

Moreover, the fragmentation of matrix-isolated molecules can be achieved by using the heavy atom effect of xenon (route A₂).

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Organic Quantum-Confined Structures through Molecular Layer Epitaxy**

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Organic multilayered structures have attracted significant attention because they are potential substitutes for regular elemental components in electronic and electrooptic devices as well as excellent objects for experimental studies of basic quantum-mechanical models and principles of solid-state physics.^[1] Novel layered structures of organic light emitting devices (OLEDs) were reported to exhibit three-color emission.^[2] The study of organic field effect transistors (OFETs) fabricated from organic conjugated heterocyclic compounds has shown that an electron mobility as high as 1.3 cm² V⁻¹ s⁻¹ is achievable in molecular electronic devices.^[3] Recently the first OLED- and OFET-integrated optoelectronic devices were reported.^[4]

Multilayered structures such as self-assembled monolayers,^[5] electrostatic polymer assemblies,^[6] and Langmuir–Blodgett films,^[7] can be obtained by solution-derived methods, whereas ultra high vacuum (UHV) deposition,^[8] organic molecular beam epitaxy (OMBE),^[9] and molecular layer deposition^[10] were used for vapor-phase assembly of organic heterostructures. However, there is as yet no straightforward vapor-phase deposition method for assembling organic superlattices that enable epitaxial growth with covalent bonding. Inorganic atomic layer epitaxy (ALE)^[11] is the main vapor-phase method that can be used to build covalently bonded epitaxial multilayers in a layer-by-layer fashion.

We developed a new method for deposition of organic multilayers, molecular layer epitaxy (MLE), which is based on four levels: deposition of a template layer, self-limiting, vapor-phase reactions, covalent (“c axis”) interlayer bonding, and π stacking in the *xy* plane. A template layer is firstly deposited on an oxide surface, such as Si/SiO₂, quartz, or glass/indium tin oxide (ITO; Figure 1 a, step 1), exposing propylamine functionalities toward the interface and in turn dictating epitaxial growth. We choose the siloxane coupling network to enhanced thermal stability. This coupling reaction on silicon’s native oxide yields an ordered monolayer. However, on rougher surfaces such as ITO this reaction flattens the surface by a less controlled condensation reaction that can result in the assembly of two to three layers. Then discrete pulses of reactants, liquids or solids that undergo self-limiting reactions, are carried to the surface by an inert carrier gas in an MLE deposition reactor

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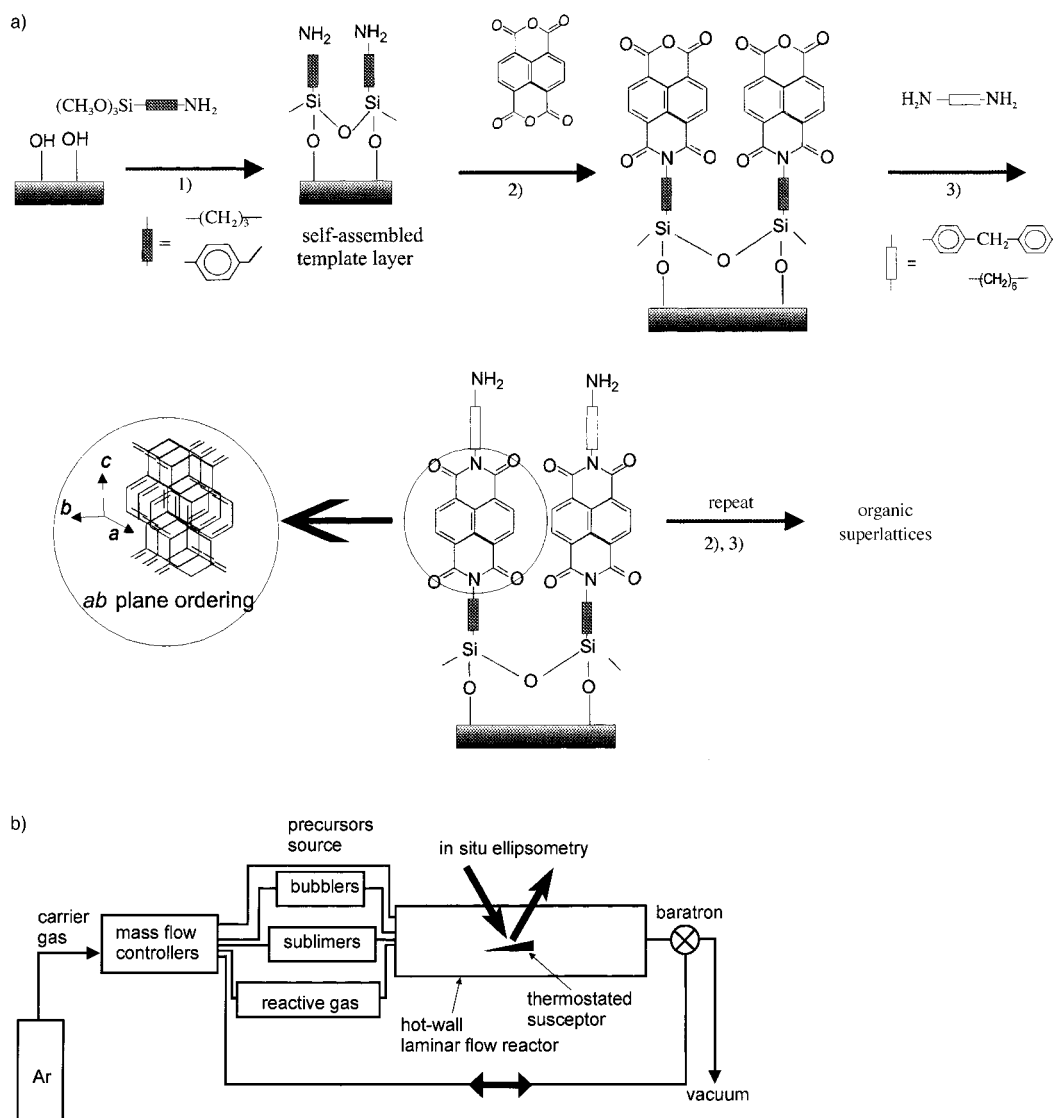


Figure 1. The molecular assembly approach and reactor for molecular layer epitaxy (MLE): a) MLE surface chemistry, b) laminar flow MLE reactor setup.

(Figure 1b). An alkylamine-containing surface is hit with a pulse of 1,8:4,5-naphthalenetetracarboxylic dianhydride (NTCDA) precursor (Figure 1a, step 2), forming imide linkages.^[12] Then a pulse of a vaporized aromatic or aliphatic diamine spacer (Figure 1a, step 3) is added to regenerate amine functionalities on the surface, which can again react with the dianhydride. Repeated cycling through these steps (Figure 1a, steps 2 and 3) leads to the formation of organic superlattices based on 1,8:4,5-naphthalenetetracarboxydiimide (NTCDI).

Those superlattices are organized by two motifs: individual structural units held together by covalent bonds perpendicular to the surface and, parallel to the surface, interplanar π stacking of aromatic groups (see the *ab* plane ordering in Figure 1a). The MLE-derived multilayers are stable with respect to heat (up to 300 °C) and most organic solvents and acids.

The structural regularity of the resulting NTCDI-based multilayers was tested by variable angle spectroscopic ellipsometry (VASE). Figure 2 shows measured and fitted ellipso-

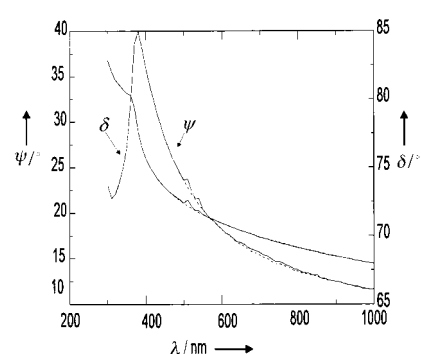


Figure 2. Variable angle spectroscopic ellipsometry (VASE) to determine the structural regularity in MLE-derived organic superlattices: generated (—) and experimental ellipsometric data (---) for nine bilayers of NTCDI-HM. Ψ = real, δ = imaginary part of the complex index of refraction.

metric data for a superlattice containing the aliphatic spacer hexamethylene (HM) with nine bilayers, (NTCDI-HM)₉. Interplanar spacing along the molecular *c* axis are 7.01 ± 0.03 Å for NTCDI and 6.90 ± 0.02 Å for the hexamethylene

spacer. The structural ordering of the system should be viewed as a two-dimensional “smectic-like” liquid crystal, with the confinement of NTCDI building blocks in a single layer without interpenetration of neighboring layers. In this plane ordering NTCDI might have a herring-bone structure,^[13] as is also suggested from the measured tilt angle of 23°. To verify the dimensional parameters of MLE-derived multilayers and the spectroscopic data, we synthesized the two low molecular weight model compounds *N,N'*-dihexyl-NTCDI (**1**) and *N,N'*-diphenyl-NTCDI (**2**).^[14] Model compounds of dialkylated NTCDI (see Experimental Section) exhibited smectic phases at elevated temperatures. Such spontaneous ordering might be induced by the MLE-derived topotactic chemistry.

Excitons play a fundamental role in the optical properties of solids, and are suggested to be responsible for finite size effects in the absorption spectra of organic multilayered structures.^[9] The size-dependent characteristics in NTCDI-based superlattices were investigated by optical absorption signature. The blue shift of the absorption peak and the increase in transition energy ΔE predicted for multilayers of decreased thickness were observed for PTCDA/NTCDA multilayers (PTCDA = 3,4,9,10-perylenetetracarboxylic dianhydride).^[15] The same trend is observed for the peak shift of the lowest energy absorption of NTCDI superlattices. An energy decrease of about 12 meV (Figure 3 a) is measured for the fewer number of layers showing a NTCDI multilayered structure with the aliphatic HM spacer. We considered the organic multiple quantum well (OMQW) energy levels to be consistent with a narrow potential well for NTCDI semiconduction placed in between very high potential barriers (aliphatic spacers). In this OMQW design both the electron and hole were approximated as being confined in the NTCDI layer. Conductivity-type anisotropy of the hole and electron in NTCDI-like molecular solids was established recently.^[16] Thus a model of a confined Wannier exciton in the quantum wells was considered by us.^[17] Minimizing of the binding exciton energy ($E_{1s} = \langle \psi | \mathcal{H} | \psi \rangle$) was applied to fit the blue-shifted absorption peak (marked in the insert of Figure 3 a).

Conjugated polymers or molecular stacks are organic semiconductors by virtue of the delocalization of electrons on the π molecular orbitals in the stacking direction. Such materials frequently exhibit electroluminescence (EL) when incorporated into a device. In an OLED device, excitation is caused by the injection of an electron into the conduction band (LUMO) and a hole into the valence band (HOMO), which recombine with emission of visible light. We fabricated MLE-derived OLEDs as devices that were as small as 4–6 nm thick.^[18] The EL spectra of OLEDs formed by assembling of two and four bilayered NTCDI structures with a diphenylmethane (DPM) spacer in the glass/ITO/OMQW/Al configuration at 8 V are shown in Figure 3b. It is clearly observed that two different centers emit under these conditions. The blue EL is attribute to radiative recombination on a single NTCDI molecule, and the red EL is assigned to radiative recombination within NTCDI molecules. The coexistence of two emitting centers within the same layer is an indication for two different excitation paths, intramolecular

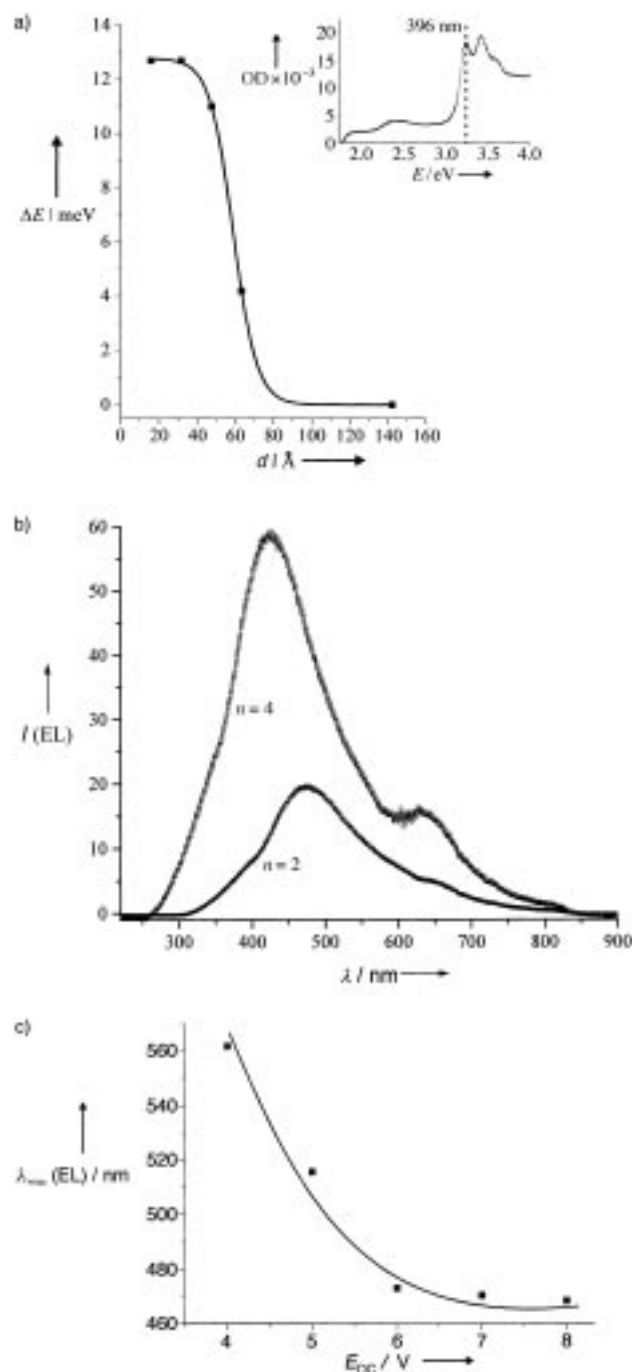


Figure 3. Dependence of effects on size in MLE-derived organic superlattices: a) Energy shift ΔE of the NTCDI-HM superlattice absorption peak (marked in the insert) as a function of thickness d . The symbols ■ correspond to experimental data, and the solid curve is the fit to the model described in the text. Insert: Absorption spectrum of a (NTCDI-HM)₂ multilayer sample; OD = optical density. b) Dependence of the EL on thickness in (NTCDI-DPM)_n for $n=2$ and 4 in MLE-based OLEDs at $E_{DC} = 8$ V. c) Dependence of the EL on the DC voltage for (NTCDI-DPM)₄-based OLEDs.

excitons and intermolecular excitons,^[19] and is a sign for homogeneous structure. The same trend for the appearance of a new EL peak due to epitaxial ordering was observed in perylene-based OLEDs^[20] and the single crystal of **1**.^[21]

Another finite size effect was observed for the EL of MLE-derived structures: the dependence of the EL of (NTCDI-

DPM)_n on thickness (Figure 3b). The EL maxima at 480 nm for (NTCDI-DPM)₂ was shifted by almost 50 nm upon doubling of the thickness. This blue-shifted EL can be explained by the electric field modulated Stark shift effect^[6] observed in inorganic^[22] and organic low-dimensional structures.^[23] The EL can be shifted to the blue by ramping the applied potential in the same (NTCDI-DPM)_n, OMQW-based devices (Figure 3c). At low voltage the red emission of the stacked NTCDI molecules (intermolecular excitons) dominate the EL spectrum, since these centers have a lower energy gap for excitation and charge recombination. Increasing the applied potential led to charge recombination at the higher energy gap (intramolecular excitons) and to blue-shifted EL. In summary, EL tunability is governed by finite size effects and the direct current (DC) field.

Figure 4a demonstrates the voltage dependence of the EL and current curves of MLE-derived OLEDs with a turn-on voltage of about 0.5 V, which is in contrast to the 5 to 10 V required to turn on most OLEDs. The current–voltage curve of an organic thin film of (NTCDI-DPM)₂ having a thickness

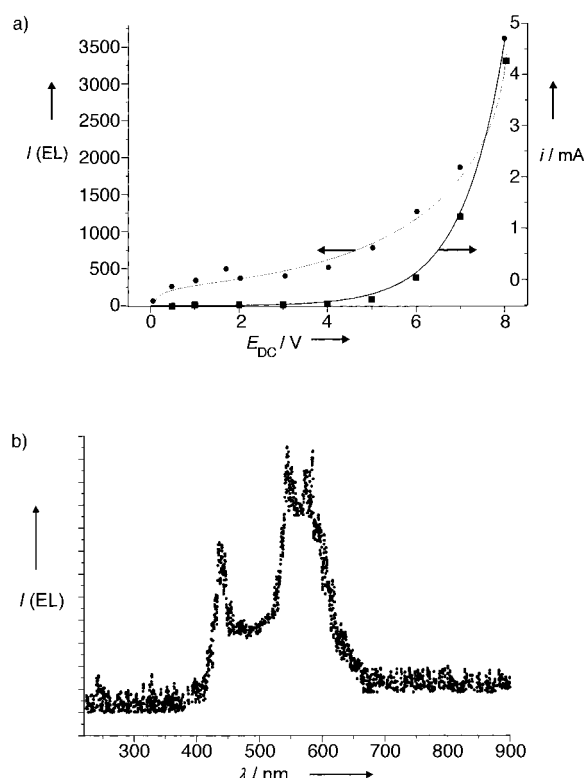


Figure 4. Electrical characteristics and capacitor effects in MLE-derived OLED's: a) Dependence of the EL intensity I (●) and the current i (■) on the voltage for (NTCDI-HM)₄. b) Anomalous emission of (NTCDI-HM)₄ at $E_{DC} = 0$ V.

of about 30 Å exhibits an archetypical semiconductor character with an EL lifetime of more than 100 hours (room temperature, ambient environment, $E_{DC} = 4$ V). Following the first cycle of EL, (NTCDI-HM)_n structures that incorporate aliphatic spacers act like tiny capacitors and emit light for a few hours after the voltage source was turned off; a spectrum is shown in Figure 4b. The EL band at 438 nm is narrower and sharper than for the DC-derived EL (FWHM = 10 nm).

We connect this unusual EL with the barrier structure of OMQW, which can trap the injected charges in the potential well structure and thus slow the radiative recombination. In terms of operation stability the MLE-derived devices are also robust in their ability to operate at a DC field of 3×10^7 V cm⁻¹, which is comparable to the operation values of amorphous silicon and positioned in the high range of dielectric breakdown in organic materials.

In summary, we have introduced a new synthetic route for the assembly of organic superlattices, the MLE approach. The combination of *c*-axis bonding and in-plane stacking led to the formation of densely packed and highly regular organic multilayers. The chemical and temporal stability of these organic structures were proved to be useful in device operation. Finite size effects have a major role in the optical properties of MLE-derived OMQWs. The aliphatic spacers produced heterostructures with capacitor-like behavior, and aromatic spacers led to the formation of highly efficient OLEDs. We expect that the molecular layer epitaxy approach will contribute to the fields of molecular optoelectronics as well as fundamental and applied sciences.

Experimental Section

Substrate cleaning: Quartz and silicon wafers were cleaned in aqueous detergent, rinsed copiously with deionized water, cleaned for 1 h in an ultrasonic bath in a hot (90 °C) "piranha" solution (H₂SO₄/H₂O₂ 70/30 v/v), and then allowed to cool to room temperature over the course of 1 h while sonicating. The cleaned substrates were rinsed then with deionized water. Further cleaning was carried out with H₂O/H₂O₂/NH₃ (5/1/1). After subsequent washing with deionized water, the substrates were immersed for 5 min in pure methanol, then in methanol/toluene (1/1), and finally in dry toluene.

Growth of organic multilayers: The template layer was obtained on precleaned hydroxylated substrates by liquid-phase silanization reaction with 3 mm (3-aminopropyl)trimethoxysilane in dry toluene at 90 °C for 8 h under a N₂ atmosphere. After the template layer was deposited all of the following film growth steps were conducted in the CVD reactor: The NTCDI precursor was vaporized at $T = 200$ – 250 °C to react with the surface-bound amine; 1,6-diaminohexane and 4,4'-methylenedianiline precursors were vaporized at $T = 35$ – 40 °C and 90 – 110 °C, respectively. Imidization in both steps was carried out at a substrate temperature of 280 – 290 °C for 15–25 min at a total pressure of 0.05 Torr. The laminar flow MLE reactor setup (Reynolds number < 250) was equipped with a spectroscopic ellipsometer for in situ process monitoring. Following the assembly of each monolayer, the reaction zone was cleaned by resublimation of unchanged precursors under a N₂ flow for 5 min. The reactor walls were independently heated to 330 °C.

Model compounds **1** and **2** were synthesized according to procedures in reference [24]. The modified synthesis will be reported elsewhere.

UV/Vis spectra were recorded on a Shimadzu UV-Vis-NIR 3101 PC scanning spectrophotometer. Luminescence was measured on a RF-5301 PC spectrofluorimeter. Electroluminescence was observed on a home-made setup consisting of RF-5301 PC and the source measure unit Keithley 236.

The variable angle spectroscopic ellipsometer (Woollam Co.) VASE 32 PC was used for measuring ellipsometry with 5-nm intervals in the range 300–800 nm. The structural model for fitting ex situ ellipsometry data uses the data of three different incident angles; in Figure 2 only the 75° data is shown. The fitting model includes the real (refractive index) and imaginary parts (extinction coefficient) of optical constants and the thickness of the layers. The multilayered structure that we studied consists of two different layers. These layers have a different free volume distribution and electron density: NTCDI is a highly dense layer with heteroatomic units, and the aliphatic spacer is a more diluted layer with properties closer to those of

polyethylene or monolayers containing long alkyl chains. The molar extinction coefficients (ϵ) were obtained from absorption spectra of MLE precursors, and the refractive index (n) was defined by surface plasmon resonance measurements on physisorbed films (50-nm-thick layer of NTCDA precursor). The starting values for the fitting model^[25] were taken from crystallographic data on compounds **1** and **2**, in accordance with literature data.^[13]

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Highly Efficient, Enantioselective Total Synthesis of the Active Anti-Influenza A Virus Indole Alkaloid Hirsutine and Related Compounds by Domino Reactions**

Lutz F. Tietze* and Yifa Zhou

In memory of Ulrich Schöllkopf

Owing to their high bond forming efficiency, domino reactions allow the construction of complex molecules in a few steps from simple substrates.^[1] Within this context, we have developed inter alia a domino Knoevenagel–hetero-Diels–Alder reaction in which a highly reactive 1-oxa-1,3-butadiene is formed by condensation of a 1,3-dicarbonyl compound with an aldehyde and then transformed into a functionalized dihydropyran in a subsequent hetero-Diels–Alder reaction with an enol ether or an alkene.^[2] This three- or four-component reaction^[3] also proceeds on a polymer support and is thus suitable for combinatorial synthesis.^[4] Recently, we reported the preparation of the Vallesiachotamine alkaloid dihydroantirrhine by a domino Knoevenagel/hetero-Diels–Alder reaction.^[5]

We describe here the application of this method to the highly efficient, enantioselective synthesis of the corynanthe indole alkaloids^[6] hirsutine^[7] (**1**) and dihydrocorynantheine (**2**).^[8] Hirsutine (**1**) and related compounds are currently of great interest as it has been shown that **1** exhibits a strong inhibitory effect against the influenza A virus (sub-type H3N2), with an EC₅₀ value of 0.40–0.57 µg mL⁻¹.^[9] It is

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