

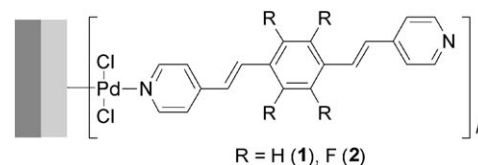
Designing Surface-Confined Coordination Oligomers

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Oligomers with a high degree of delocalization, such as oligo(phenylene ethylenes) (OPEs) and oligo(phenylene vinylenes) (OPVs), are important materials for device fabrication.^[1] As such, the charge-transport properties of these and related materials have been examined both experimentally and theoretically.^[2] Their electronic properties can be systematically controlled by the addition of electron-donating or -withdrawing functional groups (e.g., NO₂, NH₂, CN, SH, and halogens).^[3] Fluorine substitution is especially attractive because of its strong electronegativity and compact size. For example, Gierschner and co-workers showed the versatility of fluorination to control the electronic structure of a number of π -conjugated molecules, including oligoacenes and distyryl benzenes.^[3b,f] Moreover, fluorine substitution of oligothiophenes can change the charge transport between p- and n-type oligothiophenes.^[1a,3d,h] The electronic properties of monolayers and vapor deposition films of fluorinated OPEs and terphenyls have also been studied.^[3c,e,i] In all these cases, relatively short oligomers were considered, apparently because of solubility restrictions that limit the synthesis of longer chains or the assembly of organized films. In some instances, these limitations may be overcome by functionalizing the monomer with side chains.^[3g] However, the additional substitutions ultimately influence the conduction.^[3e,4] Another approach described by Grill and co-

workers involved covalently polymerized long molecular chains on metal surfaces.^[5] Electronic properties of conjugated polymers can be enhanced by linking them into 2D networks.^[6]

Herein we demonstrate the assembly of fluorinated surface-bound coordination-based oligomers. The oligomers (>10 nm long) form high-quality films with optical and structural characteristics distinctly attributable to the fluorinated central ring of the chromophore. DFT calculations demonstrate the feasibility of ligand substitution for controlling the electronic properties of these systems. These oligomers were assembled by using our iterative deposition strategy that involves coordinating PdCl₂ and either the bis(pyridylethenyl)benzene (**1**) or bis(pyridylethenyl)tetrafluorobenzene (**2**) chromophore to a siloxane-based template layer (Scheme 1 and Scheme S1 in the Supporting Informa-



Scheme 1. Coordination-based oligomers ($n=2-6$) demonstrated in this study bound to a silicon-based substrate (dark gray) through a pyridyl-terminated template layer (light gray; Scheme S1 in the Supporting Information).^[7,10]

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tion).^[7,8] The resulting films were characterized by UV/Vis spectroscopy, spectroscopic ellipsometry, semicontact atomic force microscopy (AFM), and synchrotron X-ray reflectivity (XRR). The assemblies were found to be low refractive index materials. Calculations predicted that the energy gap is lower for the fluorinated oligomers and comparable to common heterogeneous semiconductors.^[9]

The growth of the oligomers is linear with each deposition step (i.e., either **2** or PdCl₂). This is evident from both the UV/Vis spectra or by spectroscopic ellipsometry (see Figure 1 and Figure S1 in the Supporting Information). The

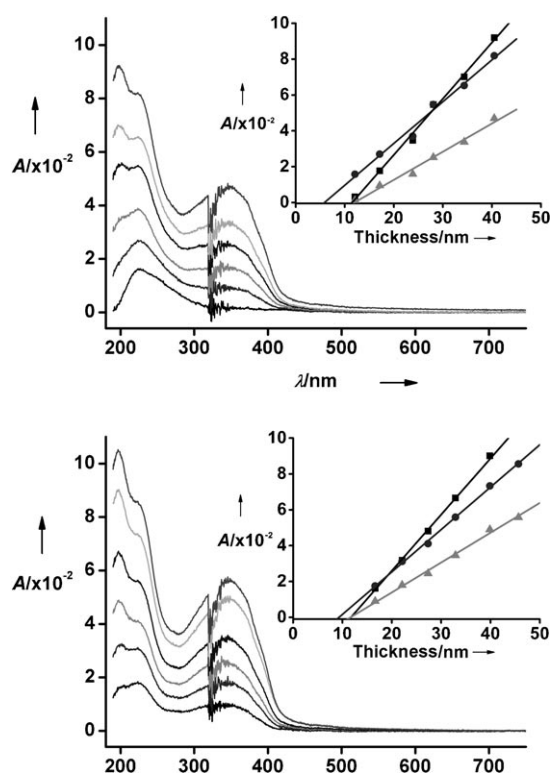


Figure 1. UV/Vis spectra of (top) palladium- and (bottom) chromophore-terminated assemblies. Insets: UV/Vis absorbance intensity versus ellipsometrically determined thickness for palladium- and chromophore-terminated layers, respectively (\blacksquare , $\lambda=197$ nm; \bullet , $\lambda=224$ nm; \blacktriangle , $\lambda=350$ nm; $R^2 > 0.99$). The absorption of the template layer has been subtracted (Scheme S1 in the Supporting Information).^[7,10]

absorption bands at 197 and 350 nm increase with each additional organic unit, whereas the intensity of the peak at 224 nm increases with the addition of the metal moiety (Figure S1 in the Supporting Information). Significantly, there is no shift in the position of any of the band peaks as the oligomers grow. Furthermore, there is no change in the intensity of the chromophore bands by the addition of metal fragments or vice versa. This implies that although chromophore **2** is conjugated, the coordination of an additional **2**-PdCl₂ unit does not lead to a change in the overall electron distribution along the oligomers. Likewise, the assembly packing is not affected. This is in contrast with our observations with the analogous oligomers incorporating the non-fluorinated chromophore **1**, in which there is a 23 nm red shift in the maximum of the main chromophore band as the oligomers length is increased from one to six units.^[7] Furthermore, the intensities and positions of all the bands in the spectra are affected during the growth process.

Figure 2 shows representative 500 × 500 nm and 3 × 3 μm semicontact AFM scans of a **2**-PdCl₂ assembly. The image reveals a smooth surface composed of large grains (>100 nm); grains of the **1**-PdCl₂ assemblies were more than an order of magnitude smaller.^[7] It is possible that this morphological difference can be explained by a difference in packing arrangements. Gierschner et al. found that distyryl-

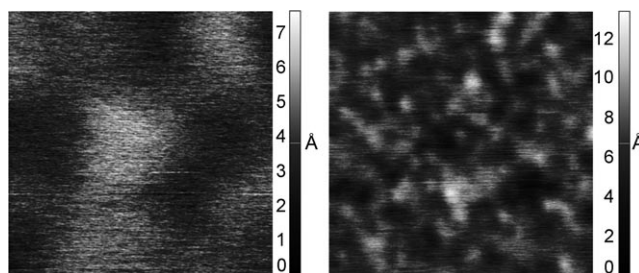


Figure 2. Semicontact AFM images of a 500 × 500 nm (left) and a 3 × 3 μm (right) scan area on silicon-based substrate of a 4.5 nm thick assembly ($R_{\text{rms}}=0.09$ nm; peak-to-peak: 0.76 nm and $R_{\text{rms}}=0.15$ nm; peak-to-peak: 1.4 nm, respectively).

benzene organizes in a face-to-edge herringbone manner whereas the fluorinated analogue aligns in a face-to-face manner.^[3] That said, the UV/Vis spectra of **2**-PdCl₂ assemblies do not indicate one way or another the presence of π - π bonding or other weak interactions between the individual oligomers.^[11]

The root-mean-square roughness (R_{rms}) of the assemblies is less than 0.1 nm, which is about the same as the roughness of the bare silicon substrates used or almost two orders of magnitude less than the assembly thickness. The deposition strategy used had previously resulted in assemblies with roughness values in the range of 0.3–2 nm, with **1**-PdCl₂ assemblies being the least rough.^[7,8,12,13]

The thickness determined from fitting the XRR data is 4.5 nm (Figure 3). Based on the thicknesses of the assembly and template layers (Figure 2) and the length of the oligo-

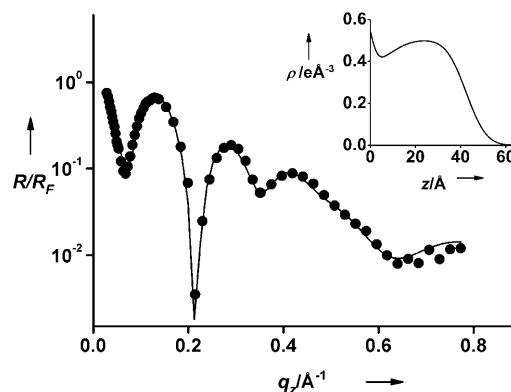


Figure 3. Specular XRR spectra for a six-deposition cycle **2**-PdCl₂ assembly on a functionalized silicon-based substrate. The line is a fit based on a previously described model.^[17] Inset: Electron density profile obtained from the XRR data.

mers (from DFT calculations, see below), the tilt angle can be approximated as about 20°. This tilt results from both the well-defined coordination chemistry around palladium and from the inherent structure of the template layer.^[7] Dipole-dipole interactions in this system are expected to be minor. The Kiessig fringes imply a smooth surface that is in line with the AFM data; no Kiessig fringes were evident for the

structurally similar **1**-based oligomers.^[7] The XRR-derived roughness for a spot of 20 mm² is approximately 0.55 nm. This is of the same order of magnitude as the roughness of bare Si, but is higher than the nominal AFM roughness value of 0.1 nm (see above).^[14] The electron density profile, with values in the range 0.4–0.5 eÅ⁻³ is similar to that reported for the **1**-PdCl₂ assembly.^[7] By using the XRR-obtained thickness, it is possible to estimate from the ellipsometry spectroscopic data that the index of refraction (*n*) of the **2**-PdCl₂ assembly is 1.45. This is significantly lower than for other coordination-based oligomers, such as the **1**-PdCl₂ oligomers (*n* in the range of 1.8–2.0).^[7,8] Fluorinated polyynes and fluorinated monolayers are known to be low-*n* materials.^[15] Materials with *n* values of approximately 1.45 are potentially useful because of their match to SiO₂-based optical components,^[16] which are suitable supports for our assemblies.

A series of model oligomers of **1** and **2** with two to five chromophore units was studied by DFT at the M06/SDB-*pc1*//M06-L/SDD(d)/DFBS level of theory (see the Supporting Information for full computational details).^[18] Representative results are illustrated in Figure 4 showing the HOMO and LUMO for the four-chromophore long oligomers, which are approximately 7.7 nm in length; the other oligomers are depicted in the Supporting Information. This analysis (Figure 4 and Figure S3 in the Supporting Information) reveals that the electrons in the frontier molecular orbitals of the **1**-PdCl₂-based oligomers tend to be delocalized over the entire chain. The length of the chains seems to have relatively little effect on the conjugation. This observation is consistent with the evidence of hybridization between d-

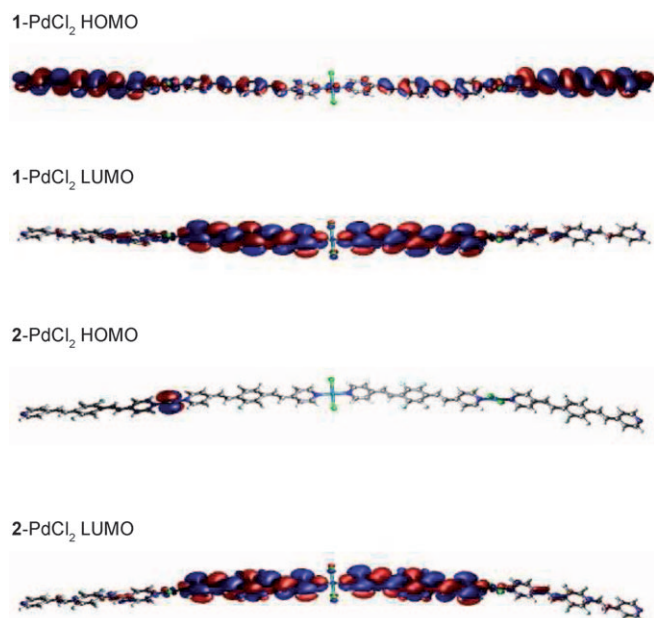


Figure 4. Calculated HOMO and LUMO of **1**-PdCl₂ (top) and **2**-PdCl₂ (bottom) with four chromophore and three PdCl₂ units (≈ 7.7 nm long). Atomic color scheme: F=light blue, Cl=green, Pd=teal, C=gray, H=white, N=dark blue. In contrast to the surface-bound oligomers, the calculated model structures do not have a terminal pyridinium salt.

and π -orbitals in metal-containing polyynes.^[19] For the fluorinated system the picture is more complex: the LUMO tends to show a significant degree of delocalization whereas the electrons in the HOMO are centered on the metal (see the Supporting Information). These results might indicate that the electron-transport properties of these oligomers will be distinctly different because conductivity is essentially achieved in the unoccupied orbitals. The energy levels of the frontier orbitals of these oligomers are compared in Figure 5. Several significant observations can be made. The

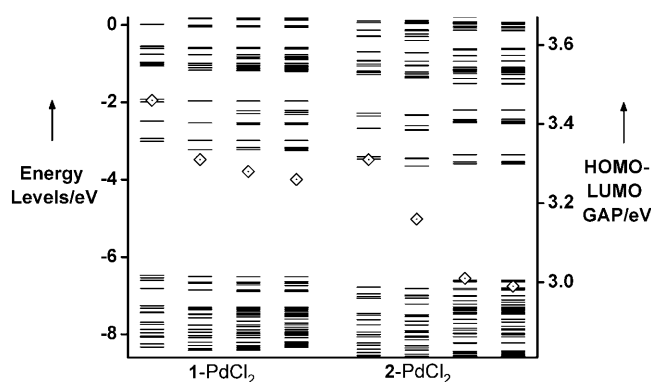


Figure 5. DFT-derived energy levels (—, left axis) and nominal energy gaps (\diamond , right axis) for **1**-PdCl₂ and **2**-PdCl₂ oligomers that are 2–5 units long (from left to right). A plot of the HOMO–LUMO gap versus the number of chromophore units is presented in Figure S2 in the Supporting Information.

HOMO–LUMO gap is slightly narrower in the **2**-based oligomers. In both cases, the gaps continue to shrink with increasing length (Figure 5, \diamond), and level off around five units in length. This nonlinearity in the band gap with extension of the conjugation length for relatively long oligomers is consistent with the Kuhn equation and has been observed by others.^[20] Although the energy levels of the unoccupied orbitals remain almost constant, for the fluorinated **2**-PdCl₂ oligomers the HOMO and LUMO occur at lower energy levels. Subtle changes in electronic structure of conjugated oligomers have been previously predicted by DFT calculations.^[3b,d,21,22]

In conclusion, we have demonstrated the ability to tune the band gaps of relatively long (> 10 nm), surface-bound metal–organic oligomers,^[7,8,12,23] while preserving the adopted structure and chemical framework. HOMO–LUMO engineering to generate small band-gap materials is an important challenge in building up materials with potential electronic functionality.^[20a] In addition, the index of refraction of the fluorinated system matches well with SiO₂-based materials allowing integration into various electrooptical devices.^[16] The current study demonstrates a viable systematic strategy to improve and control electrical properties of organic materials to this important end.

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Keywords: coordination polymers • density functional calculations • HOMO–LUMO engineering • oligomers • solid-state structures

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