Single-crystal organic charge-transfer interfaces probed using Schottky-gated heterostructures

Ignacio Gutiérrez Lezama¹, Masaki Nakano², Nikolas A. Minder¹, Zhihua Chen³,⁴, Flavia V. Di Girolamo¹,⁵, Antonio Facchetti³,⁴ and Alberto F. Morpurgo¹

¹ DPMC and GAP. University of Geneva, 24 quai Ernest Ansermet, CH1211 Geneva, Switzerland
² CERG, RIKEN Advanced Science Institute, Wako, Saitama 351-0198, Japan
³ Polyera Corporation, 8045 Lamon Avenue, Skokie, Illinois 60077, USA
⁴ CHEM, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, USA
⁵ CNR-SPIN and University of Naples, p.le Tecchio 80 80125 Naples, Italy
1. Electrical characterization of rubrene and PDIF-CN\(_2\) crystals using FETs realized by lamination

The fabrication of Schottky-gated heterostructures relies on the lamination of thin and flat molecular single crystals of rubrene and PDIF-CN\(_2\) that are grown using conventional vapor phase transport techniques\(^{S1}\). We have extensively investigated the properties of these same crystals by using them for the realization of field-effect transistors, in combination with several different gate dielectrics (for rubrene\(^{S2, S3}\): vacuum, parylene, SiO\(_2\), Al\(_2\)O\(_3\), Si\(_3\)N\(_4\), and Ta\(_2\)O\(_5\); for PDIF-CN\(_2\)\(^{S4}\): vacuum, Cytop, and PMMA). All these FET devices were also fabricated by means of the same lamination technique. Field-effect transistor measurements are highly reproducible and show that the carrier mobility depends on the dielectric constant of the gate dielectric\(^{S3}\). In particular, when vacuum is used as gate dielectric, band-like transport\(^{S5}\) (i.e., mobility increasing with lowering temperature) is observed both for holes in rubrene (room temperature mobility values up to 20 cm\(^2\)V\(^{-1}\)s\(^{-1}\) have been reproducibly observed\(^{S5}\) and for electrons in PDIF-CN\(_2\) (reproducible room-temperature mobility values\(^{S4}\) up to 5 cm\(^2\)V\(^{-1}\)s\(^{-1}\)). On gate insulators with a relative dielectric constant of 3, comparable to that of organic crystals, the typical mobility values are somewhat lower (approximately 9 cm\(^2\)V\(^{-1}\)s\(^{-1}\) at room temperature for holes in rubrene with parylene gate insulator\(^{S3}\); approximately 2.5 cm\(^2\)V\(^{-1}\)s\(^{-1}\) for electrons in PDIF-CN\(_2\) with PMMA gate insulators\(^{S4}\)). In these devices an increase in mobility near room temperature –albeit small- is still observed with lowering temperature. In both cases, however the mobility decreases exponentially with lowering temperature below 150 K, to values that are orders of magnitude smaller than 1 cm\(^2\)V\(^{-1}\)s\(^{-1}\) at temperatures below 50 K. The results obtained for the electron mobility in the Schottky-gated heterostructures discussed in the main text can be directly compared to those of PDIF-CN\(_2\) FETs, and from this comparison we find that electrons in Schottky-gated heterostructures exhibit a much more pronounced band-like transport behavior as discussed in the main text.
An explicit comment is worth on the high reproducibility (e.g., the linear temperature dependence of the electron density with the same slope in all devices; see also table S1 for the statistics of the room temperature resistivity, electron density and mobility values) that is observed despite the fact that the effects that are investigated depend sensitively on the properties of an interface that has been assembled under ambient conditions. Even though this reproducibility may seem surprising, devices that we have studied in the past based on organic single crystals and realized by a similar process commonly exhibit such a reproducibility. Past experiments have shown, for instance, an excellent reproducibility of the carrier mobility at rubrene/dielectric interfaces\textsuperscript{S2, S3}, PDIF-CN\textsubscript{2}/dielectric interfaces\textsuperscript{S4}, reproducible low contact resistance at rubrene/nickel interfaces\textsuperscript{S6} and reproducible charge transfer at TTF-TCNQ\textsuperscript{S7} and TMTSF-TCNQ\textsuperscript{S8} interfaces. Other examples from our own work, as well as from the work of other groups, can easily be found. In short, it is by now established that lamination of organic crystals in ambient conditions leads to interfaces exhibiting highly reproducible electronic properties.

2. Temperature dependence of the resistance of un-gated rubrene-PDIF-CN\textsubscript{2} interfaces

The temperature dependence of the resistance measured in un-gated rubrene-PDIF-CN\textsubscript{2} interfaces –shown in Fig. S1- is qualitatively different from that of organic single-crystal charge transfer interfaces investigated previously, based on TTF-TCNQ\textsuperscript{S7} or TMTSF-TCNQ\textsuperscript{S8}. Specifically, for rubrene-PDIF-CN\textsubscript{2} the square resistance is typically 1 M\(\Omega\) at room temperature and increases only slowly upon lowering temperature down to approximately 150 K (see Fig. S1). In contrast to this, in TTF-TCNQ\textsuperscript{S7} the typical square resistance value is \(\sim\)10 k\(\Omega\) and the temperature dependence is metallic-like; in TMTSF-TCNQ\textsuperscript{S8} the square resistance is 10-30 M\(\Omega\) and increases exponentially with lowering temperature. These differences are a manifestation of the different band alignment in the different cases, as discussed in the main text.
3. Fabrication of Schottky-gated heterostructures and characterization

The rubrene-PDIF-CN₂ heterostructures are mounted on a PDMS stamp support, according to the following procedure: We first evaporate through a shadow mask a gate electrode consisting of a strip (approximately 200 or 400 micron wide) of Ti (3 nm, adhesion layer), Au (20 nm, to improve the mechanical properties), Ti (3 nm, to avoid gold interdiffusion), and Cr (20 nm). Although simpler structures may be possible as well, we found that this layer sequence eliminates most problems associated to the mechanical properties and electrical continuity of the gate electrode. Cr was chosen because –with a work function of approximately 4.5 eV—it leads to a sufficiently high Schottky barrier at the interface with rubrene to enable Schottky gating, while being a simpler material to process and handle as compared to metals with a smaller work function. A rubrene crystal (approximately 1-2 micron thick) is subsequently manually aligned under an optical microscope and laminated on top of the gate. Gold contacts (15 nm thick) are then evaporated through a shadow mask directly on top of rubrene. Finally, a thin PDIF-CN₂ crystal is laminated onto the rubrene one, so that it makes contact with the gold electrodes and it is aligned with the underlying gate. Small (25 micron in diameter) gold wires are attached to the gold electrodes and to the gate, using solvent-free silver epoxy. Images of devices realized in this way are shown in Fig. 1 of the main text.

While being conceptually similar to the process that we commonly use for the realization of single-crystal transistors, the fabrication of heterostructures is considerably more complicated in practice, because it requires more steps and rather precise manual alignment. As a consequence, it much more frequently happens (as compared to the fabrication of single-crystal FETs) that a device is damaged during the fabrication (crystal cracking and fracturing of the gate electrode are two of the more commonly encountered problems). For this reason we carefully checked devices before starting their in-depth study, and found that it is particularly important to ensure the electrical continuity of the gate electrode and that the leakage current to the gate is sufficiently small (the leakage current can be strongly increased if the devices are damaged during the fabrication).

Transport measurements through devices that meet the above standards were mainly performed in a two terminal configuration. We found that the resistivity of the interfacial plane in all the measured devices is quite reproducible, with a value ~ 1 MΩ (see table S1 for statistics on all the properly functioning devices). Table S1 also includes the values of

See, for instance, ref. 23 in the main text. It is certainly possible that the work function of our films is somewhat different from this literature value. However, none of our conclusions depends on the precise value of the work function of Chromium, and the only essential issue is that the work function is sufficiently small to allow an effective operation of the Schottky gate.

Figure S1. Temperature dependence of the square resistance of an un-gated rubrene-PDIF-CN₂ interface, showing the weak temperature dependence between room temperature and 100 K that we referred to in the main text.
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carrier density and field-effect mobility for all devices in which these quantities could be extracted.

<table>
<thead>
<tr>
<th>No.</th>
<th>Resistivity (MΩ)</th>
<th>n (10^{12} cm^{-2})</th>
<th>μ (cm²/Vs)</th>
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<td>2.75</td>
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<td>8</td>
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<tr>
<td>15</td>
<td>2.48</td>
<td>Not gated</td>
<td></td>
</tr>
</tbody>
</table>

Table S1. Resistivity, electron density and electron mobility extracted from two-terminal measurements. These results include all the functioning devices measured at room temperature.

In this work we focused mainly on the investigation of transport in a two-terminal configuration, because of the complexity of making four-probe or Hall bar devices, in which the PDIF-CN₂ crystals have to be aligned with 4 or 6 contacts instead of two. This implies that the last alignment step needs to be carried out with much better precision, which requires lengthier manipulations of the crystals and easily results in damage and in mechanical stress which can reduce the carrier mobility. We found that this type of degradation poses particularly serious challenges to the fabrication of Hall bar devices, where alignment of the
PDIF-CN$_2$ crystal requires a precision of ~ 10 μm. We also found that the presence of additional contacts renders the devices more susceptible to cracks that appear in the crystals as devices are cooled down. For all these reasons, basing our investigations on multi-probe devices would have very seriously limited the amount of properly functioning devices that we could have studied in detail. We nevertheless succeeded in fabricating working devices with four or six probes. In these devices we could compare the square resistance extracted from two- and four-probe measurements, and we found no significant difference (even at lower temperature), as shown in Fig. S2, which illustrates the comparison between the two and four-terminal resistivity in two different devices. Fig. S2a corresponds to device S3 whose mobility and electron density are shown in Fig 4a and 4b respectively. The data in Fig S2b corresponds to device S4, on which the Hall measurements where performed and which are described in the next section. These measurements demonstrate that the contact resistance is small and does not significantly influence the results of this work.

**Figure S2.** Resistivity (at $V_G = 0$ V) of two heterostructures as a function of temperature, measured in a two-terminal (full squares) and in a four-terminal (open squares) configuration. The comparison shows that the contact resistance has a negligible contribution to the total resistivity of the heterostructures. a) corresponds to one of the devices whose two-terminal resistivity, electron density and mobility are discussed in the main text, while b) corresponds to the resistivity of the device in which the Hall effect was measured. The insets show an optical image of the devices.
4. Hall measurements on Schottky-gated heterostructures

Figure S3. Time evolution of the Hall voltage $\Delta V_{xy}$ as a function of magnetic field, at a) 290 K, b) 210 K, and c) 130 K. A voltage offset at $B = 0$ T (about 8% of the applied $V_{DS}$) has been subtracted. d) shows the Hall resistance as a function of B. The negative slope indicates electron transport.

We succeeded in measuring the Hall effect as a function of temperature on one device, and in a few other devices Hall effect measurements could also be performed, but only close to room temperature (as the devices broke upon cooling). These experiments corroborate the results obtained by FET measurements, as they provide an independent measurement of the type of charge carriers contributing to transport, and of the temperature dependence of their carrier density and mobility.
The measurements were performed in a variable temperature cryostat, in a perpendicular magnetic field up to 7 T, and sweeping rates up to 0.6 T/min. We focused on measurements of the Hall effect at $V_G = 0$ V: the Hall voltage to be measured is very small and its measurement requires very stable devices (stability of better than one part in one thousand over a few hours) and we found that the application of a gate voltage was not compatible with such a stability level (mainly because of small, slow drifts in the source drain current). The time evolution of the Hall voltage $\Delta V_{xy}$ while sweeping the magnetic field, measured at three different temperatures is shown in Fig. S3a-c. The devices are voltage biased ($V_{DS} = 10$ V) and the source drain current $I_{DS}$ decreases with lowering temperature (in this device the resistance increases with lowering temperature, see Fig. S2b), which makes the Hall signal more difficult to measure at low temperature. Nevertheless, as it can be seen from the raw data, the signal to noise ratio remains excellent even at the lowest temperatures.

From the Hall voltage we extract the Hall resistance (see Figure S3d), whose slope as a function of $B$ increases upon lowering temperature, indicating that the electron density decreases as expected. Indeed, the results shown in Fig. 4 of the main text show that the decrease in electron density is linear with $T$, and that its slope equals the one obtained from the FET analysis (i.e., it coincides with the one predicted by the model discussed in the main text).

5. Scanning Kelvin probe force microscopy across rubrene-PDIF-CN$_2$ heterostructures

Scanning Kelvin probe force microscopy (SKPFM) is a non-contact scanning probe technique commonly used to measure the work function of metals$^{S10}$ and semiconductors$^{S11}$. In this technique, a conductive atomic force microscope tip is scanned above a grounded sample, and is capacitively coupled to it. The work function difference between tip and sample results in a contact potential difference (CPD) between the two, which causes an electrostatic force acting on the tip. The SKPFM measurement consists in zeroing this electrostatic force by applying
an external voltage that equals the CPD: the value of this voltage corresponds to the work
function difference between tip and sample. If the work function of the tip is known, one
directly obtains the work function of the sample (for more details see ref. S10). SKPFM has
been widely applied to organic semiconductors\textsuperscript{S12}, for instance to measure their work
function\textsuperscript{S13}, to probe the electrostatic potential profile of field-effect transistor under biased
conditions\textsuperscript{S14}, and to investigate the influence of illumination on the electrostatic profiles at
organic interfaces in solar cell structures\textsuperscript{S15}.

The measurements on rubrene/PDIF-CN\textsubscript{2} interfaces were performed in ambient conditions,
with an Asylum Cypher scanning force microscope, in a two-scan mode. In the first scan, the
topography is measured and during the second scan the measured height profile is used to
maintain a constant distance between tip and sample, while measuring the CPD as a function
of position. We performed SKPFM measurements on rubrene/PDIF-CN\textsubscript{2} interfaces, on actual
devices (see Fig. S4a) and on interfaces assembled on different substrates. As an example,
Fig. S4b and Fig. S4c show the topography and CPD measured in the area delimited by the
red-line in Fig. S4a. On the left side of the image, the surface of the rubrene crystal is exposed
and on the right side, the rubrene crystal is covered by a PDIF-CN\textsubscript{2} crystal. The height
difference between the two –corresponding to the thickness of the PDIF-CN\textsubscript{2} crystal- is
clearly apparent in Fig. S4b. Fig. S4c shows that in correspondence of the height step, a CPD
step is present. For a quantitative analysis, Fig S4d shows the averaged height and CPD step
perpendicular to the interface, over the entire area of the images. The difference in CPD on
the two materials gives their work function difference irrespective of the absolute value of the
work function of the tip (which is an important point to achieve high accuracy, because
uncertainties in the work function of the tip can give large calibration errors in absolute
measurements). We performed measurements on more than 10 interfaces, using two different
type of tips (i.e. with different work functions) and found that the work function difference
between rubrene and PDIF-CN\textsubscript{2} single crystals is 410 meV +/- 50 meV.
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Together with transport measurements performed on individual rubrene and PDIF-CN₂ crystals, the work function difference measured by SKPFM can be used to verify the level alignment between the valence band of rubrene and the conduction band on PDIF-CN₂ crystals. As mentioned in the main text, we know from transport measurements (on individual rubrene and PDIF-CN₂ crystals) that the energy difference between the Fermi level and the
top of the valence band in rubrene is about 300 meV (with sample-to-sample fluctuations of about 100 meV –see inset of Fig. 2d), while the energy difference between the Fermi level and the bottom of the conduction band of PDIF-CN₂ is about 100 - 120 meV. Hence if the valence band of rubrene and the conduction band of PDIF-CN₂ are aligned, one would expect a work function difference of about 400 meV, with an uncertainty of about 100 meV. This finding is in excellent agreement with the work function difference found via SKPFM measurements, and provides an independent quantitative confirmation of the alignment of the level in rubrene and PDIF-CN₂ which was assumed to model the interfacial transport data (see main text and next section).

6. Interfacial charge transfer and band diagram of Rubrene-PDIF-CN₂ heterostructures

Here we analyze in more detail the band diagram that determines the electronic properties of rubrene-PDIF-CN₂ Schottky-gated heterostructures, as well as the two different contributions to the density of electrons present at the rubrene-PDIF-CN₂ interface. We start by discussing the interface between semi-infinite rubrene and PDIF-CN₂ crystals, and see later what is the effect of the presence of a Schottky gate at a finite distance from the rubrene-PDIF-CN₂ interface.

As mentioned in the main text, our experimental observations indicate the absence of both any sizable gap or band overlap between the top of the valence band of rubrene and the bottom of the conduction band of PDIF-CN₂, i.e., before bringing the material into contact, the top of the valence band of rubrene is aligned with the bottom of the conduction band of PDIF-CN₂. The discussion of the entire band-diagram also requires the –at least approximate– knowledge of the position of the chemical potential in the bulk of the two semiconductors. As we discussed in the main text, the chemical potential is approximately 300 meV above the top of the valence band in rubrene (see ref. 28 and the considerations in main the text about the activation energy of the space charge limited current that flows through the rubrene crystal.
upon biasing the Schottky gate) and 100 meV below the bottom of the conduction band of PDIF-CN$_2$ (as determined from the activation energy of the residual conductivity measured in individual PDIF-CN$_2$ crystals). Before bringing the two materials into contact, therefore, the relative position of the levels and chemical potentials in the two materials is as depicted in the left side of Fig. S5$^\text{ii}$

Upon bringing the two materials into contact, electrons redistribute to create a uniform electrochemical potential through the entire structure. There are two contributions to the charge redistribution: a surface contribution, and a contribution due to the displacement of charge in the bulk of the semiconductors potential. The surface contribution is confined to a layer of the thickness of one (or at most few) molecules on each side of the interface, the same thickness that characterizes the accumulation layer in organic field-effect transistors. This contribution involves an equal number of electrons at the surface of PDIF-CN$_2$ and holes at the surface of rubrene, because electrons are excited from the valence band of rubrene to the conduction band of PDIF-CN$_2$. It generates an electrostatic dipole that shifts apart the top of the valence band in rubrene and the bottom of the conduction band in PDIF-CN$_2$, effectively opening a gap proportional to the density of transferred surface charge. The bulk contribution, on the contrary, displaces electrons from a deeper region of the rubrene crystal to the PDIF-CN$_2$ crystal. It is driven by the chemical potential in the bulk of the rubrene crystal, which is higher than that in the bulk of PDIF-CN$_2$. The characteristic length scale for this contribution to the charge redistribution is the usual screening length of doped semiconductors, which for

$^\text{ii}$ We are discussing the electronic properties of organic semiconductors in full analogy with those of conventional semiconductors, how it is often done. In this context, we consider that the position—in energy—of the valence and conduction bands in the two organic crystals also includes terms such as the re-organization energy, which are relevant for organic materials but not for inorganic ones. Additionally, correlation energies due to electron-electron interactions—that could be important in organic semiconductors owing to their rather narrow band-width—are neglected because the density of interfacial charge carriers is about 0.01 per molecule (much smaller than 1 per molecule).
the small doping levels typical of high-quality organic crystals corresponds to several hundreds of nanometers. The final band diagram therefore is the one depicted on the right of Fig. S5.

\[ n_S = \int_{\frac{\Delta}{2}}^{\infty} 2N_S e^{-\frac{E}{kT}} dE \]  
(S1)

**Figure S5** Left: alignment of the bands in rubrene and PDIF-CN\(_2\), and position of the chemical potentials in the two materials before bringing them into contact. Right: band-diagram in the interface region after establishing contact between the two materials. The gap between the top of the valence band of rubrene and the bottom of the conduction band of PDIF-CN\(_2\) is due to the surface charge density \(n_s\) transferred between the two materials. Band bending in the bulk, away from the interface occurs on a length scale determined by the doping level (typically few hundreds
where \(N_S\) is the density of states per unit surface (which is approximately the same for rubrene and PDIF-CN2, and is given by the density of molecules \(-1 \times 10^{15} \text{ cm}^{-2}\) divided by the bandwidth, \(-0.5 \text{ eV}\); the factor 2 in the expression comes from spin degeneracy). Even though for rubrene-PDIF-CN2 no gap is present before charge transfer (i.e. \(\Delta = 0\) before bringing the two semiconductors together) a gap is effectively opened by the electrostatic dipole created by the surface charge transfer, once the two semiconductors are brought into contact. From simple electrostatics, the expression for this gap (i.e., electrostatic potential associated to the dipole) is:

\[
\Delta = \frac{n_Se}{\varepsilon \varepsilon_0}d
\]

(S2)

Here, \(d\) is the distance between the electron and hole layers at the two surfaces (layer which we take to be 1 nm) and \(\varepsilon\) is the relative dielectric constant of the organic materials (which we take to be 3). We therefore get a self-consistent equation for \(n_S\):

\[
n_S = \int_{n_S e^2d \over 2\varepsilon \varepsilon_0}^{\infty} 2N_S e^{E \over kT} dE = 2N_S kT e^{n_S e^2d \over 2\varepsilon \varepsilon_0 kT}
\]

(S3)

which is equation (1) in the main text.

Charge transfer from the rubrene to the PDIF-CN2 surfaces generates as many electrons on the PDIF-CN2 surface as holes on the rubrene surface. However, the alignment of the electrochemical potential in the bulk of the two crystals gives an additional electron contribution (see Fig. S5) that fills the hole states, which is why only electron transport is observed. The total electron density at the interface is then determined by the values of the chemical potentials in the two materials, which, in turn, is determined by the amount of unintentional dopants present and by the disorder-induced density of states inside the band-
gap of the two semiconductors, and that therefore fluctuates from sample to sample. This is why the total electron density that we find in different devices is different.

It is now simple to understand the effect of the finite thickness of the rubrene crystal, and of the Schottky barrier formation. The Schottky barrier at the Cr/rubrene interface leads to the formation of the usual depletion region. If the rubrene-PDIF-CN\textsubscript{2} interface is further away from the Cr gate electrode (i.e., if the thickness of the rubrene crystal is much larger than the depletion region associated to the formation of the Schottky barrier), the band bending due to the Schottky barrier itself and to the rubrene-PDIF-CN\textsubscript{2} interface are spatially separated (see Figure S6).

**Figure S6** Band diagram of Schottky-gated rubrene-PDIF-CN\textsubscript{2} heterostructures for different thicknesses of the rubrene crystal. Left: the rubrene crystal is thicker than the depletion region associated to the Schottky barrier. The band bending due to the Schottky barrier formation does not overlap with the band bending due to the charge accumulated at the interface (as indicated by a flat band region in between the two) and can be treated independently. Middle: if some overlap is present between the depletion region and the charge accumulation region at the rubrene-PDIF-CN\textsubscript{2} interface, the net result is to shift the Fermi level at the interface closer to the bottom of the conduction band in PDIF-CN\textsubscript{2} (as can be easily understood by considering the case –on the right- in which the interface is much closer to the Schottky gate). Indeed it may be possible to accumulate rather high electron densities at the interface in devices with a sufficiently thin rubrene crystal (although very interesting, these devices are harder to fabricate and are expected to exhibit higher leakage current at room temperature, even though at lower temperature the leakage current may still be completely suppressed).

It is now simple to understand the effect of the finite thickness of the rubrene crystal, and of the Schottky barrier formation. The Schottky barrier at the Cr/rubrene interface leads to the formation of the usual depletion region. If the rubrene-PDIF-CN\textsubscript{2} interface is further away from the Cr gate electrode (i.e., if the thickness of the rubrene crystal is much larger than the depletion region associated to the formation of the Schottky barrier), the band bending due to the Schottky barrier itself and to the rubrene-PDIF-CN\textsubscript{2} interface are spatially separated (see Figure S6).
left scheme in Fig. S6) and can be treated independently. In practice, the depletion region can extend up to nearly 1 micron (similarly to what has recently been found for rubrene metal-semiconductor transistors\textsuperscript{51}), at least for the devices in which the concentration of dopants is lowest. In this case the depletion region due to the Schottky barrier can have some overlap with the region (in the rubrene crystal) where band bending originating from the rubrene-PDIF-CN\textsubscript{2} interface is present (see middle scheme in Fig. S6). The result of this overlap is to further shift upward the electrochemical potential at the interface (as it can be simply understood by considering the case of a thin rubrene crystal, see right scheme in Fig. S6), and provides an additional contribution to the electron density at the interface. The resulting complete band diagram of the Schottky gate heterostructure is shown in Fig. 5.

References


