Multifunctional organic-inorganic hybrid films deposited by the Langmuir-Blodgett technique

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Chapter 6

Ultrathin Molecule-Based Magnetic Conductors*

In this chapter we discuss the electronic and magnetic properties of multilayer organic-inorganic hybrid films which comprise arachidic acid and donor bis(ethylenedioxy)tetrathiafulvalene (BEDO-TTF) as organic component and Cu/Gd complexes as inorganic component and were deposited by the Langmuir-Blodgett technique. First we focus on the electrical transport properties arising from the π electrons in the donor BEDO-TTF layer. The conductivity of the hybrid films signals the existence of a metallic state at high temperature, which at low temperature (T < 150 K) evolves into a state described by two-dimensional variable-range-hopping. To gain further insight into the intrinsic electronic behaviour of these hybrid LB films, their optical properties were studied in the IR range. The presence of a Drude term in the optical response confirmed their metallic character. In the second part of this chapter, the magnetic properties are discussed. A long range ferromagnetic order with an ordering temperature of ~ 1 K was found for the film containing Gd ions. The LB films containing Cu ions showed more extended ferromagnetic exchange interactions than the ones containing Gd ions.

* This chapter is based on N. Akhtar, M. C. Donker, T. Kunsel, T. T. M. Palstra and Petra Rudolf, “Ultrathin Molecule-Based Magnetic Conductors” ready for submission.
6.1. Introduction

Conventional electronics make extensive use of inorganic materials because they exhibit a wide range of robust electronic and magnetic properties along with their thermal and mechanical stability\(^1\). However, incorporating inorganic materials in electronic devices involves expensive processing and fabrication steps. Organic materials, on the other hand have received considerable attention as candidates for inexpensive, flexible and wearable devices or clean and renewable energy sources\(^2\)-\(^5\). Significant progress is being made in the development of a new generation of electronic devices and the prototypes like the world’s first rollable full-colour organic light emitting diode display (see http://www.youtube.com/watch?v=9OvTLg4i2_U) developed by SONY and Philips’ full-colour electronic paper (see http://www.youtube.com/watch?v=8gekv6psBp0) have already been available for a few years.

Organic-inorganic hybrids represent a new class of smart materials that could benefit from the best of both worlds, organic and inorganic\(^6\). Such materials can be prepared through self-assembly, intercalation or grafting of one species onto another one. They are capable of providing co-existent multiple functionalities in one system, a trait which is difficult or impossible to achieve in a continuous lattice. One such example involves the molecular materials wherein conductivity or superconductivity is coupled with magnetism\(^7\). Over the last decade various types of molecule-based magnetic conductors where the conducting properties stem from \(\pi-\pi\) stacking of organic radicals and the magnetic properties arise from magnetic counter ions have been studied\(^8\). In this context, tetrathiafulvalene (TTF) and its derivatives have been extensively used due to their strong tendency to self-assemble forming charge transfer salts. The electronic properties of these materials are extremely sensitive to the intermolecular distance between neighbouring molecules within the organic layer. For a detailed review on TTF-based magnetic molecular conductors is referred to E. Coronado et al.\(^9\).

In recent years, many low dimensional molecular conductors and magnetic conductors have been prepared as single crystals\(^10\)-\(^11\). Single crystals are generally very suitable for examining the structural and transport properties of hybrids but incorporation in electronic devices requires growing hybrid thin films. Moreover, to tune their physical and chemical properties one has to be able to predetermine and influence the organization of the molecular assemblies. In this context, an old but elegant deposition method, the Langmuir-Blodgett technique, provides precise control over the film growth through simple external
parameters. Hence, uniquely tailored new supramolecular architectures can be formed from novel molecular building blocks in this fashion\textsuperscript{12}.

Here, we employed the Langmuir Blodgett technique to construct quasi-two-dimensional electronic networks formed by arachidic acid and bis(ethylenedioxy)tetrathiafulvalene (BEDO-TTF) molecules sandwiched between magnetic inorganic layers consisting of Cu\textsuperscript{2+} or Gd\textsuperscript{3+} complexes. The choice of BEDO-TTF among the TTF molecular family is motivated by its strong tendency to form organic metals due to its low ionization energy and the ability to self-aggregate\textsuperscript{13}. In most salts BEDO-TTF forms a similar stacking pattern based on strong intermolecular C-H..O hydrogen bonds. The deposition protocol along with structural properties of our hybrid LB films was discussed in detail in chapter 5. Here we shall focus on the electrical transport and magnetic properties.

6.2. Results and discussion

6.2.1. DC electrical transport properties

The sheet resistance, $R_s$, is a measure of the resistance of thin films that are nominally uniform in thickness. The advantage of $R_s$ is that it is directly measured using a four-terminal sensing measurement (also known as a four-point probe measurement) as explained in Chapter 2. The temperature dependence of the in-plane DC sheet conductance ($G_s = \frac{j}{R_s}$) for the 30-layer thick hybrid LB films is shown in figure 6.1. The room temperature conductance was $50 \pm 1$ and $142 \pm 2$ µS/sq for the C\textsubscript{20}+BEDO-TTF+Gd and C\textsubscript{20}+BEDO-TTF+Cu LB films, respectively. These values are higher than the quantum conductance of $e^2/h = 40$ µS/sq, at which a metal-to-insulator transition is typically expected. For the C\textsubscript{20}+BEDO-TTF+Cu LB film, conductance increased slowly while cooling down from 300 to 260 K and then decreased very slowly with decreasing temperature ($\sigma_{260K}/\sigma_{150K} = 1.47$) between 260-150 K. Upon further cooling from 150 K to 8 K, a rapid decrease in conductance was observed instead. The C\textsubscript{20}+BEDO-TTF+Gd LB films showed a very slow decrease in conductance with decreasing temperature from 300 to 150 K ($\sigma_{300K}/\sigma_{150K} = 1.15$) and a rapid decrease upon further cooling down to 8 K.

A decreasing conductivity with decreasing temperature is typically associated with a semiconducting behaviour. However, it is also commonly observed for granular metallic systems for which the grain boundaries disrupt the continuous metallic path\textsuperscript{14}. Hence, variable-range-hopping model\textsuperscript{15} can also be observed in granular systems. In the hybrid LB films, the temperature dependence of the sheet conductance, $G_s$, in the temperature range
150-8 K, presented in figure 6.1, is fairly well reproduced by a variable-range-hopping model\textsuperscript{15}:

\[ G_S \propto e^{-\left(\frac{T_0}{T}\right)^n} \]  

(6.1)

where \( n \) is the dimensionality of the electronic system, \textit{i.e.} \( n=2 \) in the present case for both hybrid LB films, and \( T_0 \) the hopping term described by the following expression:

\[ T_0 = \frac{27\alpha^2}{\pi k_B N(E_f)} \]  

(6.2)

where, \( \alpha^{-1} \) is the localization length and \( N(E_f) \) the density of states at the Fermi level. The value of \( T_0 \) for the C\textsubscript{20}+BEDO-TTF+Cu LB film obtained from the fit was \( T_0 =6028\pm300 \) K, while for the C\textsubscript{20}+BEDO-TTF+Gd LB film \( T_0 \) was lower, namely \( 2048\pm50 \) K. However, the room temperature sheet conductance was higher for the former than for the latter. The higher value of \( T_0 \) could be a consequence of a smaller \( \alpha^{-1} \) or a smaller \( N(E_f) \).

Figure 6.1. Sheet conductance measured parallel to film plane as a function of temperature for 30-layer thick C\textsubscript{20}+BEDO-TTF+Cu LBfilm (left panel) and 30-layer thick C\textsubscript{20}+BEDO-TTF+Gd LB film (right panel). The corresponding fits using equation 2 are plotted as solid lines.
From the X-ray diffraction studies discussed in Chapter 5, we know that the lateral packing of BEDO-TTF molecules is similar in both LB films. This implies almost the same order of magnitude for $N(E_f)$ in both films. However, the X-ray diffraction data also indicate that the C$_{20}$+BEDO-TTF+Cu LB films are less ordered than the C$_{20}$+BEDO-TTF+Gd LB films and the localization length $\alpha^{-1}$ becomes shorter with increasing disorder. Hence, the higher value of $T_0$ for C$_{20}$+BEDO-TTF+Cu LB films is most likely due to a smaller $\alpha^{-1}$.

6.2.2. Optical conductivity

Since the temperature dependence of the DC sheet conductivity of the hybrid LB films can be modelled at low temperatures with variable-range-hopping it indicates that the charge transport is limited by the inter-crystallite barriers at the grain boundaries. To determine electrical transport within grains and the intrinsic conductive properties of such granular samples consisting of randomly oriented grains with highly resistive grain boundaries we measured the optical conductivity ($\sigma_{opt}$) in IR range, which is not sensitive to the presence of grain boundaries. Moreover, the optical properties of the organic molecular conductors in the IR range can provide very important information on the charge transfer properties. Figure 6.2 presents the transmitted intensity ($T_T$) at the normal incidence measured as a function of wavenumber in the range 900-11500 cm$^{-1}$ for 10-layer thick C$_{20}$+BEDO-TTF+Cu and C$_{20}$+BEDO-TTF+Gd LB films as well for a pure C$_{20}$+BEDO-TTF LB film also obtained in 5 deposition cycles.

It is evident that the optical response of C$_{20}$+BEDO-TTF+Cu and C$_{20}$+BEDO-TTF+Gd LB films is qualitatively similar to that of C$_{20}$+BEDO-TTF LB film, pointing to a similar conduction mechanism in all three films. The absorption features observed in the optical spectra are typical for most BEDT-TTF and BEDO-TTF based crystals. The low frequency spectral region is dominated by vibronic effects arising from a strong coupling of electronic excitations with the totally symmetric intra-molecular vibrations of C=C bonds in the TTF-based organic molecule. The electron-molecular vibration (e-mv) coupling theory was formulated by M. J. Rice for a dimer system. The two molecules, within the dimer, induce an oscillatory dipole moment through intermolecular charge transfer as a result of anti-phase vibrations.

The optical dispersion above 2000 cm$^{-1}$ is usually seen in the context of Drude model in these organic crystals. We take this approach also in the case of the hybrid LB films based on the fact that i) LB films of C$_{20}$+BEDO-TTF have been found to be metallic when studied through DC electrical measurement; ii) the conductive properties of C$_{20}$+BEDO-TTF+Cu
and C₂₀+BEDO-TTF+Gd LB films are also arising from BEDO-TTF molecular layer; and
iii) the room temperature conductivity values show a high density of mobile carriers in
these films. So \( T_\tau(\omega) \) was analysed in the context of the Drude-Lorentz model\(^{23}\) with the
dielectric function as described below:

\[
\epsilon = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma} - \frac{\Omega_{pl}^2}{\omega^2 - \omega_{0i}^2 + i\omega\gamma_i} \tag{6.3}
\]

where \( \epsilon_\infty \) is the background dielectric constant that takes into account the effects of high
frequency inter-band transitions. The frequency dependent first term represents the Drude
model where the free charge carriers are described via \( \omega_p \), the plasma frequency, and \( \Gamma \), the
damping constant. The second term models the Lorentz oscillators that include the
absorption in IR range due to charge transfer and inter-band transitions, where \( \omega_{0i}, \gamma_i \), and
\( \Omega_i \) are the resonance frequency, line width, and strength of the \( i^{th} \) Lorentz oscillator.

The details of how we applied the model calculation to our specific experimental geometry
are reported in the Appendix of this chapter. In short, the Sellmeier equation\(^{24}\) for CaF\(_2\) was used for
the substrate refractive index while ignoring the multiple reflections in the thick
substrate. However, multiple (Fabry-Perot) internal reflections in film were taken into
account in calculations. As clearly seen in figure 6.2, all three LB films showed two broad
bands around 1100 cm\(^{-1}\) and around 2000 cm\(^{-1}\) originating from vibronic excitation based
on a strong electron–phonon coupling effect, referred to as electron–molecular vibration (e–
mv) coupling,\(^{25-26}\) and charge transfer\(^{18,27}\), respectively. These two features along with CH\(_2\)
symmetric and anti-symmetric modes (2849 cm\(^{-1}\), 2916 cm\(^{-1}\)) were fitted with Lorentz
oscillators. The fitted curves are superimposed on the experimental data in figure 6.2. Other
modes that involve intra-molecular vibrations in low frequency regime were neglected in
model fitting. A very good fit to the experimental data was obtained in the spectral region
above 2000 cm\(^{-1}\) while it was reasonably good in the low frequency region. The parameters
which gave the best fit are given in Table 6.1. The oscillator strength of the CH\(_2\) symmetric
and anti-symmetric modes was extracted \( \leq 250 \) and \( \leq 400 \) cm\(^{-1}\), respectively for all LB
films, while \( \gamma \) was constrained to \( < 20 \) cm\(^{-1}\) in the fitting procedure.
Figure 6.2. Transmittance spectra for 10-layer thick C\textsubscript{20}+BEDO-TTF (a), C\textsubscript{20}+BEDO-TTF+Cu (b) and C\textsubscript{20}+BEDO-TTF+Gd (c) LB films deposited on CaF\textsubscript{2}. The solid grey lines represent the corresponding fits. See text for details.

The optical conductivity $\sigma\text{opt}(0)$ was calculated from the extracted parameters using the expression:

$$\sigma\text{opt} \ 0 = \frac{\varepsilon_0 \omega_p^2}{\Gamma} \quad (6.4)$$

The values of the plasma frequency and the damping constant for charge carriers extracted from the optical data are reasonable when compared with those reported for other BEDO-TTF containing metallic crystals. This is very convincing evidence for the metallic nature of these hybrid LB films. However, $\omega_p$ and $\sigma\text{opt}(0)$ were slightly smaller for the C\textsubscript{20}+BEDO-
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TTF+Gd LB film as compared to the C$_{20}$+BEDO-TTF and C$_{20}$+BEDO-TTF+Cu LB films. A smaller value of $\omega_p$ indicates a relatively lower number of free charge carriers in this film. This observation is consistent with the lower value of the average charge on the BEDO-TTF molecule in C$_{20}$+BEDO-TTF+Gd LB film as deduced from positions of the IR bands discussed in Chapter 5.

The optical conductivity for all three LB films is much higher than the DC conductivity measured at room temperature: $\sigma_{DC} = 16.7$ S/cm while $\sigma_{opt} = 532$ S/cm for the C$_{20}$+BEDO-TTF LB film, $\sigma_{DC} = 12.6$ S/cm while $\sigma_{opt} = 521$ S/cm for C$_{20}$+BEDO-TTF+Cu LB film and $\sigma_{D} = 6.1$ S/cm while $\sigma_{opt} = 467$ S/cm for C$_{20}$+BEDO-TTF+Gd LB film. This is in line with what was observed in (BEDO-TTF)$_2$ReO$_4$(H$_2$O) single crystals$^{28,29}$. The higher values of $\sigma_{opt}(0)$ as compared to $\sigma_{DC}$ can be understood in the view of the frequency dependent carrier mobility since $\Gamma$ in equation (6.4) is frequency dependent$^{30,31}$. The optical data analysis evidenced the similar conduction mechanism in all three films and hence testifies to their intrinsic metallic character.

Table 6.1. Best fit parameters obtained from fitting the experimental transmittance spectra for three LB films. Optical conductivity is calculated using equation 5 for each LB film.

<table>
<thead>
<tr>
<th>LB Film</th>
<th>$\varepsilon_{\infty}$</th>
<th>$\omega_p$</th>
<th>$\Gamma$</th>
<th>$\omega_01$</th>
<th>$\gamma_1$</th>
<th>$\Omega_1$</th>
<th>$\omega_02$</th>
<th>$\Gamma_2$</th>
<th>$\Omega_2$</th>
<th>$\sigma_{opt}$ (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{20}$+BEDO-TTF</td>
<td>4.0 ±0.005</td>
<td>7500</td>
<td>1761</td>
<td>1120</td>
<td>299</td>
<td>1646</td>
<td>2200</td>
<td>2220</td>
<td>3104</td>
<td>532</td>
</tr>
<tr>
<td>C$_{20}$+BEDO-TTF+Cu</td>
<td>3.5 ±0.01</td>
<td>7500</td>
<td>1800</td>
<td>1125</td>
<td>160</td>
<td>754.5</td>
<td>2200</td>
<td>2200</td>
<td>3500</td>
<td>521</td>
</tr>
<tr>
<td>C$_{20}$+BEDO-TTF+Gd</td>
<td>4.5 ±0.01</td>
<td>7000</td>
<td>1750</td>
<td>1090</td>
<td>298</td>
<td>1610</td>
<td>2200</td>
<td>2500</td>
<td>3131</td>
<td>467</td>
</tr>
</tbody>
</table>

6.2.3. Magnetic properties

The temperature dependence of the magnetic susceptibility for the hybrid LB films is shown in figure 6.3. The data are corrected for the substrate contribution and normalized to the total number of layers. The easy axis of magnetization for both C$_{20}$+BEDO-TTF+Cu and C$_{20}$+BEDO-TTF+Gd LB films lies in the film plane. For both films the temperature dependence of susceptibility was fitted using the Curie-Weiss law:
\[ \chi = \chi_\pi + \frac{C}{T - \theta} \quad (6.5) \]

where the temperature independent susceptibility, \( \chi_\pi \), represents the Pauli paramagnetic contribution from conduction electrons\(^{13,32} \) and is related to the density of states \( (N(E_f)) \) at the Fermi level, \( C \) is the Curie constant, and \( \theta \) is the Weiss temperature. The susceptibility for the C\(_{20}\)+BEDO-TTF+Gd LB film showed a deviation from Curie-Weiss law below 10 K, while for the C\(_{20}\)+BEDO-TTF+Cu film \( \chi \) obeyed this law in the whole data range. The least-squares fit gives \( \chi_\pi = 3.6 \times 10^{-4} \) (4.0\( \times \)10\(^{-4} \) emu/mol), \( C = 7.85 \) emu.K/mol (0.36 emu.K/mol), \( \theta = 0.80 \pm 0.1 \) K (0.2\( \pm \)0.05 K) for the C\(_{20}\)+BEDO-TTF+Gd (C\(_{20}\)+BEDO-TTF+Cu) LB film. The obtained values of \( \chi_\pi \) for the hybrid LB films are in good agreement with the reported values for other related conducting organic materials\(^{13,33} \).

The \( C \) values are very close to those calculated for non-interacting Gd\(^{3+} \) (\( S = 7/2 \))\(^{34} \) and Cu\(^{2+} \) (\( S = 1/2 \))\(^{35} \), while the small and positive \( \theta \) values point to a weak ferromagnetic interaction between the f-f spins in the C\(_{20}\)+BEDO-TTF+Gd LB film and between the d-d spins in the C\(_{20}\)+BEDO-TTF+Cu LB film. The \((\chi - \chi_\pi)T\) product when plotted as a function of temperature \( (T) \), showed a rapid rise below 12 K as shown in figure 6.4. It is thus the same as the observation of a positive theta. In the mean field (MF) approximation\(^{36} \), \( \theta \) is related to the magnetic exchange integral \( J \) for magnetic systems through the following equation:

\[ J = \frac{3k_B \theta}{2zS(S + 1)} \quad (6.6) \]

where \( S \) is the spin quantum number, \( k_B \) the Boltzmann constant and \( z \) the number of nearest neighbours. According to this equations \( \theta \) should be 21 times smaller for Cu with \( S = 1/2 \) than for Gd with \( S = 7/2 \) but the value deduced for the C\(_{20}\)+BEDO-TTF+Cu LB film was only 4 times smaller than that for the C\(_{20}\)+BEDO-TTF+Gd LB film. This indicates that the d-states in Cu are more extended than the f-states for Gd in these hybrid LB films.
Figure 6.3. Temperature dependence of the magnetic susceptibility (χ) for a 700-layer-thick C_{20}+BEDO-TTF+Cu film (left panel) and a 200-layer-thick C_{20}+BEDO-TTF+Gd film (right panel). For comparison the data were normalised to the total number of layers in each case. The solid line in each graph represents the Curie-Weiss fit as described by equation 6.5. The measurements were done in a magnetic field of 1 T applied parallel to the film plane.

Figure 6.4. Temperature dependence of the in-plane (χ−χ₀)T product for the C_{20}+BEDO-TTF+Cu LB film (left panel) and the C_{20}+BEDO-TTF+Gd LB film (right panel) as deduced from the data reported in figure 6.3.

To gain further insight into the magnetic properties of the hybrid LB films, the magnetization was also studied as a function of the applied magnetic field (H). The top left panel in figure 6.5 displays the magnetization versus field behaviour of the C_{20}+BEDO-TTF+Gd LB film at different temperatures. The most interesting feature observed in the M(H) data is the opening of hysteresis loops at higher fields testifying to the field-induced ferromagnetic ordering in this film. The onset of the opening of the hysteresis loop shifts towards higher applied fields as temperature increases. The temperature dependence of the
field-induced ferromagnetic ordering becomes clearer by the field-temperature phase diagram extracted from M(H) loops and displayed in figure 6.5 (top right panel). For each temperature, the field value which marks the onset of loop opening is plotted (H_{irreversible}). The positive slope of the plot implies the presence of long range ferromagnetic order in this film. The M(H) for the C_{20}+BEDO-TTF+Cu LB film presented in the bottom panel of figure 6.5 did not show any opening of a hysteresis loop even at temperatures as low as 4 K.

Long range magnetic ordering has been observed in various types of low-dimensional hybrids at relatively high temperatures\textsuperscript{37} although it is not allowed in low-dimensional Heisenberg systems according to Mermin and Wagner\textsuperscript{38}. Perovskite-based two-dimensional organic-inorganic hybrids with the chemical formula \((C_6H_5CH_2CH_2NH_3)_2MCl_4\) are reported to be canted antiferromagnets for \(M = Fe, Mn\) and ferromagnetic for \(M = Cu\)\textsuperscript{39}. Although these three hybrids present a similar structure with a 2-dimensional perovskite layer, the occurrence of ferromagnetism in the latter is attributed to the Jahn-Teller effect of the Cu\textsuperscript{2+} ions and interlayer ferromagnetic interactions.

The origin of long range magnetic ordering in these systems with out-of-plane interlayer distance larger than 10 Å is attributed to the cooperative divergence of the in-plane magnetic correlation length. In the present case of hybrid LB films, the exact magnetic structure of the inorganic lattice is not clear due to insufficient information concerning the structure (see discussions in Chapter 5). However, we can speculate that given the substantial conjugation in the BEDO-TTF molecules, the π-electrons act as mediating channel for the ferromagnetic exchange interaction between magnetic ions. A π-electron-mediated ferromagnetic exchange interaction was also observed in the (EDT-TTFVO)\textsubscript{2}FeBr\textsubscript{4} charge transfer salt below 15 K where the Fe atoms interact with neighbouring atoms via π-spins provided by the EDT-TTFVO layer\textsuperscript{40}. The existence of long range ferromagnetic order in hybrid LB films with a large (> 5 nm) interlayer distance between inorganic layers can be understood in the context of the divergence of the in-plane magnetic correlation length.

Hybrid LB films of gadolinium stearate (C\textsubscript{18}+Gd) prepared without donor BEDO-TTF have been found not to show spontaneous magnetization even at 100 mK\textsuperscript{41}. However, the presence of long range ferromagnetic order as indicated by the magnetic memory at high fields in the C\textsubscript{20}+BEDO-TTF+Gd LB film emphasizes the significance of the interface between the π-conjugated BEDO-TTF molecular layer and the Gd acetate layer for tailoring the magnetic properties\textsuperscript{42-43}.
Figure 6.5. Top left panel: In-plane magnetization (M) measured as a function of applied magnetic field (H) at different temperatures for a 200-layer thick $C_{20}$+BEDO-TTF+Gd LB film. Top right panel: Phase diagram for the transition between the ferromagnetic and the paramagnetic state in the $C_{20}$+BEDO-TTF+Gd LB film as extracted from M(H) loops. Bottom panel: In-plane magnetization (M) measured as a function of applied field (H) at 4 K for a 700-layer thick $C_{20}$+BEDO-TTF+Cu LB film. The magnetization is normalized to the total number of layers for both hybrid LB films.

6.3. Conclusion

DC electrical transport studies demonstrated the metallic character of hybrid LB films comprising arachidic acid and donor bis(ethylenedioxy)tetrathiafulvalene (BEDO-TTF) as organic component and Cu/Gd complexes as inorganic component at high temperature. However, the conductance decreases upon cooling below 150 K. Such behaviour is
common in organic polycrystalline samples that have less conducting or insulating grain boundaries. To better understand the intrinsic conduction mechanism in these films, optical studies were carried out that can probe the intra-grain transport properties. Transmittance spectra clearly showed the presence of a plasma edge that confirmed the metallic nature of the hybrid LB films. Moreover, optical transport parameters as extracted from the Drude-Lorentz fitting for C$_{20}$+BEDO-TTF+Cu and C$_{20}$+BEDO-TTF+Gd LB films were similar to those for metallic C$_{20}$+BEDO-TTF LB films. Hence, the electrical conduction in these films arises from the π-conjugated BEDO-TTF molecules. The magnetic characterization revealed ferromagnetic exchange interaction in both C$_{20}$+BEDO-TTF+Cu and C$_{20}$+BEDO-TTF+Gd LB films. However, it is found that the d-states of Cu$^{2+}$ are more extended than the f-states of the Gd$^{3+}$ ion. The long range magnetic order in C$_{20}$+BEDO-TTF+Gd LB films revealed by the presence of a magnetic hysteresis loop emphasizes the importance of the interface between the BEDO-TTF molecular layer and the Gd acetate sheet for tailoring the magnetic properties.

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Appendix

Transmittance of an absorbing thin film on a transparent substrate including an infinite amount of multiple reflections within the film

Here is given the details of the Drude-Lorentz model used to analyze the optical transmission spectra of 10-layer thick hybrid LB films deposited on CaF$_2$ substrates. The general terms are defined followed by a set of equations used to calculate the total transmittance $T_T$.

Data: Transmittance ($T$) as function of $\omega$ in cm$^{-1}$

**Fit parameters:**

- $(\Omega_{pi}, \omega_{0i}, \gamma_i) =$ Drude-Lorentz model parameters in cm$^{-1}$.
- $(\varepsilon_{\infty}) =$ (L) = film thickness in m.

**Constants:** speed of light, $c=2.9979\times10^8$ m/s.

**Sample:** vacuum(1)/film(2)/substrate(3)/vacuum(4)

**Refractive index substrate (N):** Sellmeier equation for CaF$_2$ in the 0.23-9.7 $\mu$m range at room temperature.

The equations used in the fitting procedure are based on the following complex amplitude transmission coefficients for a vacuum/film/substrate/vacuum sample (medium 1/2/3/4) at an angle of incidence (A.O.I.) of 0º. We neglect multiple reflections in the thick substrate.

1. $t = \left( \frac{t_{12}t_{23}e^{i\phi}}{1 - r_{23}r_{21}e^{i2\phi}} \right) t_{34}$, total transmission coefficient for A.O.I.=$0^\circ$

2. $r_{ij} = \left( \frac{N_i - N_j}{N_i + N_j} \right)$, reflection coefficient at the boundary $i/j$.  

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(3) \( t_{ij} = \left( \frac{2N_i}{N_i + N_j} \right) \), transmission coefficient at the boundary \( i/j \).

(4) \( \varphi = \left( \frac{N\omega L}{c} \right) \), complex phase for a film with thickness \( L \).

(5) \( \varepsilon_{\text{real}} = \varepsilon_{\infty} + \sum_i \Omega_{p,i}^2 \left( \frac{\omega_{0,i}^2 - \omega^2}{\gamma_i^2 \omega^2 + \omega_{0,i}^2 - \omega^2} \right) \), real part of the dielectric function

(Drude-Lorentz model)

(6) \( \varepsilon_{\text{imaginary}} = \sum_i \Omega_{p,i}^2 \left( \frac{\omega_{0,i}^2 - \omega^2}{\omega_{0,i}^2 - \omega^2 + \gamma_i^2 \omega^2} \right) \), imaginary part of the dielectric function (Drude-Lorentz model)

(7) \( n = \frac{1}{\sqrt{2}} \sqrt{\varepsilon_{\text{real}} + \varepsilon_{\text{real}}^2 + \varepsilon_{\text{imaginary}}^2} \), real part of the refractive index

(8) \( k = \frac{1}{\sqrt{2}} \sqrt{-\varepsilon_{\text{real}} + \varepsilon_{\text{real}}^2 + \varepsilon_{\text{imaginary}}^2} \), imaginary part of the refractive index

The total transmittance (T) is obtained by multiplying \( t \) with its complex conjugate (\( t^* \)):

(9) \( T_T = tt^* \)

The fitting procedure will give us \( \Omega_{p,i}, \omega_{0,i} \) and \( \gamma_i \), which are the plasma frequency, the resonance frequency and the damping parameter in wavenumbers [cm\(^{-1}\)]. From these we can obtain the electron density \( (n_e) \), the scattering time \( (\tau) \) and the DC conductivity \( (\sigma \text{ at } \omega=0) \) for the Drude term \( (\omega_\sigma=0, \Omega_p = \omega_p, \gamma = \Gamma) \) through the following relations

(10) \( n_e = \frac{\varepsilon_0 m \omega_p^2}{e^2} \)

(11) \( \tau = \frac{1}{\Gamma} \)
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(12) \[ \sigma_{DC} = \frac{\varepsilon_0 \omega^2}{\Gamma} \]

After having applied Eq. (1-8), we obtained the following equation for \( T_T \) that we used in the fitting procedure; here \( n, k \) are the real and the imaginary part of the complex refractive index of the film, \( N \) is the real part of the complex refractive index of the substrate; the imaginary part of the complex refractive index of the substrate is 0 (refractive index vacuum =1).

\[ T_T = \frac{M}{R_{multi}} \frac{4N^2}{(N + 1)^2} \]

Where

\[
M = \frac{16e^{-2B}(k^2 + n^2)}{(k^2 + n^2 + 2n + 1) + (N^2 + 2Nh + k^2 + n^2)}
\]

\[
N = \sqrt{1 + \frac{0.568(\lambda_\mu)^2}{(\lambda_\mu)^2 - (0.0503)^2} + \frac{0.471(\lambda_\mu)^2}{(\lambda_\mu)^2 - (0.1004)^2} + \frac{3.848(\lambda_\mu)^2}{(\lambda_\mu)^2 - (34.649)^2}}
\]

\( \lambda_\mu = \) Wavelength in cm\(^{-1} \)

\[
R_{multi} = 1 + [C^2 + D^2]e^{-2B} + [2D \sin(2A) - 2C \cos(2A)]e^{-2B}
\]

\[
A = \frac{nL\omega}{c}
\]

\[
B = \frac{kL\omega}{c}
\]
\[ C = -\frac{N^2(k^2 + n^2 - 1) + k^2(4N - k^2 - 2n^2 + 1) - n^4 + n^2}{(k^2 + n^2 + 2n + 1)(N^2 + 2Nn + k^2 + n^2)} \]

\[ D = \frac{2k(N + 1)(k^2 + n^2 - N)}{(k^2 + n^2 + 2n + 1)(N^2 + 2Nn + k^2 + n^2)} \]