Supporting Information

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Oligothiophene-Based Phosphonates for Surface Modification of Ultraflat Transparent Conductive Oxides

*Melanie Timpel,* *Marco V. Nardi,* *Berthold Wegner,* *Giovanni Ligorio,* *Luca Pasquali,* *Jana Hildebrandt,* *Michael Pätzl,* *Stefan Hecht,* *Hiromichi Ohta,* and *Norbert Koch*
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1. **Synthesis of T5-tP/iP**

**Organic Synthesis.** All solvents and other starting materials were commercial and used as received. The NMR spectra were recorded on a 500 MHz Bruker AVANCE II 500 spectrometer at room temperature. $^1$H-NMR and $^{13}$C-NMR spectra were referenced to 7.26 ppm and 77.16 ppm, respectively, for CDCl$_3$ and 5.32 ppm and 53.8 ppm, respectively, for CD$_2$Cl$_2$. UPLC-MS was performed on a Waters UPLC Acquity equipped with a Waters LCT XE Mass Detector for UPLC-HRMS, with Waters Alliance systems.

**Synthesis of T5-tP**

![Chemical Structure](image)

$\text{Bu}_3\text{Sn}$

**5-Tributylstannyl-5'-diethoxyphosphoryl-[2,2']-bithiophene 2.** To a solution of $n$BuLi (5.70 mL, 12.48 mmol, 2.2 M in hexane) in THF (100 mL) was added dropwise diisopropylamine (1.77 mL, 12.59 mmol) at -78 °C. The mixture was warmed to 0 °C for 5 min and then cooled to -78 °C. A solution of 5'-diethoxyphosphoryl-[2,2']-bithiophene 1 (3.40 g, 11.24 mmol) in THF (10 mL) was added dropwise and the mixture was stirred for 1 h at this temperature. Bu$_3$SnCl (3.35 mL, 12.37 mmol) was added at -78 °C. After stirring for 4 h at this temperature, the mixture was allowed to warm to room temperature overnight. The
solvent was removed under reduced pressure, the residue was diluted with CH$_2$Cl$_2$ (150 mL) and washed with NH$_4$Cl-solution (100 mL). The organic layer was dried over MgSO$_4$, filtered and the solvent was removed under reduced pressure. The resulting brownish oil was subjected to column chromatography (AcOEt) to afford 1.80 g (27%) of compound 2. $^1$H NMR (CDCl$_3$, 300 MHz), δ[ppm] = 0.90 (m, 9H), 1.14 (m, 5H), 1.34 (m, 13H), 1.57 (m, 6H). HRMS (ESI+): Calc. for [C$_{24}$H$_{42}$O$_3$PS$_2$Sn$^+$]: 593.1335; Found 593.1354.

2-Diethoxyphosphoryl-[5,2’;5’,2”’;5”,2”’’;5”’,2”’’’]-quinquethiophene 4. 2-Iodo-terthiophene 3 (1.367 g, 3.652 mmol), Pd$_2$(dba)$_3$ (126 mg, 0.122 mmol), Ph$_3$P (128 mg, 0.487 mmol) and 5-stannyl-bithiophene 2 (1.800 g, 3.043 mmol) are suspended in toluene (50 mL). CuCl (54 mg, 0.548 mmol) was added at room temperature and the mixture was refluxed for 2 h. After cooling to room temperature 2 M aqueous KF-solution (25 mL) was added and the mixture was allowed to stir at this temperature for 1 h. The reaction mixture was filtrated over Celite and diluted with AcOEt (100 mL). The organic phase was washed with brine (100 mL) and was dried with MgSO$_4$. After removal of the solvents under reduced pressure the residue obtained was subjected to column chromatography (CH$_2$Cl$_2$ : MeOH = 100 : 2) to afford 1.12 g (66%) of 4 as an orange powder. $^1$H NMR (CDCl$_3$, 300 MHz), δ[ppm] = 1.29 (m, 6H), 4.07 (m, 4H), 6.95 (m, 1H), 7.02 (m, 5H), 7.11 (m, 3H), 7.16 (m, 1H), 7.48 (m, 1H).

2-Phosphono-[5,2’;5’,2”’;5”,2”’’;5”’,2”’’’]-quinquethiophene T5-tP. In 4 mL of acetonitrile, phosphonate 4 (100 mg, 0.182 mmol) was dissolved, to which iodo(trimethyl)silane (0.111 mL, 0.819 mmol) was added at ambient temperature and the mixture was stirred at this temperature overnight. The solvent was removed under reduced pressure, followed by addition of MeOH (5 mL) and stirring for further 12 h. A saturated
Na₂S₂O₃-solution (10 mL) was added, followed by stirring, filtration of the precipitated crystals, washing with distilled water, MeOH, CHCl₃, and diethyl ether to obtain 45 mg (100%) of T5-tP as an orange powder. Anal. Calcd. C₂₀H₁₃O₃PS₅: C: 48.77, H: 2.66, S: 32.54. Found C: 47.55, H: 2.79, S: 29.17.

**Synthesis of T5-iP**

3-Diethoxyphosphoryl-2,5-bis(tributylstannyl)thiophene 6. To a solution of nBuLi (32.0 mL, 69.70 mmol, 2.2 M in hexane) in THF (250 mL) was added dropwise diisopropylamin (9.79 mL, 69.70 mmol) at -78 °C. After stirring for 1h the solution was added to 3-diethoxyphosphoryl-thiophene 5 (6.14 g, 27.88 mmol) in THF (75 mL) at -78 °C. The reaction mixture was allowed to stir at this temperature for further 2 h. Bu₄SnCl (18.91 mL, 69.70 mmol) dissolved in THF (50 mL) was added and the reaction was stirred for 4 h at -78 °C. The pH was adjusted to 7 by addition of a Na₂HPO₄/NaH₂PO₃-buffer (125 mL). The mixture was extracted with AcOEt (3x70 mL). The combined organic phases were washed with brine (200 mL) and dried over MgSO₄. The solvent was removed under reduced pressure and the resulting brownish oil was subjected to column chromatography (petroleum ether : AcOEt = 10 : 1) to afford 13.50 g (61%) of compound 6. ¹H NMR (CDCl₃, 300 MHz ,)
\[ \delta[\text{ppm}] = 0.88 (m, 18H), 1.19 - 1.23 (m, 11H), 1.28 - 1.33 (m, 18H), 1.57 (m, 8H), 4.00 - 4.07 \] (m, 4H), 7.47(m, 1H).

**4”-Diethoxyphosphoryl-[2,2’;5’,2″;5″;2‴;5‴;2‴′];-quinquethiophene 7.** 5’-iodo-[2,2’]-bithiophene (4.178 g, 14.30 mmol), Pd\(_2\)(dba)\(_3\) (269 mg, 0.260 mmol), Ph\(_3\)P (262 mg, 1.04 mmol) and 3-diethoxyphosphoryl-2,5-bis(tributylstannyl)thiophene 6 (5.189 g, 6.500 mmol) are dissolved in toluene (100 mL). CuCl (116 mg, 1.170 mmol) was added at room temperature and the mixture was refluxed for 2 h. After cooling to room temperature, 2 M aqueous KF-solution (50 mL) was added and the mixture was allowed to stir at this temperature for 1h. The reaction mixture was filtrated over Celite and diluted with AcOEt (100 mL). The organic phase is dried with MgSO\(_4\). After removal of the solvents under reduced pressure the residue obtained was subjected to column chromatography (AcOEt : \(\text{CH}_2\text{Cl}_2 = 7 : 3\)) to give 0.85 g (24%) of 7 as an orange solid.\(^1\)H NMR (300 MHz, CD\(_2\)Cl\(_2\)), \[ \delta[\text{ppm}] = 1.20 (m, 6H), 4.03 (m, 4H), 6.93 (m, 2H), 7.00 (m, 2H), 7.06 (m, 1H), 7.09 (m, 1H), 7.15 (m, 3H), 7.37 (m, 1H), 7.42 (m, 1H). \] HRMS (ESI+): Calc. for [C\(_{24}\)H\(_{22}\)O\(_3\)PS\(_5\)\(^+\)]: 548.9910; Found 548.9956.

**4”-Phosphono-[2,2’;5’,2″;5″;2‴;5‴;2‴′];-quinquethiophene T5-iP.** In 8 mL of acetonitrile, phosphonate 7 (150 mg, 0.273 mmol) was dissolved, to which iodonitrilesilane (0.111 mL, 0.819 mmol) was added at ambient temperature and the mixture was stirred at this temperature overnight. The solvent was removed under reduced pressure, followed by addition of MeOH (10 mL) and stirring for further 12 h. A saturated Na\(_2\)S\(_2\)O\(_3\)-solution (10 mL) was added, followed by stirring, filtration of the precipitated crystals, washing with distilled water, MeOH, CHCl\(_3\), and diethyl ether to obtain 134 mg (100%) of T5-iP as an orange powder.
$^1$H NMR (300 MHz, CD$_2$Cl$_2$), $\delta$[ppm] = 7.03 (m, 2H), 7.11 (m, 2H), 7.16 (m, 1H), 7.22 (m, 2H), 7.33 (m, 2H), 7.53 (m, 1H), 7.81 (m, 1H).

HRMS (ESI -): Calc. for [C$_{20}$H$_{12}$O$_3$PS$_5$]$: 490.9128$; found 490.9128.

2. Binding of PAs to ultraflat TCOs

The molecules’ binding to the ITO/ZnO metal oxide surfaces was evaluated by O 1s core level fitting analysis (Figure S1). The fitting was carried out with energetic positions corresponding to two binding modes (stable configurations) of the PA’s oxygen to the substrate, namely bidentate and tridentate binding.

**Figure S1.** O 1s core level spectra (background subtracted) of the unmodified, T5-tP-modified, and T5-iP-modified ITO (left panel) and ZnO (right panel) surface as indicated in the figure.
3. **Optical absorption (UV/Vis) spectroscopy**

Optical absorption (UV/Vis) spectroscopy (*Perkin-Elmer Lambda 900* spectrometer) was performed to estimate the surface coverage N/A (i.e., molecules/nm²) of oligothiophene-based PA monolayers on transparent conductive oxides (TCOs). For this purpose, the newly synthesized quinquethiophene (T5) with the PA group in internal position (T5-iP) fulfills the requirements to be a suitable reference molecule: i) the T5 moiety absorbs in the UV/Vis region (see Figure S2a); ii) the main transition dipole moment $\mu_T$ of T5 is polarized parallel to its long axis,[1] thus, after forming a monolayer of T5-iP on TCOs, $\mu_T$ lies approximately parallel to the substrate surface, rendering it suitable for quantitative measurements via UV/Vis spectroscopy.

3.1 **UV/Vis in solution**

In order to check for any influence of the PA group on the optical properties, T5 and T5-iP molecules were dissolved in THF, and UV/Vis absorption spectra were measured with different concentrations (Figure S2a and b). By comparison of the free T5 with the T5-iP absorption spectrum, a similar line shape with a slight blue shift of the main maximum and several side maxima in the UV region can be observed. These findings verify that the PA group does not remarkably influence the spectroscopic properties of the T5 moiety.
Figure S2. UV/Vis absorption (extinction) spectra of (a) T5, (b) T5-iP in solution (THF); (c) extinction coefficient $\varepsilon$ (linear interpolation $A = \varepsilon \cdot c \cdot d$) of T5-iP at 409 nm; (d) UV/Vis absorption spectra of T5-tP/iP in solution (THF); the onsets in (d) correspond to the optical gaps of the molecules.

Assuming a linear relationship between absorbance and molar concentration $c$ of the absorbing molecules ($c < 10^{-3}$ mol/l), the Beer-Lambert law\cite{2} for the absorbance $A$ (= absorption, neglecting any contribution of reflection and scattering) can be written as:

$$A = -\log(T) = \varepsilon \cdot c \cdot d,$$

where $\varepsilon$ is the extinction coefficient (molar absorptivity), and $d$ is the optical path length (= thickness of quartz glass cuvette, $d = 10$ mm). In turn, $\sigma = c \cdot d$ corresponds to the molecular
coverage of a thin film, giving an estimation of the surface coverage of T5-iP-modified (transparent) surfaces via UV/Vis spectroscopy.

In Figure S2c, the absorbance (extinction) at the peak maximum (409 nm) was plotted vs. the concentration \( c \) of the T5-iP molecules in solution. The linear fit gives an extinction coefficient of \( \varepsilon_{\text{sol}} = (3.3 \pm 0.3) \times 10^3 \text{ m}^2/\text{mol} \) for T5-iP, whereas for T5 it amounts to \( \varepsilon_{\text{sol}} = (4.3 \pm 0.9) \times 10^3 \text{ m}^2/\text{mol} \) (linear fit not shown here). The obtained values for the extinction coefficients coincide within their measurement uncertainties. It can be concluded, that the PA group has only small influence on the absorption of the T5-iP molecule and therefore the assumption can be made, that the influence of the PA group binding to the ITO surface can be neglected.

### 3.2 UV/Vis of T5-iP multilayers

In a second step, T5-iP multilayers were evaporated in UHV onto ITO substrates (Thin Film Devices Inc., California, USA) with different thicknesses. The evaporation rate was monitored with a quartz crystal microbalance and set to ca. 1 Å film mass-thickness per minute, using a density of 1.384 g cm\(^{-3}\) and assuming the same sticking coefficient on the Au-coated quartz and the ITO surfaces. The thicknesses were then calibrated via AFM height images on a multilayer (scratched away via a scalpel blade) with a nominal thickness of \( d_{\text{nom}} = 32 \text{ nm} \).

UV/Vis absorption spectra of each ITO were collected before and after multilayer deposition, and the spectra of the bare ITO were subtracted from those of the corresponding T5-iP multilayers on ITO. It is noteworthy that the obtained differential spectra show negative absorbance in the wavelength regions around the molecule’s main absorption (i.e., between \( \lambda = 300 – 370 \text{ nm} \) and \( \lambda > 550 \text{ nm} \)). This is mainly due to the fact that the UV/Vis experimental setup used in the present study only allows for the detection of transmitted light.
and, therefore, any changes of light reflection and scattering are neglected. We assume that the reflectivity at the T5-iP/ITO interface with respect to the bare ITO (i.e., T5-iP layers instead of ambient air) is constantly decreased for each sample.

**Figure S3.** (a) Differential UV/Vis absorption (extinction) spectra of T5-iP multilayers on ITO (evaporated in UHV) with defined thicknesses d; (b) extinction coefficient $\varepsilon^*$ (linear interpolation $A = \varepsilon c d = \varepsilon^* d$) of T5-iP bulk material at the corresponding wavelength $\lambda$ of the absorption maximum.

As it is obvious from Figure S2b, the T5-iP molecule in solution does not absorb in the wavelength region around $\lambda = 600$ nm. Therefore, a constant shift along the y axis was applied for each differential spectrum to bring the observed minimum at around $\lambda = 600$ nm (e.g., see black curve in Figure S3a) to zero absorption. The as-processed differential UV/Vis absorption spectra of the T5-iP multilayers are reported in Figure S3a. The additional negative absorption in the UV region of the thickest T5-iP multilayer ($d = 25.5$ nm) cannot be unambiguously accounted for, since there occurs an overlap with the absorption tail of the molecule (see Figure S2b). However, it was neglected at this stage, because this region does not contribute to the maximum absorbance (which is the determined value needed for further calculations).
It can be seen that the absorbance maximum of the thinnest layer \((d = 1.6 \text{ nm})\) lies at 409 nm, which corresponds to the value found for the molecules in solution (see Figure S2b). This finding indicates that at this layer thickness there is no significant molecule-molecule interaction that could influence the absorption behavior of the molecules. With increasing thickness the maximum of the absorbance exhibits a red shift due to increasing molecular interaction. In Figure S3b, the maximum absorbance is plotted against the film thickness. The linear fit proves the linear behavior also for the solid T5-iP multilayers. The obtained extinction coefficient \(\varepsilon^* = 2.16 \times 10^{-3} \text{ nm}^{-1}\) can be further used to determine the thickness of T5-iP monolayers on TCOs (see below).

### 3.3 Estimation of surface coverage of T5-iP-modified ITO

The linear behavior between absorbance and layer thickness in the case of T5-iP multilayers supports the previous assumption that the PA group does not have a strong influence on the absorption behavior, even after PA binding to the metal oxide surface, and that the extinction coefficient in solution \(\varepsilon_{\text{sol}}\) can be used to determine the molecular coverage \(\sigma\) of the T5-iP monolayers on TCOs.

At this point, it has to be considered, that the molecules also bind to the backside of the sample, i.e. the glass substrate, during the wet-chemical monolayer preparation (see experimental section for preparation details). Therefore, our first assumption to roughly estimate the surface coverage of T5-iP-modified ITO is that the absorbance of the molecules on the backside of the glass substrate \((\tilde{A}_{\text{glass}})\) contributes equally to the overall absorbance \((\tilde{A}_{\text{tot}})\):

\[
\tilde{A}_{\text{tot}} = \tilde{A}_{\text{SAM}} + \tilde{A}_{\text{glass}}
\]

\[
\tilde{A}_{\text{SAM}} = \frac{1}{2} \tilde{A}_{\text{tot}}
\]  

(2)
This assumption is based on our preliminary work with other phosphonic acid derivatives, where we found that the maximum surface coverage is very similar on most oxide surfaces (ZnO, ITO, SiO2, glass, etc.)[3].

A second assumption accounts for the difference between the extinction coefficient of the molecules in a bound monolayer (\(\varepsilon_{SAM}\)) and of those in solution (\(\varepsilon_{sol}\)). In a monolayer, the transition dipole moment \(\mu_T\) of T5-iP lies approximately parallel to the surface of the substrate (as it is a requirement for the reference molecule), whereas in solution the transition dipole moments are homogenously distributed. With simple geometrical considerations, one can determine this difference to be:

\[
\varepsilon_{SAM} = \frac{3}{2} \varepsilon_{sol}
\]

In the present study, we obtained for the T5-iP-modified ITO a maximum absorbance of \(\tilde{A}_{SAM} = 4.3 \times 10^{-3}\). Thus, with eq. (1) the molecular coverage \(\sigma\) of the T5-iP-modified ITO can the estimated to be:

\[
\sigma_{T5-iP} = c \cdot d = \frac{\tilde{A}_{SAM}}{\varepsilon_{SAM}} = \frac{2}{3} \frac{\tilde{A}_{SAM}}{\varepsilon_{sol}} = 5.2 \times 10^{13} \text{ molecules/cm}^2
\]

\[
= 0.5 \text{ molecules/nm}^2
\]

Considering ITO surface unit-cell dimensions of 24.79 Å \(\times\) 14.32 Å,[4] this corresponds to 1.9 molecules/unit-cell, which is in good agreement with the assumption that ITO can theoretically bind up to 2.0 molecules/unit-cell (based on the most densely packed geometry in agreement with steric hindrance of the T5-iP molecules).

The estimation of the surface coverage via UV-Vis absorbance was cross-checked via the XPS signal of the In 3d core level before and after surface modification (see Figure S4).
case of T5-ip on ITO, the In 3d signal was attenuated by about 22 % after surface modification. This attenuation roughly corresponds to a molecular coverage of \( \sim 2 \) molecules/unit-cell, which is in good agreement with the value obtained by UV-Vis absorbance.

![Figure S4. XPS In 3d core level of unmodified and T5-iP-modified ITO.](image)

Using the extinction coefficient \( \varepsilon^* \) obtained from the T5-iP multilayers (see section 3.2), the layer thickness \( d \) of the T5-iP monolayer on ITO can be estimated to be:

\[
d_{T5-iP} = \frac{2 \delta_{SAM}}{3 \varepsilon^*} = 1.3 \text{ nm}
\]

(5)

The estimated thickness of 1.3 nm for a T5-iP monolayer is in agreement with the theoretically expected value of the free-molecule T5-iP equilibrium geometry (i.e., in our calculations the perpendicular distance from the lowest oxygen to the highest hydrogen in the T5-iP molecule amounts to about \( \sim 1 \) nm). The small discrepancy might be due to the fact that the phosphonate bonds for the T5-iP monolayer are forced to be highly strained as the T5 moiety has to tilt on the ITO surface (see discussion in the main text). Thus one can reasonably assume that the overall monolayer thickness is larger than the size of the molecule.
4. **Transition dipole moment and XAS data of T5-iP-modified ITO/ZnO**

![Diagram of T5-tP/iP molecules orientation](image1)

**Figure S5.** (a) Orientation of the transition dipole moment of the T5-tP/iP molecules; (b,c) experimental C K-edge XAS spectra of the T5-iP-modified (a) ITO and (b) ZnO surface, showing no preferential orientation of the molecule.

5. **References for Supporting Information**

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