Ambipolar transistors based on chloro-substituted tetrphenylpentacene

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<td>Complete List of Authors:</td>
<td>Sato, Ryonosuke; Tokyo Institute of Technology, Department of Organic and Polymeric Materials Eda, Shohei; Kwansei Gakuin University - Kobe Sanda Campus; Institute of Physical and Chemical Research Sugiyama, Haruki; Tokyo Institute of Technology; Keio University - Hiyoshi Campus Uekusa, Hidehiro; Tokyo Institute of Technology, Hamura, Toshiyuki; Kwansei Gakuin University, Department of chemistry Mori, Takehiko; Tokyo Institute of Technology, Department of Organic and Polymeric Materials</td>
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</table>
Ambipolar transistors based on chloro-substituted tetraphenylpentacene†

Ryonosuke Sato,*,a Shohei Eda,b,c Haruki Sugiyama,d,e Hidehiro Uekusa,d Toshiyuki Hamura,c and Takehiko Mori*a

Thin-film transistors of halogen-substituted tetraphenylpentacenes are investigated. These compounds exhibit mainly hole transport, but the chlorine compound shows considerably higher performance than the fluorine and bromine compounds. In addition, the chlorine compound shows ambipolar properties, though the hole mobility is by four times larger than the electron mobility. These compounds have basically the same crystal structures, but the remarkable halogen dependence is explained from the critical location of the LUMO levels as well as the intermolecular transfers, which sensitively changes depending on the stacking geometry. In particular, hole and electron transfers exhibit different periodicity depending on the slip distance along the molecular long axis, and this is related to the appearance of the electron transport properties.

Introduction

Transistors of rubrene have been extensively studied owing to the highest performance in single-crystal organic transistors.1–5 Rubrene has a uniformly stacking structure,6 and it is comparatively difficult to make the thin-film transistors. On the other hand, pentacene is a representative transistor material,7,8 and the thin-film transistors have been investigated for a long time. A variety of the related compounds have been investigated as transistor materials,9–11 among which the tetramethyl and dibromo derivatives have been reported to show hole-transporting properties with the mobility of 0.2–0.3 cm²V⁻¹s⁻¹,12,13 and perfluoropentacene is known to show electron-transporting properties.14 In this connection, tetraphenylpentacene is interesting (X = H in Scheme 1), which has been reported to show the hole mobility of 10⁻³ cm²V⁻¹s⁻¹ in the thin-film transistors.15

Usually pentacene shows only hole transport, and electron transport is observed only when calcium is used as the electrode material.16 However, ambipolar transport is observed using Ag electrodes on poly(methyl methacrylate) (PMMA),17 and Ag/AI electrodes on tetratetracontane (TTC).18 TTC is an excellent passivation layer even when Au electrode is used, which enables the observation of ambipolar transistor properties in copper phthalocyanine,18–20 indigos,21–24 quinoidal oligothiophene,25 semiquinones,26 diketopyrrolopyroles,27,28 and isoindigos.29,30

We have recently developed a versatile synthetic route to prepare substituted acenes using cycloaddition reactions.31–33 Using this route, we can directly obtain acenes where the terminal hydrogens are substituted by halogens. Carrier polarity is sensitive to terminal halogens because of the induced polarization.9 In the present paper, thin-film transistors of halogen-substituted tetraphenylpentacenes (4X4Ph, where X = F, Cl, and Br in Scheme 1) are investigated.

Experimental

Synthesis

The halogen-substituted tetraphenylpentacenes 4X4Ph were prepared in two ways by using dibromodiphenylisobenzofuran 2c as a synthetic building block (Scheme 2). Thus, the one-pot successive [4+2] cycloadditions of dihaloarynes and isobenzofurans efficiently gave diepoxy pentacenes 4X4Ph_epoxy (X = F, Cl),31 which were converted to
pentacenes 4F4Ph and 4C14Ph by reductive aromatization (Scheme 2a). On the other hand, due to the poor site-selectivity in the bromine–lithium exchange of the tetrabromopentacene 3c for generation of arylene, pentacene 4Br4Ph was alternatively prepared in four-steps including double Diels–Alder reactions of isobenzofuran 2c and 1,4-benzoquinone as a key reaction (Scheme 2b).

\[
\begin{align*}
\text{(a)} \\
\begin{array}{c}
\text{X} \\
\text{O} \\
\text{X} \\
\text{O} \\
\text{X} \\
\text{O} \\
\text{X} \\
\text{O} \\
\end{array} \\
\begin{array}{c}
\text{Br} \\
\text{n-BuLi} \\
\text{n-BuLi} \\
\text{Br} \\
\text{Br} \\
\text{Br} \\
\text{Br} \\
\text{Ph} \\
\end{array} \\
\begin{array}{c}
\text{X} \\
\text{O} \\
\text{X} \\
\text{O} \\
\text{X} \\
\text{O} \\
\text{X} \\
\text{O} \\
\end{array} \\
\begin{array}{c}
1a: X = F \\
1b: X = Cl \\
2c: X = Br \\
3a: X = F \\
3b: X = Cl \\
4F4Ph \\
4C14Ph \\
\end{array} \\
\end{align*}
\]

\[
\begin{align*}
\text{(b)} \\
\begin{array}{c}
\text{O} \\
\text{Br} \\
\text{X} \\
\end{array} \\
\begin{array}{c}
\text{Cl} \\
\text{AlBr}_3 \\
\text{SiCl}_4 \\
\end{array} \\
\begin{array}{c}
\text{CHCl}_3 \\
\text{4F4Ph} \\
\text{4C14Ph} \\
\end{array} \\
\begin{array}{c}
4F4Ph_{\text{epoxy}} (62\%, 2 \text{ steps}) \\
4C14Ph_{\text{epoxy}} (43\%, 2 \text{ steps}) \\
\text{4F4Ph: X = F (51\%)} \\
\text{4C14Ph: X = Cl (50\%)} \\
\end{array} \\
\end{align*}
\]

Scheme 2. Syntheses of pentacenes 4X4Ph.

Device fabrication

Thin-film transistors were fabricated onto an n-doped Si substrate with a thermally grown SiO2 dielectric layer (300 nm, \(C = 11.5 \text{ nF cm}^{-2}\)). The passivation layer tetratetracontane (C_{44}H_{190}, TTC, \(e = 2.5\)) with a thickness of 20 nm was evaporated under a vacuum of \(10^{-4} \text{ Pa}\) on the substrates,\(^{19,20}\) where the calculated overall capacitance of the gate dielectrics was 10.4 nF/cm\(^2\).\(^{34}\) Then 4X4Ph with a thickness of 50 nm was evaporated. The top-contact electrodes were patterned by Au thermal deposition through a metal mask; the channel length (\(L\)) and width (\(W\)) were 100 \(\mu\text{m}\) and 1000 \(\mu\text{m}\), respectively. The measurements were conducted under the vacuum of \(10^{-3} \text{ Pa}\) by using a Keithley 4200 semiconductor parameter analyzer. The mobilities were estimated from the saturated-region transfer characteristics.

Results and discussion

Energy levels

The highest occupied molecular orbital (HOMO) levels and the lowest unoccupied molecular orbital (LUMO) levels together with the energy gaps are summarized in Table 1. The HOMO levels are estimated from the oxidation potentials of the cyclic voltammograms, and the energy gaps are obtained from the absorption edges (Figs. S2 and S3, ESI†). Accordingly, the LUMO levels are evaluated by adding the energy gaps to the HOMO levels. Energy levels of the halogen substituted compounds are lower than those of the unsubstituted pentacene (HOMO/LUMO = \(-5.0/-3.2 \text{ eV}\))\(^{35}\) and the tetrphenylpentacene (\(X = \text{H, } \sim -4.95/\sim -3.07 \text{ eV}\)).\(^{36}\) In general, a \(F\) substituted compound is a stronger acceptor than the corresponding Cl and Br compounds. In the present series, however, the LUMO levels indicate that 4F4Ph is a weaker acceptor than 4C14Ph and 4Br4Ph. The HOMO levels are not largely different, but the optical gaps of 4C14Ph and 4Br4Ph are obviously smaller than that of 4F4Ph. The difference of the LUMO levels may be attributed to the spread of the molecular orbitals to the halogen atoms. It has been reported that hole-transporting properties appear when the HOMO level is higher than \(-5.6 \text{ eV}\), whereas electron-transporting properties appear when the LUMO level is lower than \(-3.2 \text{ eV}\).\(^{37}\) The HOMO levels of these compounds are much within the threshold. The LUMO levels of 4C14Ph and 4Br4Ph are certainly within the electron transporting limit, but 4F4Ph and 4H4Ph are critically out of the limit. Therefore, the energy levels indicate hole dominant ambipolar transport, but the electron transport may potentially depend on the substituents.

<table>
<thead>
<tr>
<th>(X)</th>
<th>(E_{\text{HOMO}} (\text{eV}))</th>
<th>(E_{\text{LUMO}} (\text{eV}))</th>
<th>Absorption edge (nm)</th>
<th>(E_c (\text{eV}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>–5.01</td>
<td>–3.07</td>
<td>638</td>
<td>1.94</td>
</tr>
<tr>
<td>F</td>
<td>–5.17</td>
<td>–3.18</td>
<td>622</td>
<td>1.99</td>
</tr>
<tr>
<td>Cl</td>
<td>–5.19</td>
<td>–3.29</td>
<td>651</td>
<td>1.90</td>
</tr>
<tr>
<td>Br</td>
<td>–5.20</td>
<td>–3.31</td>
<td>656</td>
<td>1.89</td>
</tr>
</tbody>
</table>

Transistor properties

Thin-film transistors with bottom-gate top-contact geometry were fabricated onto a TTC-treated SiO2 layer, where 4X4Ph was thermally evaporated. The transfer and output characteristics are shown in Fig. 1. From these characteristics, the transistor parameters are extracted as summarized in Table 2. All compounds show hole transport, whereas only 4C14Ph shows ambipolar transport. The hole mobility of 4C14Ph (0.016 cm² V⁻¹ s⁻¹) is much higher than those of 4F4Ph and 4Br4Ph. This mobility is also much larger than the reported value (10⁻³ cm² V⁻¹ s⁻¹) of 4H4Ph.\(^{15}\) The hole mobility of 4C14Ph is by four times larger than the electron mobility. The electron threshold voltage is also considerably larger than the hole threshold voltage. Then, the hole transport is obviously dominant. This is also evident

Table 2. Transistor properties of 4X4Ph.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>(\mu_{\text{hole}} [\mu\text{m}^2 \text{V}^{-1} \text{s}^{-1}])</th>
<th>(V_{th} (\text{V}))</th>
<th>(L/I_{on})</th>
</tr>
</thead>
<tbody>
<tr>
<td>4F4Ph</td>
<td>(4.4 \times 10^{-3} [6.0 \times 10^{-4}])</td>
<td>–9</td>
<td>5 \times 10⁵</td>
</tr>
<tr>
<td>4C14Ph</td>
<td>(0.013 [0.016])</td>
<td>–5</td>
<td>3 \times 10⁵</td>
</tr>
<tr>
<td>4Br4Ph</td>
<td>(3.3 \times 10^{-3} [6.4 \times 10^{-4}])</td>
<td>58</td>
<td>2 \times 10⁵</td>
</tr>
<tr>
<td>4H4Ph</td>
<td>(2.3 \times 10^{-4} [2.9 \times 10^{-4}])</td>
<td>3</td>
<td>3 \times 10⁴</td>
</tr>
</tbody>
</table>
in the output characteristics (Fig. 1d), where the inverse current due to the electron transport is comparatively small, whereas large inverse current due to the hole transport is observed even from a positive $V_D = 20$ V in Fig. 1e.

Crystal structures

The crystal data are listed in Table 3. These compounds are approximately isostructural, where the stacking structure has close resemblance to rubrene (Fig. 2). Torsion angles of phenyl groups from the pentacene skeleton are $58.7 - 66.0^\circ$ in 4F4Ph, $62.0 - 72.9^\circ$ in 4Cl4Ph, and $67.6 - 86.7^\circ$ in 4Br4Ph, which tend to be smaller than $80.8^\circ$ in rubrene (Table S1, ESI†). In addition, the rubrene molecule is located on an inversion center, whereas the present molecules are located on a general position. In contrast to rubrene with uniform stacks, the present compounds have dimerized stacks similar to tetrafluorotetraphenylanthracene. Here, $c_1$ with the distance between the molecular centers $R \sim 4.9$ Å makes a dimer (Table 4), and $c_2$ ($R > 8.7$ Å) corresponds to the interdimer interaction.

In order to analyze the intermolecular interactions, the transfer integrals $t$ are calculated for HOMO ($t_h$) and LUMO ($t_e$) as listed in Table 4. Interstack transfers are negligibly small, and not shown in Table 4. The transfers are estimated from the HOMO and LUMO overlaps. As another method, the transfers are evaluated from the level splitting of the diads. Although the signs of transfers are not determined in the later method, both of these two calculation methods show the same tendency: $|t_h| > |t_e|$, indicating hole dominant transport. The comparatively high LUMO levels are the principal reason of the hole dominant transport, but the small electron bandwidth is also responsible.

The bandwidth is determined by $c_2$, and the interdimer $|t_e|$ ($c_2$) of 4Br4Ph (1.9 meV) is particularly small; this may be related to the absence of electron transport in 4Br4Ph. It is
characteristic of 4Cl4Ph that the intradimer $|t_c|$ ($c1$) is larger than those of 4F4Ph and 4Br4Ph. In particular, the intradimer $|t_c|$ of 4F4Ph is even smaller than $c2$, and the bandwidth is limited by $c1$. This is a reason that the electron transport in 4F4Ph is hampered rather than naively expected from the geometry.

Since transfer integrals are sensitive to the geometry of the diads,\textsuperscript{40} slip distances along the molecular long axis ($D_l$) and along the molecular short axis ($D_s$) are evaluated as well as the interplanar distances ($D_t$) (Table 4). It is reasonable that $c2$ interaction with large $D_t$ ~ 7.9 Å affords a smaller transfer than the $c1$ interaction with small $D_s$ ~ 3.1 Å. Since the HOMO and LUMO have nodes on each benzene ring,\textsuperscript{40} the transfer is a periodical function of $D_t$ (Fig. 3). The previous calculation indicates that the HOMO transfer has peaks at $D_t$ = 0, 2.8, 5.6, and 8.5 Å, in which 2.8 Å corresponds to the size of a benzene ring.\textsuperscript{40} The $c1$ and $c2$ overlaps are not far from the second and fourth peaks, leading to a comparatively large $|t_c|$. The LUMO transfer periodicity is slightly smaller than this, which makes peaks at $D_t$ = 0, 2.3, 4.5, 6.7, and 8.9 Å. This is because the HOMO spreads to the outer rings, but the LUMO spreads to the inner rings (Fig. 3).\textsuperscript{40} Accordingly, the LUMO transfer has nodes at $D_t$ = 1.2, 3.5, 5.8, and 8.0 Å. The actual $D_t$ values of the present crystals are not definitely on the LUMO peaks, and particularly that of $c2$ ($D_t$ ~ 7.9 Å) is close to the node. $D_t$ values of 4Cl4Ph and 4Br4Ph for $c1$ are 3.1 Å, but that of 4F4Ph $c1$ is 3.3 Å (Table 4), which is around the node of the LUMO transfer ($D_t$ = 3.5 Å).\textsuperscript{40} This is the reason of significantly small $c1$ in 4F4Ph. Similar $D_t$ sensitivity has been recently reported in halogenated tetraazapentacenes as well.\textsuperscript{41}

### Table 3. Crystallographic data of 4X4Ph (X = F, Cl, and Br).

<table>
<thead>
<tr>
<th>Crystal</th>
<th>4F4Ph</th>
<th>4Cl4Ph</th>
<th>4Br4Ph</th>
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<tbody>
<tr>
<td>Formula</td>
<td>C₆H₄F₄</td>
<td>C₆H₄Cl₄</td>
<td>C₆H₄Br₄</td>
</tr>
<tr>
<td>Formula weight</td>
<td>654.67</td>
<td>720.47</td>
<td>898.31</td>
</tr>
<tr>
<td>Crystal size (mm³)</td>
<td>0.07 × 0.06 × 0.02</td>
<td>0.122 × 0.071 × 0.031</td>
<td>0.099 × 0.048 × 0.033</td>
</tr>
<tr>
<td>μ (mm⁻¹)</td>
<td>0.789</td>
<td>0.388</td>
<td>5.826</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
<td>P-1</td>
<td>P-1</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>a (Å)</td>
<td>10.0390(2)</td>
<td>10.3770(13)</td>
<td>10.3811(3)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>13.0700(2)</td>
<td>12.874(2)</td>
<td>13.2135(4)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>13.4090(2)</td>
<td>13.3509(17)</td>
<td>13.8306(4)</td>
</tr>
<tr>
<td>α (deg)</td>
<td>112.658(1)</td>
<td>86.033(6)</td>
<td>81.924(2)</td>
</tr>
<tr>
<td>β (deg)</td>
<td>103.943(1)</td>
<td>77.911(4)</td>
<td>77.158(2)</td>
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<tr>
<td>γ (deg)</td>
<td>92.256(1)</td>
<td>74.579(5)</td>
<td>72.986(2)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>1558.15(5)</td>
<td>1681.14(4)</td>
<td>1762.94(9)</td>
</tr>
<tr>
<td>ρ (g cm⁻³)</td>
<td>1.395</td>
<td>1.423</td>
<td>1.692</td>
</tr>
<tr>
<td>Total reflns.</td>
<td>18385</td>
<td>16286</td>
<td>20752</td>
</tr>
<tr>
<td>Unique reflns. (Rint)</td>
<td>5593 (0.0399)</td>
<td>7546 (0.0693)</td>
<td>6332 (0.1139)</td>
</tr>
<tr>
<td>R1 (F² &gt; 2σ(F²))</td>
<td>0.0677</td>
<td>0.0694</td>
<td>0.0685</td>
</tr>
<tr>
<td>wR2 (All reflections)</td>
<td>0.2312</td>
<td>0.2303</td>
<td>0.1983</td>
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<tr>
<td>GOF</td>
<td>0.968</td>
<td>1.029</td>
<td>1.013</td>
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<tr>
<td>Temperature (K)</td>
<td>173(2)</td>
<td>93(2)</td>
<td>123(2)</td>
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### Table 4. Intermolecular transfer integrals and slip distances in 4X4Ph.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Transfer integrals (meV)</th>
<th>Slip distances (Å)</th>
<th>R</th>
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<tr>
<td></td>
<td>$t_c$</td>
<td>$t_c$</td>
<td>$D_s$</td>
</tr>
<tr>
<td>4F4Ph</td>
<td>c1</td>
<td>−58.1 (48.2)</td>
<td>4.4 (0.8)</td>
</tr>
<tr>
<td></td>
<td>c2</td>
<td>−19.4 (16.8)</td>
<td>−5.9 (9.0)</td>
</tr>
<tr>
<td>4Cl4Ph</td>
<td>c1</td>
<td>−51.1 (43.2)</td>
<td>15.9 (9.4)</td>
</tr>
<tr>
<td></td>
<td>c2</td>
<td>−8.2 (8.8)</td>
<td>−6.6 (8.4)</td>
</tr>
<tr>
<td>4Br4Ph</td>
<td>c1</td>
<td>−39.6 (34.6)</td>
<td>8.8 (5.2)</td>
</tr>
<tr>
<td></td>
<td>c2</td>
<td>4.8 (3.2)</td>
<td>−1.9 (2.9)</td>
</tr>
</tbody>
</table>

* From orbital overlaps. Values in the parentheses are from level splittings.

* Slip distances in a diad from the definitions indicated below. $R$ is the distance between the molecular centers.
Thin-film properties

X-ray diffraction (XRD) patterns, and atomic force microscopy (AFM) images of the thin films deposited on the tetratetracontane (TTC)-modified Si/SiO₂ substrates were observed. As shown in Fig. 4a, the XRD patterns show diffraction peaks around 2θ = 7.1°–7.4°. The d-spacings, 11.9–12.5 Å, correspond to b sinα of the crystal lattice, indicating that the crystallographic ac plane is aligned parallel to the substrate (Fig. 4b). Not only the (010) peaks but also the (020) peaks are observed in the three films, and the (040) peaks are observed in the 4Cl4Ph and 4Br4Ph films. The pentacene core has the side-on arrangement rather than the end-on arrangement. Then, the terminal halogen atoms do not contribute to the polarization at the gate interface. This is a reason that charge polarity does not depend on the halogen electron negativity. The molecular planes are tilted by 65.4° (4F4Ph), 70.2° (4Cl4Ph), and 74.6° (4Br4Ph) with respect to the substrates.

The 4Br4Ph molecules are standing most close to the perpendicular direction to the substrate. It has been generally known that the mobility attains a maximum at the perpendicular molecular arrangement. This may be the reason that the mobility of 4Br4Ph is five times larger than that of 4F4Ph.

Atomic force microscopy (AFM) images of the thin films are shown in Figs. 4c-e. Grains of three films are in the same size of about 1 μm. However, in the 4F4Ph and 4Br4Ph films, rod-like microcrystals cover the substrate, but in the 4Cl4Ph film, plate-like microcrystals densely cover the substrate. The 4F4Ph and 4Br4Ph films show relatively sparse coverage in comparison with the 4Cl4Ph film. The 4F4Ph film shows larger roughness than the 4Cl4Ph and 4Br4Ph films, and this may be related to the absence of the (040) XRD peak in the 4F4Ph film. The thin-film quality is to some extent responsible for the largely different mobilities of these materials.

Conclusions

Thin-film transistors of 4X4Ph show mainly hole transport. 4Cl4Ph exhibits higher performance than 4F4Ph and 4Br4Ph. In addition, 4Cl4Ph shows electron transport as well. These compounds have basically the same crystal structures, but the remarkable halogen dependence as well as the hole dominant transport is explained from the critical location of the LUMO levels as well as the intermolecular transfers which sensitively changes depending on the stacking geometry. In particular, the periodicity of the LUMO transfer is different from that of the HOMO transfer, and sensitively influences the appearance of electron transport.
Acknowledgments

We thank Dr. H. Kojima (Nara Institute of Science and Technology) for the results in Fig. 3, which are taken from Ref. 40. This work was partly supported by ACT-C Grant Number JPMJCR12YY and JPMJCR12ZB from JST, Japan, a Grant-in Aid for Scientific Research (No. 16K13974, 18H02044, and 15H05840) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan, and Takahashi Industrial and Economic Research Foundation. The authors are grateful to the Tokyo Institute of Technology Center for Advanced Materials Analysis for XRD measurement and Prof. Kakimoto for AFM measurements.

Notes and references

† Electronic supporting information (ESI) available: Additional information for preparative details, structure analysis, and transfer integrals. CCDC 1887275-1887277.

The table of contents entry

Title
Ambipolar transistors based on halogen-substituted tetraphenylpentacenes

Text (one sentence, of maximum 20 words, highlighting the novelty of the work)
Transistor properties of halogen-substituted tetraphenylpentacenes sensitively change depending on the slip distance along the molecular long axis.

Keywords
organic transistors, ambipolar transistors, transfer integral

Authors
Ryonosuke Sato, Shohei Eda, Haruki Sugiyama, Hidehiro Uekusa, Toshiyuki Hamura, and Takehiko Mori

ToC figure (maximum size 8 cm x 4 cm)