to 450 nm, maximum photoluminescence spectrum at 504 nm (excitation at 405 nm) and sheet resistance of 148 Ω sq$^{-1}$. The roughness and homogeneity are comparable to those of commercially-acquired FTO films, with the advantage that its morphology can favor reduction of the tip effects and the accumulation of charge in small regions of the electrode. In the Cu$_{2-x}$Se/MEH-PPV/Al IOHLED there is a transition from tunneling FN to DT, with a barrier height of 27 meV. With the addition of an intermediate layer of PEDOT:PSS hole carrier, the IOHLED featured only the DT charge injection mechanism. This explains the considerable decrease in its operating voltage, demonstrating that even under high electric fields there is no significant reduction in the energy barrier. As a result, the direct tunneling in the Cu$_{2-x}$Se/PEDOT:PSS interface allows for a low operating voltage in the device, despite the increased sheet resistance. In both devices the charge transport mechanism via hopping must occur along with the tunneling mechanism in these interfaces. The PEDOT:PSS device did not show detectable electroluminescence in our experimental apparatus, probably due to the significant imbalance of charge injection. In the device without PEDOT:PSS, the EL curve shows a red shift in relation to the PL spectrum. While the wide emission spectrum is not suitable for emission of pure colors, it creates the opportunity to fabricate devices for lighting. Its emission region may be possibly controlled by changing the thickness of the Cu$_{2-x}$Se layer or the organic active layer. The optical and electrical results are demonstration of the possible use of Cu$_{2-x}$Se films as transparent, flexible electrodes in hybrid light-emitting devices processed at low cost and large areas.

4. Experimental Section

Cu$_{2-x}$Se Films: Cu$_{2-x}$Se substrates were obtained by evaporating a thin (≤ 50 nm) layer of copper onto a transparent polyester sheet (polyester film for inkjet printers, thickness = 100 μm) under a vacuum of ~8 × 10$^{-3}$ mbar. A sodium selenosulfate (Na$_2$SeSO$_3$) stock solution was prepared.[46] This reactant cannot be isolated in the pure state, but it can be kept stable for several months in aqueous 0.10 mol L$^{-1}$ Na$_2$SO$_3$. A mixture of selenium (5 g), Na$_2$SO$_3$ (12 g) and ultrapure water (150 mL) was boiled for 12 h using a condenser to prevent loss of solvent. The mixture was left to rest for several hours at room temperature, and residues were discarded. The actual concentration in the clear solution was determined by gravimetry. An aliquot (5 mL) of the stock solution was decomposed with concentrated HCl. Selenium precipitates were filtered, washed, dried and weighed (0.039 g). For the chemical bath deposition, the stock solution was diluted to 8.0 mmol L$^{-1}$ with 0.10 mol L$^{-1}$ Na$_2$SO$_3$, where the copper/polymer substrate was immersed for 1 min to 2 min under magnetic stirring. After removal, it was washed with ultrapure water. X-Ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDS) were carried out using, respectively, a diffractogram X-Ray Shimadzu XRD6000 and a Tescan Vega 3 LMU. XRD and EDS curves typical of berzelianite phase are shown in Figures S12 and S13, respectively, in the Supporting Information.[7,25]

Light Emitting Diodes with Inorganic–Organic Multilayers: The substrates containing copper selenide were cleaned with ultrapure water and detergent. Figure 7a depicts the film thus obtained. A nickel-plated copper wire was used as electrical contact on the copper selenide electrode (anode). Silver glue and epoxy glue were used to cover, insulate and protect the contact. Spin-coating was employed to prepare the active layer of MEH-PPV from a 3.3 mg mL$^{-1}$ solution in chloroform (Alrich).[49]
The final film thickness was ≈200 nm. The rotation speed was 1400 rpm for 60 s under a relative humidity of 20%. A second device was made by interposing a hole injection layer of PEDOT:PSS (Sigma-Aldrich), which was deposited by spin coating at 3000 rpm for 60 s from a 1.3% dispersion in chloroform. The sample was then heated under vacuum at 120 °C for 1 h. Finally, aluminum was evaporated under vacuum of ≈8 × 10⁻³ mbar and the active area of the devices was 7.1 mm². Figure 7b,c shows the IOHLED architectures which is referred to as Cu₂X₃Se/PEDOT:PSS/MEH-PPV/Al and Cu₂X₃Se/MEH-PPV/Ali, respectively.

**Device Characterization:** Optical absorption measurements were performed using the UV-VIS 800XI Femto spectrophotometer and surface morphology was studied using an atomic force microscope (AFM) Shimadzu SPM-9600. For continuous current (CC) four-probe electrical measurements, a Keithley 2410-C voltage source was used. Photoluminescence spectra were obtained using the Laser Line iZi as the excitation source at 405 nm, and the light emitted by the sample was guided by a set of biconvex lenses and detected with a portable USB4000 spectrometer from Ocean Optics. A 450 nm cutoff high-pass filter was placed in front of the spectrometer to cut the corresponding excitation wavelength. In the electroluminescence measurements, a Keithley 2410-C voltage source was used as CC source and the emitted light was collected using the Keithley 2410-C source. For continuous current (CC) four-probe electrical measurements, a Keithley 2410-C voltage source was used. The emitted light was detected as described above. Conductivity measurements in CC condition were performed at various sample temperatures (90–370 K) and detected as described above. Conductivity measurements in CC condition were performed at various sample temperatures (90–370 K) and detected as described above.

**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**

The data that supports the findings of this study are available in the Supporting Information of this article.

**Keywords**

copper selenide, direct tunneling, electrical characterization, hole injector electrodes, inorganic–organic light emission diodes

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[1] H. Kim, C. M. Gilmore, A. Piquet, J. S. Horwitz, H. Mattoussi, H. Murata, Z. H. Kafafi, D. B. Chrisey, J. Appl. Phys. 1999, 86, 6451.
[2] A. E. Rakshani, Y. Mankidi, H. A. Ramazaniyan, J. Appl. Phys. 1998, 83, 1049.
[3] A. C. Rabelo, A. Marletta, R. A. Silva, N. M. B. Neto, O. L. Bottecchia, Synth. Met. 2009, 159, 2318.
[4] N. Thejo Kalyani, S. J. Dhoble, Renewable Sustainable Energy Rev. 2012, 16, 2696.
[5] H. Hiramoto, I. Koizumi, K.-B. Kim, H. Yanagi, T. Kaniya, M. Hirano, N. Matsunami, H. Hosono, J. Appl. Phys. 2008, 104, 113723.
[6] K. Tyagi, B. Gahtori, S. Bathula, S. Auluck, A. Dhar, Appl. Phys. Lett. 2014, 105, 173905.
[7] S. R. Gosavi, N. G. Deshpande, Y. G. Gudage, R. Sharma, J. Alloys Compd. 2008, 448, 344.
[8] B. Güzeldir, M. Sağlam, Spectrochim. Acta, Part A 2015, 150, 111.
[9] O. Arellano-Ternor, M. C. Acosta-Enríquez, R. Ochoa-Landín, R. Iñiguez-Palomares, T. Mendívil-Reynoso, M. Flores-Acosta, S. J. Castillo, Chalcogenide Lett. 2014, 11, 13.
[10] I. A. Ezenwa, N. A. Okereke, L. N. Okoli, Int. J. Eng. Sci. Technol. Innov. 2013, 2, 82.
[11] G. Juška, V. Gulbinas, Lith. J. Phys. 2010, 50, 233.
[12] P. Peranathan, Y. L. Jeyachandran, C. Viswanathan, N. N. Praveena, P. C. Chitra, D. Mangalaraj, S. K. Narayandas, Mater. Charact. 2007, 58, 756.
[13] A. M. Hermann, L. Fabick, J. Cryst. Growth 1983, 61, 658.
[14] A. Mondal, P. Pramanik, J. Solid State Chem. 1984, 55, 116.
[15] G. K. Padam, Thin Solid Films 1987, 150, L89.
[16] H. Pathan, C. Lokhande, D. Amalnerkar, T. Seth, Surf. Coat. Technol. 2003, 211, 48.
[17] S. Deka, A. Genovese, Y. Zhang, K. Misztal, G. Bertoni, R. Krahne, C. Giannini, L. Manna, J. Am. Chem. Soc. 2010, 132, 8912.
[18] C.-T. Yang, H.-I. Hsiang, Mater. Res. Bull. 2018, 97, 30.
[19] J. Choi, N. Kang, H. Y. Yang, H. J. Kim, S. U. Son, Chem. Mater. 2010, 22, 3586.
[20] T. Sakuma, K. Sugiyama, E. Matsubara, Y. Waseda, Mater. Trans., JIM 1989, 30, 365.
[21] A. Ghosh, C. Kulsi, D. Banerjee, A. Mondal, Appl. Surf. Sci. 2016, 369, 525.
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