Mixed Self-Assembled Multilayer of 4,4′-Dimercaptobiphenyl and 1,8-Octanedithiol

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Mixed multilayers from aromatic (biphenyl) and aliphatic (octane) dithiols, using Cu(II) ions, have been prepared and characterized by ellipsometry, FTIR, and XPS. The data support the formation of multilayers in which interlayer disulfide linkages connect the 4,4′-dimercaptobiphenyl layers and intralayer disulfide bonds connect 1,8-octanedithiol molecules. Cu(I) ions connect the aromatic and aliphatic layers.

Molecular self-assembly is a simple method of preparing organic films with molecular level controlled structure, thickness, and surface behavior.[1] Control on this scale is necessary to efforts being put forth for the development of molecular scale electronic devices. Such devices are generally made from molecules that systematically incorporate aromatic moieties along with a variety of functional groups to give a specific electronic behavior such as a transistor, switch, and diode. These molecules usually include three to four aromatic rings; they may have aliphatic side chains to increase solubility and may variously include donor acceptor atoms and or transition metals. Synthetic approaches have made complex molecules increasingly accessible, but controlling molecular assembly motifs on larger scales and in two or three dimensions is still one of the most challenging problems. Multilayers of molecules for electronic devices made by self-assembly may be one solution. Due to synthetic and purification difficulties, trichlorosilane-based multilayers have been limited to aliphatic molecules[2] or molecules containing one phenyl ring.[3] Metal−bisphosphonate multilayers have been prepared using aromatic systems containing more than one phenyl ring.[4] Recently, other organometallic systems have been used in multilayer formation.[5] A while back, we reported the formation of organometallic multilayers of ω-mercaptoalkanoic acids [HS(CH$_2$)$_n$COOH], based on the interaction of Cu(II) ions with carboxylic acids and thiols.[6] Later it was confirmed that the Cu(II) ions were reduced to Cu(I).[7] Bard and co-workers reported the self-assembly of multilayers on gold using ω-mercaptoalkanethiols [HS(CH$_2$)$_n$SH] and Cu-(II) ions. XPS data confirmed a Cu(I) oxidation state and the formation of a multilayer with intralayer disulfide bonds.[8] Multilayers of α,ω-dithiols are of special interest, since the connection of two sulfur atoms through a transition metal ion and the effective interactions of their d-orbitals may allow for the design of simple long molecular conductors. This, however, requires the use of aromatic dithiols.[9]

SAMs of rigid 4-mercaptobiphenyls on gold and silver surfaces[10] attracted attention because of their ability to form stable model surfaces[11] and their potential as electron beam resists.[12] Recently, we reported the formation of multilayers using 1,4-dimercaptobiphenyl (DMBP) and Cu(II) ions.[13] There, we observed only Cu(I) in the multilayer films and suggested a possible formation of interlayer disulfide linkages. Here we report the formation of mixed multilayers from DMBP and 1,8-octanedithiol (ODT). Our aim is to investigate the introduction of an insulating linkage in a potential molecular conductor. This might make possible the design of systems with molecular control of conducting segment length and the position and length of insulating units.

The preparation of DMBP is described elsewhere. Copper-(II) perchlorate hexahydrate (Cu(ClO$_4$)$_2$·6(H$_2$O), 98%) was obtained from Aldrich and used as received. 1,8-Octanedithiol was obtained from Aldrich and used as received.

Details of the thermal evaporation of gold on glass have been published elsewhere.[14] *It is important to note that the quality of the SAMs depends strongly on the quality of the gold substrates. Good SAMs could be prepared only when annealed gold substrates were used.* The reproducible optical constants for the gold substrates prepared according to this procedure are $N_s = 0.186 \pm 0.01$ and $K_s = 3.40 \pm 0.05$. These substrates were used for ellipsometry and Fourier transform infrared (FTIR) spectroscopic measurements. Substrates used for XPS measurements were prepared according to a procedure by Bard and co-workers.[15]

Multilayer films were constructed by first immersing a freshly prepared gold substrate into a 1 μM solution of DMBP in ethanol for approximately 3 h, under nitrogen. After confirmation of monolayer formation by ellipsometry, the substrates were thoroughly rinsed with fresh ethanol and immediately exposed to a 50 mM Cu(ClO$_4$)$_2$·6H$_2$O solution in ethanol for 3 h. After a thorough rinsing with water and ethanol and drying with a jet of nitrogen, the film was exposed to an ethanol solution of DMBP or ODT, according to Figure 1. The film was left overnight for ODT adsorption.

Layer thickness was estimated by ellipsometry using a Rudolph Research AutoEL ellipsometer (He−Ne laser, angle of incidence 70°). Measurements of three separate points were carried out on each sample, using an assumed refracted index of 1.462. The FTIR spectra were obtained using a Nicolet MAGNA-IR 760 spectrometer equipped with a nitrogen-cooled MCT-A detector. For each sample, 2500 scans were collected, with a resolution of 1 cm^{-1}. X-ray photoelectron spectra were obtained with a Physical Electronics 5700 monochromatic XPS system. The Al anode (1486.7) was operated at 300 W with a 2 mm filament (24 mA emission) to produce a ∼1.5 to ∼0.6 mm X-ray spot at the sample. Samples were mounted with a spring clip so that the Au film supporting the SAM was at

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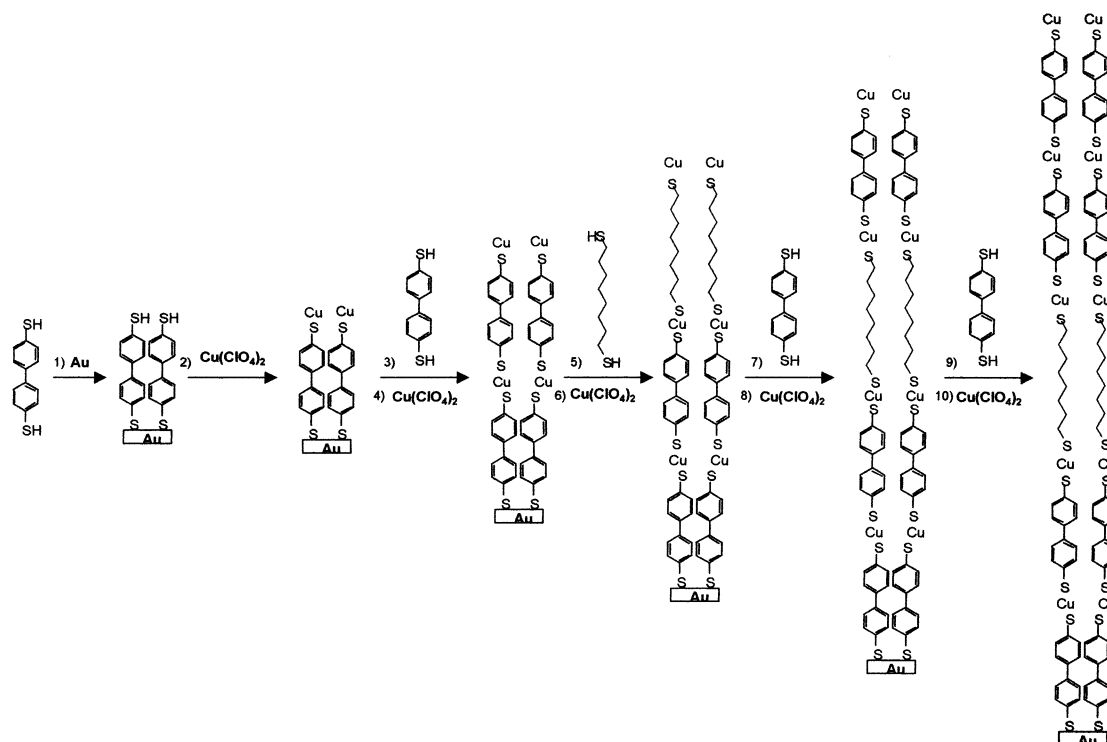
Figure 1. Adsorption scheme of mixed self-assembled multilayer of 4,4′-dimercaptobiphenyl and 1,8-octanedithiol. The odd steps represent the organic layer, and the even steps represent the Cu ions. The scheme does not represent the actual structure of the multilayers.

electrical ground. The pressure in the analysis chamber was at $\sim10^{-8}$ Torr during experiments. Spectra were monitored at an electron takeoff angle of 75°. To compensate for surface charging effects, all binding energies were referenced to the Au $4_{7/2}$ at 83.99 eV. Deconvolution of complex peaks was performed using the XI Spectral Data Processor v2.0 software with the full width at half-maximum (fwhm) of Gaussian line shape of 1−1.2 eV. Quantitative measurements were made by correction of integrated peak intensities with the Scofield correction factors. The peak area ratios for various elements were corrected by experimentally determined instrumental sensitivity factors and may be subject to a maximum error of ±20% error.

DMBP-ODT multilayers were prepared by first adsorbing a monolayer of DMBP on gold, followed by alternate exposure to Cu(II) ions and DMBP, shown as steps 1−4. Next, the film was immersed in an ethanol solution of ODT under nitrogen overnight, this is shown as step 5 in Figure 1. The subsequent steps 6−10 are the multilayer being formed by alternate exposure to Cu(II) ions and DMBP or ODT.

Figure 2 demonstrates the linear relationship between the ellipsometric thickness and the number of layers. The exact value of the real part of the multilayer refractive index is not known, and the thickness reported is based on a refractive index of 1.462 for both the aliphatic and aromatic portions of the multilayer. The slope of the line is 1.7 nm. Given the average length of DMBP is 1.2 nm and ODT is 1.0 nm, the data are in agreement with the multilayer system described in Figure 1. On average, however, a larger than expected thickness was observed for a single layer of ODT. Since it is known that the refractive indices must be different, the change in the ellipsometric parameter, Δ, a function of surface reflectivity, with respect to the experimental step in the construction of a DMBP-ODT multilayer on gold has also been plotted (Figure 3). The highly regular decrease in Δ for each experimental step indicates the formation of an ordered multilayer for the mixed system.[5b]
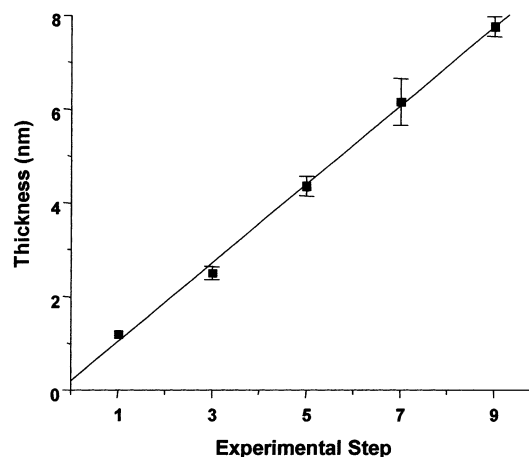

Figure 2. Ellipsometric thickness data for a mixed multiplayer film of DMBP and ODT. The measurements were taken after the addition of organic layers, steps 1, 3, 5, 7, and 9.

The aliphatic and aromatic vibrations are easily distinguished in the infrared spectrum. Figure 4 is the ER-FTIR spectrum of a sample taken after step 9. In the aliphatic CH_2 stretching region, the two expected $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ bands appear at 2926 and 2852 cm^{-1}, respectively. The positions of these bands are consistent with the liquidlike state alkyl chains in SAMs of alkanethiolates on gold when the number of carbon atoms of the alkanethiol is less than 10.[1a] The three aromatic bands were described earlier,[16] and their positions in the multilayer samples are in agreement with band maxima in SAMs of 4-mercapto-biphenyl derivatives on gold surfaces.[12,16]

The positions of the C1s emission of alkyl and aromatic moieties differ noticeably. Observing the presence and relative amounts of the C1s signal due to the two multilayer components is an essential part in determining the success of the assembly of mixed multilayer assembly. Figure 5a is the C1s region of a DMBP double layer. Peak deconvolution reveals one peak at
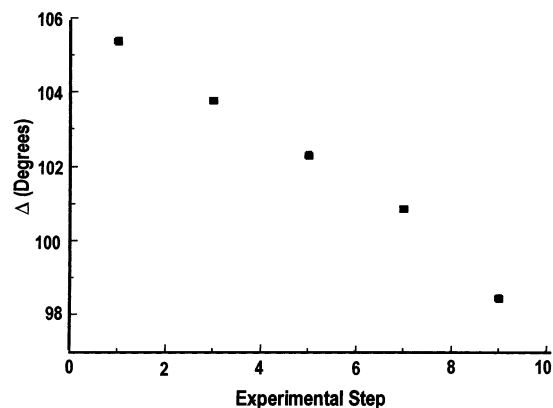
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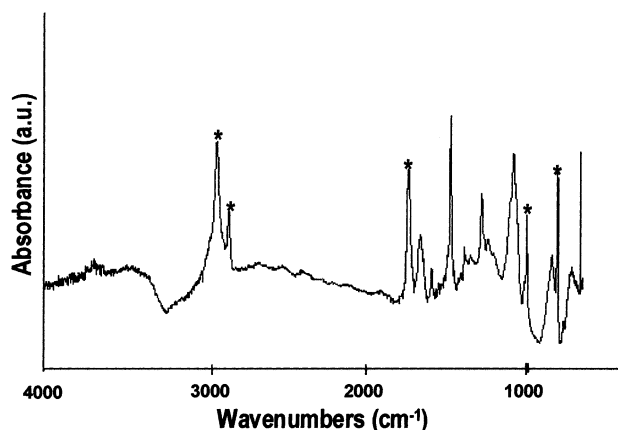**Figure 3.** Change in ellipsometric parameter, Δ, with the experimental step according to Scheme 1.

Figure 4. FTIR spectrum of a five-layer film. The relevant bands are marked. ν_{as} (CH$_2$) 2962 cm^{-1}, ν_s (CH$_2$) 2852 cm^{-1}, aromatic semicircle stretch 1475 cm^{-1}, aromatic C$-$C$-$C parallel bending 1001 cm^{-1}, aromatic CH wagging vibration 807 cm^{-1}.

284.16 eV with 85.6% of the total signal and another at 286.1 eV with 14.4% of the total signal. The former component is assigned to the aromatic carbon, while the latter is assigned to an electron-deficient carbon bonded to an electronegative sulfur.[17] Figure 5b shows the C1s region taken at step 5. Finally, Figure 5c is the C1s region taken after step 7. In both Figures 5b and 5c deconvolution of the C1s region can be fitted with two peaks. The larger peak located at 284.3$-$284.5 eV is assigned to an aromatic carbon, and the peak at 284.9$-$285.0 eV is assigned to an aliphatic carbon.[18] For the sample in Figure 4c, the aromatic carbon makes up 77.8% of the signal, while the aliphatic signal makes up 22.2%. Taking the ratio of 36 aromatic to 8 aliphatic carbons, the theoretical composition should be 81.81% aromatic and 18.19% aliphatic carbons. Clearly, the XPS data support the formation of mixed multilayers as described above. Interestingly, the data show no significant loss of the aliphatic carbon upon Cu(II) ion and DMBP deposition, suggesting that exchange of aliphatic by aromatic thiolate is insignificant.

The spectrum of the Cu region is given in Figure 6. The binding energy of Cu2p$_{3/2}$ is 932 eV, and the kinetic energy of copper Auger line Cu(L$_3$VV) is 918.1 eV, corresponding to a Cu(I) state, thus excluding the presence of Cu(II), in agreement with our observation for DMBP multilayers[13] and Bard and co-workers' report on ODT multilayers.[8] Two S2p (1/2, 3/2) doublets are visible, after peak deconvolution, in Figure 7, corresponding to two atomic species, one at a S2p$_{3/2}$ binding energy of 162.0 eV, which is assigned to thiolate species, and another, at 163.1 eV, that is assigned to neutral sulfur species
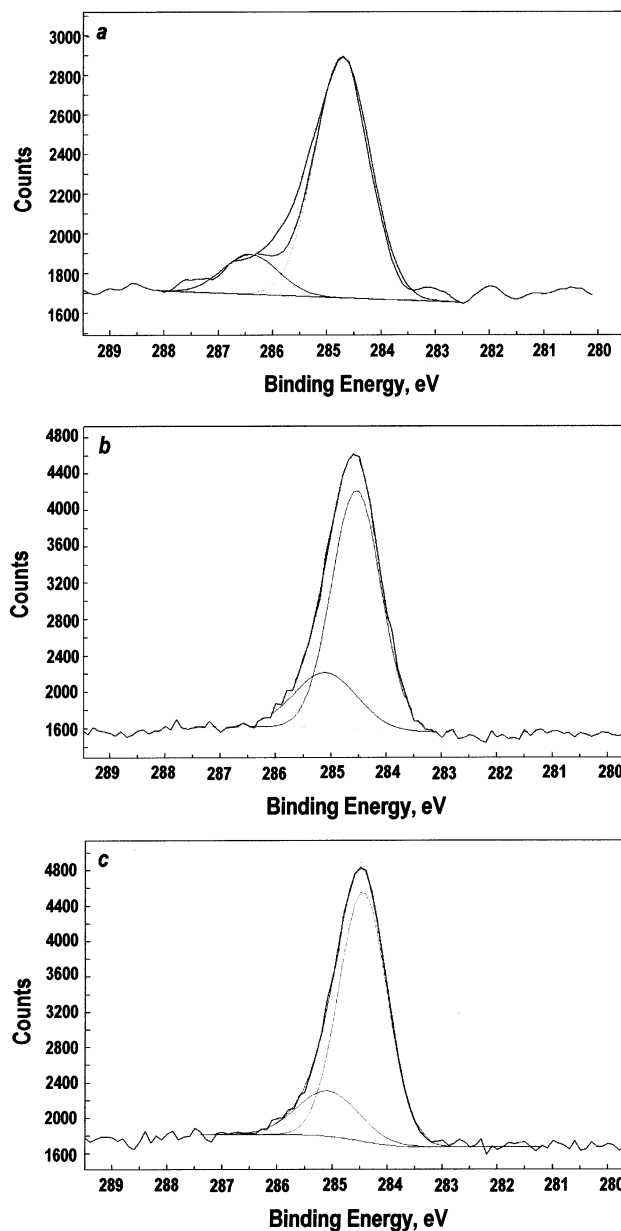

Figure 5. XPS spectra of the C1s region of (a) a film taken after step 3, (b) a film taken after step 5, and (c) a film taken after step 7.
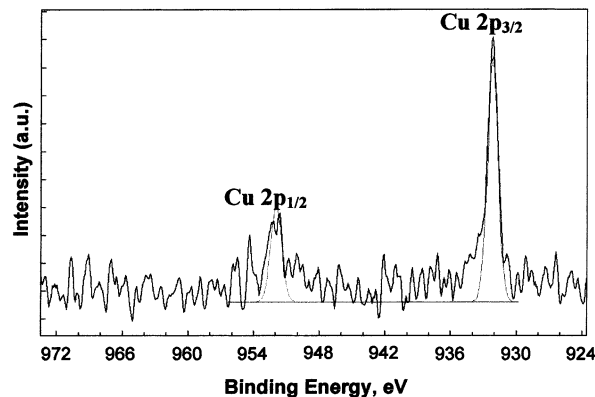

Figure 6. XPS spectrum of the Cu 2p region taken after step 9.

(e.g., disulfide). The possibility of intralayer S$-$S bonding was ruled out in the DMBP multilayer assembly,[13] because of the molecular rigidity and the imposed S$\cdots$S distance. However, interlayer S$-$S bonds are possible in the ODT layer, as was
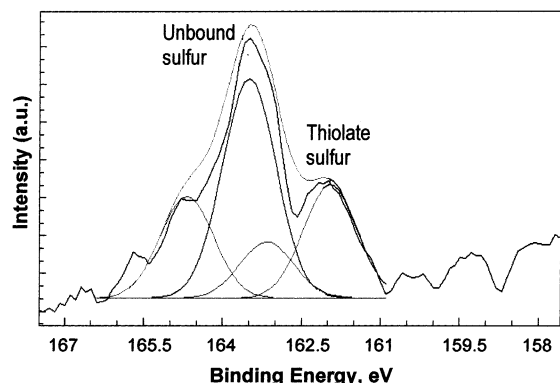
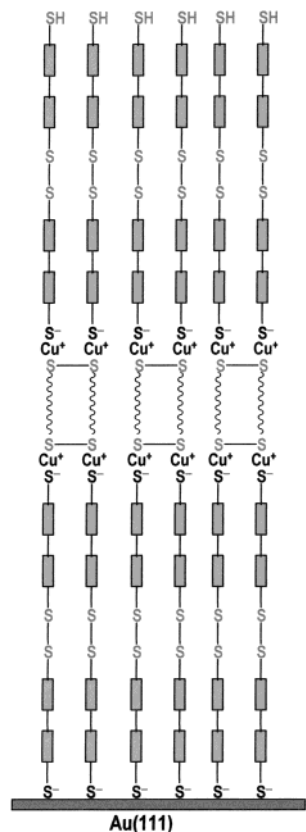**Figure 7.** XPS spectrum of the S 2p region taken after step 9.

Figure 8. Proposed structure of a five-layer sample. *Interlayer* disulfide bonds connect DMBP layers, *intralayer* disulfide bonds connect ODT, and Cu(I) ions connect the aliphatic and aromatic layers.

observed by Bard and co-workers,[8] due to their flexibility and ability to form gauche defect layers. The percentage of thiolate sulfur in the five-layer sample is ∼30% and that of unbound sulfur is ∼70%, which is in agreement with the five-layer structure proposed below (Figure 8).

Taken together, ellipsometry, FTIR, and XPS clearly support the successful buildup of mixed multilayers. Ellipsometric film thickness increases linearly with the number of layers; however, over a number of experiments the thickness at step 5 was found to be 0.45 nm higher than expected. Since the change in the ellipsometric parameter Δ decreases regularly upon addition of layers, the larger than expected final thickness is not likely due to the change in refractive index from aromatic to aliphatic species. It is possible that at times interlayer disulfide linkages allowed for the adsorption of more than one organic layer. However, since XPS data are in agreement with a mixed multilayer composed of single layers added in each step, we assume that the addition of double layers is a rare occurrence.

FTIR spectra show bands for both the DMBP and ODT and confirm that ODT and DMBP molecules are not exchanged during ODT adsorption. This is important since ODT was adsorbed at 1000× greater concentration (1 mM) than that of DMBP (1 μM) and was allowed to adsorb overnight as opposed to the 3 h adsorption time allowed for DMBP. It suggests that the strategy of mixing aliphatic segments in aromatic multilayers with the aim of controlling electrical properties is worth pursuing.

A significant conclusion from the lack of exchange is that the intermolecular disulfide model proposed for the DMBP multilayers is probably correct.[13] If these multilayers contained copper ions between the DMBP layers, not withstanding the problem of charge neutralization given that the copper is in the +1 oxidation state, one would expect that, given the high concentration of ODT, complete exchange all the way to the gold surface could have occurred. Similarly, the fact that ODT is not being replaced by DMBP, although the Cu(I) is a soft acid and alkanethiolate is a much harder base than the thiophenolate ion, provides further support to the disulfide model proposed by Bard and co-workers.[8] Hence, the mixed multilayer structure proposed here is a quite robust one.

XPS provides the most accurate quantitative analysis of this system. Three observations that are significant for proposing a multilayer structure have been made. First, the ratio of aliphatic to aromatic carbon is very close to the expected value for the multilayer system. Second, the ratio of thiolate to unbound sulfur is 3:7, which is different than the observed decrease in thiolate sulfur concentration in the DMBP multilayers to the point where it disappeared completely after five layers.[13] Third, the copper is in the +1 oxidation state. Taken together these observations suggest that the structure of the mixed multilayer is an intermediate between the structures proposed for the DMBP[13] and ODT multilayers.[8]

Figure 8 is an illustration of the proposed structure for a five-layer film. The model assumes an interlayer disulfide linkage between layers 1 and 2. After deposition of Cu(II) and of ODT, the third layer is composed of ODT disulfide dimers. Since we know that the copper on top of a DMBP layer is in the +1 oxidation state,[13] the formation of an intralayer disulfide in the ODT layer must involve oxygen. Given the amount of material on a 3−4 cm^2 substrate, there should be enough oxygen even in what is referred to as an experiment under nitrogen. The exposure of the three-layer film to Cu(II) and DMBP creates a structure similar to the first two layers, again, with intralayer disulfide bonds in the ODT and interlayer disulfide bonds between layers 4 and 5.

In conclusion, we presented ample evidence to show that mixed multilayers were prepared with aromatic (biphenyl) and aliphatic (octane) dithiols, using Cu(II) ions. The ability to deposit multilayers of desired length and to introduce insulating layers at predetermined positions allows molecular level design of organic thin film electrical properties.

References and Notes

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