1,4;5,8-naphthalene-tetracarboxylic diimide derivatives as model compounds for molecular layer epitaxy[†]

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The physical properties and finite size effects observed in 1,4;5,8-naphthalene-

tetracarboxylicdiimide (NTCDI)-based organic multilayers assembled by molecular layer epitaxy (MLE) are investigated by structure-property studies of low molecular weight model compounds. These molecules, aliphatic N,N'-dihexyl-NTCDI (1), N,N'-dihexadecyl-NTCDI (2) and aromatic N,N'-diphenyl-NTCDI (3), mimic the elemental building blocks of the solid-state heterostructures, NTCDI-based organic superlattices. Thermal analysis combined with polarized optical microscopy reveals that both 1 and 2 have polymorphic phases at an elevated temperature range. All model compounds show new absorption (abs.) and photoluminescence (PL) bathochromically shifted bands in concentrated (mM) solutions, as is also seen in MLE-derived organic superlattices. The strong tendency to aggregate and the photophysical properties of the model compounds are correlated with the PL and electrical field dependent electroluminescence (EL). This clarifies the structure-tunable emission by virtue of in-plane excitons in solid-state MLE structures. Finally, X-ray diffraction of single crystals of 1 and 3 reveal similar packing motifs for the molecules and the resulting solid-state MLE heterostructures.

Introduction

Organic multilayered structures having a characteristic layer thickness of *ca.* 1–100 nm have recently attracted significant attention in view of their possible application in molecular optoelectronic and electronic devices, such as organic light emitting diodes (OLEDs) and organic field effect transistors (OFETs).¹ Novel aspects of solid-state physics in diminished dimensions have already been recognized in organic quantum-confined structures.² The construction of stacked heterostructures usually utilizes ultra high vacuum deposition techniques like organic molecular beam deposition (OMBD), and has been demonstrated in organic superlattices built up of 1,4;5,8-naphthalene-tetracarboxylic dianhydride (NTCDA)/3,4;9,10-perylene-tetracarboxylic dianhydride (PTCDA) with a characteristic layer thickness of *ca.* 3–4 nm.³

Recently we developed a new nanotechnological approach, MLE,⁴ to assemble organic superlattices of monomolecularlayer (*ca.* 1 nm) periodicity. This method employs a vaporphase self-assembly route to enhance epitaxial growth *via* covalent bonding on the intermolecular level and forms highly ordered supramolecular layered structures. The MLE methodology comprises instrumental, synthetic and assembly aspects which are divided into four levels: (1) a template layer connecting the organic superlattice to the inorganic substrate by covalent bridges, (2) self-restricted vapor-phase reactions enabling monolayer-by-monolayer growth, (3) covalent ("c-axis") interlayer bonding and (4) π -stacking in the *x*-*y* plane. In our previous contribution⁴ we demonstrated the applicability of the MLE approach in constructing an ultra-thin (*ca.* 6 nm) OLED device.

Much like atomic layer epitaxy (ALE),⁵ the MLE approach utilizes the right balance between chemical adsorption and physical desorption and thus the monolayer's epitaxial growth is governed by self-limiting vapor phase reactions. ALE uses comparably small inorganic compounds to form multilayered structures, where in-plane ordering is achieved simultaneously with c-axis anchoring. The molecular precursors for the MLE process are larger than those of ALE, and upon c-axis anchoring they still have in-plane rotational freedom. Therefore, in-plane packing can be improved by additional face-to-face π -aggregation that in turn leads to anisotropic physical properties of the MLE-derived heterostructures. Discshaped π -conjugated organic semiconducting precursors were chosen as the building blocks of the electronically semiconductive layer, and flexible spacers were chosen as the precursors for the assembly of the electronically insulating layer. Scheme 1 shows the geometrical aspects of the model compounds, hard disc-like molecules with two flexible arms, capable of mimicking the MLE multilayers. In the case where the disc-shaped unit is mesomorphic, the multilayered structure can be viewed as an "artificial" smectic phase, in which the covalent bonding forces the precursors to adopt layered liquid-crystalline packing. Thus, the in-plane packing and π -aggregation are the key aspects in our investigation of model compounds determining the relationship between structure and electronic properties.

The chemical structures of the MLE model compounds are given in Scheme 2. We found a direct analogy between model

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Scheme 1 Electronically quantum-confined structures: model compound and MLE-derived organic superlattice.



compounds 1-3 and the NTCDI-based aromatic and aliphatic MLE heterostructures, in the mimicking of their photophysical properties. The strong tendency for face-to-face aggregation observed in the model compounds explains mesophase formation at elevated temperatures and the self-organization observed in the MLE-derived structures. The remarkable ability of liquid-crystalline material to self-organize spontaneously into highly ordered structures that, when disturbed, simply reform the original structure is implemented in the MLE processes. Most current liquid crystals (LCs) are electrical insulators and are used in applications such as flat panel displays. The recent advance in the synthesis of semiconducting LCs⁶ significantly expands the realm of potential applications, and has encouraged many studies⁷ into the use of LCs as active components in electroluminescent devices,⁸ molecular wires and fibers,9 photorefractive materials,10

photovoltaic cells,¹¹ and as a medium for high-density information storage.¹²

Furthermore, there is an independent interest in low molecular weight naphthalene-imide based compounds,13 due to their increased electron affinity which can be utilized as an electron injection layer in OLED devices or high-electron mobility n-type OFETs.¹⁴ The aromatic N,N'-diphenyl-NTCDI has an ionization potential threshold $(7.4 \text{ eV})^{15}$ that corresponds well to the good electron-injection character. This value is comparable to that of 7.7'.8.8'-tetracyanoquinodimethane (TCNQ), which is widely used in charge transfer complexes. This high ionization threshold is caused by the inductive effect of the four carbonyl electron withdrawing units distributed symmetrically around the π -conjugated naphthalene core.¹⁶ NTCDI was also utilized in blue light-emitting organic electroluminescent devices along with N-alkyl- or arenyl-4-acetylamide-1,8-naphthalimides.¹⁷ NTCDI was found to form exciplexes with diamines in the solid-state, which resulted in a long bathochromic-shifted PL emission.¹⁸ N,N'-dioctyl-NTCDI was also used as a doping material in organic photovoltaic cells.¹⁹ Doping of poly[2methoxy-5-(2'-ethylhexyloxy-p-phenylvinylene)] (MEN-PPV) with N, N'-dioctyl-NTCDI in a Schottky-type device resulted in an increase of current density and circuit voltage by factors of 10 and 6 respectively. N,N'-Dihexyl-NTCDI has also proved to be efficient in photorefractive applications.²⁰ The possible LC-like structural transformation observed in conjugated N,N'-bis(2-phenyl)perylene-3,4;9,10-bis(dicarboximide) was used for the fabrication of optical discs.²¹ In addition, the photochemical response of naphthalimides and naphthaldiimides was investigated for versatile biological applications.22

Herein we provide an example of low molecular weight model compounds that can self-assemble by π -stacking and Van der Waals interactions. In this way the system mimics the relationship between the structure and the electronic properties of MLE-deposited ultra-thin films, and enables the perfection of their assembly-performance characteristics.

Results and discussion

Imidization reactions

Formation of imide bonds between diamine-containing compounds and NTCDA, the MLE precursors, was verified by UV-Vis and FTIR spectroscopy of model compounds 1-3. UV-Vis $\lambda_{max}(\varepsilon)$ and FTIR $v_{C=O}$ spectral bands of NTCDA precursor: 369 nm ($\varepsilon = 2.1 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) and 1779 cm^{-1} . Upon imidization in the model compounds these bands were shifted to 381 nm ($\varepsilon = 2.6 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) and 1655.9 cm⁻¹ for 1; to 380 nm ($\varepsilon = 2.3 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) and 1655.5 cm⁻¹ in the case of **2**; and to 382 nm ($\varepsilon = 2.1 \times$ $10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) and 1655.7 cm⁻¹ in the case of **3**. The surface condensation reaction between the alkylamine and NTCDA was studied by FTIR measurements of an alkylamine monolayer self-assembled on an Au/SiO2/Si substrate. The free alkyl-amine peak at 3200 cm^{-1} disappeared and the imide peak at 1655 cm⁻¹ appeared following the reaction with NTCDA in MLE-derived films on gold. Finally, FTIR spectra



Fig. 1 UV-Vis spectra of model compound 1 in DMF solution at 10^{-5} M (I) and at increasing concentrations, up to 5 × 10^{-3} M (II). UV-Vis spectra of an MLE-deposited three-bilayer, SiO₂/Pr–(NTCDI–HM)₃–NH₂, on a glass substrate is shown in the inset.

comparison of surface-bound NTCDI and model compounds **1–3** provides evidence for imide-bond formation.

π -Aggregation

MLE-derived organic superlattices reveal size-dependent effects of optical, abs., PL and EL properties.⁴ Similarly we observe the formation of a bathochromically shifted band in the solutions of the model compounds (1–3). At low concentration (10^{-5} M, DMF) only UV bands, corresponding to intramolecular electronic transitions, of monomers (I) are observed, while at high concentration (10^{-3} M, DMF) an additional absorption of π -stacked molecular aggregates (II), corresponding to intermolecular electronic transitions, is

observed (see Figs. 1 and 2, 380 nm and 473 nm for 1 and 382 nm and 518 nm for 3). UV-Vis spectra of solid-state naphthalene-diimide based organic superlattices (see insets of Figs. 1 and 2) exhibit a red-shifted absorption π -aggregation band in addition to the UV band of the "isolated molecules" [380 nm and 515 nm for the MLE "1-like" structure based on DAH and NTCDA, SiO₂/Pr–(NTCDI–HM)₃–NH₂ (Pr = aminopropyl template layer; HM = hexamethylene spacer), and 381 nm and a broad band around 1100 nm for the MLE "3-like" structure, SiO₂/Pr–(NTCDI–MDP)₃–NH₂, (MDP = 4,4'-methylenediphenyl)].

MLE structures were observed to have two different PL/EL emitting centers.⁴ The blue EL is attributed to a radiative recombination process on a single NTCDI molecule, and the



Fig. 2 UV-Vis spectra of model compound **3** in DMF solution at 10^{-5} M (I) and at increasing concentrations, up to 5×10^{-3} M (II). UV-Vis spectra of an MLE-deposited three-bilayer, SiO₂/Pr–(NTCDI–MDP)₃–NH₂, on a glass substrate is shown in the inset.





Fig. 3 PL spectra of model compound **1** in DMF solution at 10^{-5} M, $\lambda_{ex(I)} = 250$ nm (I) and at 10^{-3} M, $\lambda_{ex(II)} = 380$ nm (II) (excitation spectra are not given). EL of MLE-derived three-bilayer OLED, SiO₂/ITO/(NTCDI-HM)₆/Al at 6 V is shown in the inset.

red-shifted EL is assigned to a radiative recombination process between neighboring NTCDI molecules. The coexistence of two emitting centers within the same layer is an indication of two different excitation paths: (a) *intra-molecular* excitons and (b) *inter-molecular* excitons,²³ and is a sign of dense packing. The trend of a new EL peak appearing due to epitaxial ordering was also observed in a perylene-based OLED,²⁴ and in a single crystal of model compound 1.²⁵ We separated these two emission centers in the model compounds 1–3. The emission spectra of 1 and 3 at different concentrations (10⁻⁵ M and 10⁻³ M in dimethyl formamide (DMF)) are shown in Figs. 3 and 4. In the case of the more concentrated solution, which provided conditions for aggregation, two different PL peaks were clearly observed: one in the region of 400–430 nm



Fig. 4 PL (excitation [Ex.] and emission [Em.]) spectra of model compound 3 in DMF solution at 10^{-3} M. EL of MLE-derived threebilayer OLED, SiO₂/ITO/(NTCDI-MDP)₃/Al, at 6 V is shown in the inset.

and a second broad peak at around 570 nm, which were attributed to monomer- and aggregate-centered PL respectively, in contrast to the PL spectra of the diluted solution, for which only monomer emission was observed.²⁶ The EL spectrum of MLE-derived NTCDI superlattice HM spacer in the configuration SiO₂/ITO/(NTCDI-HM)₆/Al at 6 V is shown in the inset of Fig. 3. The EL spectrum of MLE-derived NTCDI superlattice with MDP spacer in the configuration SiO₂/ITO/(NTCDI-MDP)₃/Al at 6 V is shown in the inset of Fig. 4. Applying different voltages allowed tuning of the EL of the OLED from red to blue.^{4a} At low voltage the red emission of the stacked NTCDI molecules (intermolecular excitons) dominated 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 blueshifted EL. It is clearly observed that two types of emission bands appear. The first (I) is attributed to EL of NTCDI "isolated luminophore", and the second (II) to EL of NTCDI π -aggregates. The induced aggregation in solution and the appearance of the red-shifted absorption and emission bands clearly modeled the red-shifted absorption and EL bands in the solid-state and device operation, respectively. In order to prove that the resulting MLE layers show tendency for two dimensional aggregation, atomic force microscopy (AFM) measurements were performed on SiO₂/Pr-(NTCDI-HM)_n-NTCDI superlattices (n being the number of bilayers and ranging from 0-2, see ref. 4 for detailed experimental on the MLE technique). Fig. 5 shows AFM imaging of the surfaces at various numbers of bilayers, indicating the growth in domain size as the number of MLE layers increases, ranging from 10 nm for the first NTCDA layer to about 100-120 nm for a three bilayer MLE superlattice structure (note that Fig. 5C is not an artefact, and was verified on two separate samples and at different scan sizes).

Phase behavior and liquid crystalline properties

The differential scanning calorimetry (DSC) thermogram of 1 (Fig. 6) reveals two endothermic peaks upon heating, assigned as two different polymorphs K ($T_{\rm K}$ = 187 °C, ΔH = 29.5 J g⁻¹) and M ($T_{\rm M} = 208$ °C, $\Delta H = 41.2$ J g⁻¹). The fact that no exothermic transitions can be seen even though the temperature reaches 400 °C points to the very high thermal stability of 1. Two exothermic transition peaks appeared upon cooling (with the expected hysteresis) describing the backwards phase transitions from the isotropic melt to the K' phase and finally back to the crystalline phase, and proves that these are indeed first-order phase transitions. Polarized optical images of 1 (Fig. 7A) were taken during sample cooling. Above $T_{\rm M}$ isotropic texture was observable. Around $T_{\rm M}$ we observed the formation of a different polymorph. Finally needle-like crystals appeared below $T_{\rm K}$. In order to understand the thermal properties of our material we synthesized and studied a closely related model compound 2 that has a longer aliphatic chain (Scheme 2). As predicted, we observed the lowering of the transition from the crystalline phase to the second polymorph ($T_{\rm K}$ =137 °C, ΔH = 9.2 J g⁻¹ and $T_{\rm M}$ = 150 °C, $\Delta H = 42.3 \text{ J g}^{-1}$) upon heating and cooling, again



Fig. 5 AFM imaging of 3-(aminopropyl)trimethoxysilane SAM surface (A) and MLE-derived bilayer superlattices in the form of SiO₂/Pr-(NTCDI-HM)_{*n*}-NTCDI for n = 0 (B), n = 1 (C) and n = 2 (D). Images are 950 nm × 950 nm; RMS roughnesses are 2.3 Å, 2.2 Å, 1.5 Å and 7.0 Å respectively.



Fig. 6 DSC thermograms of model compounds 1 (—) and 2 (---), recorded at a heating/cooling rate of 10 $^{\circ}$ C min⁻¹.

demonstrating the reversibility of the transitions and the very high thermal stability of the compound. Polarized optical images of 2 (Fig. 7B) were also taken during sample cooling. The images revealed melting texture above $T_{\rm M}$ and that of the second polymorph around $T_{\rm M}$. Finally needle-like crystals appear below $T_{\rm K}$ without any sign of the broken conic fanshaped texture observed for 1. DSC of 3 does not reveal any sign of another polymorph phase but again shows a very high thermal stability (up to 400 $^{\circ}$ C). The molecule seems to be too rigid for this kind of structural transformation. However, we succeeded in growing a single crystal of this compound enabling us to define the crystalline structure.

The growth of MLE structures with aromatic spacers was done using MDA. The existence of a methylene unit between the aniline groups (which are equal to the phenyl groups in compound 3) allows enough flexibility for the buildup of an MLE multilayer. Working with 1,4-phenylenediamine didn't result in ordered multilayer growth due to the high rigidity, emphasizing the need for a flexible spacer inbetween the rigid NTCDI units.

The phase transitions in our models, compounds 1 and 2, point to layered polymorphic structures in MLE-derived nanolayers exhibiting thermal stability at elevated temperatures. Similarly, systems based on dioxotriazole derivatives of perylene¹² show large LC ranges. It is not yet clear what minimal structural features are required to produce an LC phase. However, as for the cases of porphyrins and phthalocyanines, that have aromatic cores slightly larger than NTCDI, eight side chains are usually required to induce liquid crystallinity. In the LC porphyrin, zinc octakis(octylethylether) porphyrin,¹⁴ for example, the ratio of side chain atoms (excluding hydrogens) to atoms in the aromatic core is 3.6, whereas for 1 and 2 this ratio is 0.6 and 0.7 respectively. Although we have substituted the NTCDI unit with a long



Fig. 7 POM images of 1 (A) and 2 (B) at 187 $^{\circ}$ C and 137 $^{\circ}$ C respectively (magnification ×100).

alkyl tail (C_{16}), the result does not show mesomorphic behavior. In relation to this, it is noteworthy to look at the work in ref. 6*a* that shows that an insertion of phenyl-ether units does result in LC properties. For electronic applications, this is highly advantageous, because the benefits from liquid crystallinity may be utilized while keeping the volume of the electro-inactive (insulating) side chain moiety to a minimum.

Polarized optical microscopy (POM) images of model compounds 1 and 2 (Fig. 7A and B respectively) were taken at 187 °C and 137 °C respectively, temperatures that are below the melting point of each compound. Both molecules show more than two phases by polarized microscopy in the temperature range from room temperature to above the melting point, corresponding well with the DSC data presented earlier.

X-Ray crystal analysis

In order to understand the packing motifs in the model compounds and related MLE structures, crystals were grown. Successful crystallization of model compounds **1** and **3** gave the opportunity to do single crystal X-ray analysis.^{27,28} The structural motifs of compound **3** are shown in Fig. 8. The diffraction pattern in the crystalline phase of **1** could be indexed on a triclinic unit cell of dimensions a = 8.264 Å; b = 14.504 Å; c = 4.888 Å and a molecular length of 18.864 Å, and that of **3** could be indexed on a monoclinic unit cell of dimensions a = 5.136 Å; b = 7.522 Å; c = 25.623 Å and a molecular length of 15.429 Å. In both cases the molecules are



Fig. 8 Crystal packing of model compound 3 deduced from single crystal X-ray analysis.

located at inversion centers. The packing of the naphthalenediimide cores in model compound 1^{29} adopts a coplanar motif, while a herringbone motif is adopted in the case of **3**. Katz *et al.* reported a fluorinated-tail version of compound **1** which was used as an n-type semiconductor,³⁰ but the crystal structure of this compound adopted a herringbone motif similar to that of **3**. In contrast to the herringbone structure, the coplanar structure showed by **1** was also seen in an NTCDI-based compound with an aromatic ether-imide tail reported by Dingemans *et al.*^{6a}

Conclusions

Electronic transitions in organic structures are essentially controlled by the π -conjugation length. Reviews of the experimental data, the theoretical calculations and the relationship between the size of the π -conjugation and absorption spectra have been published.³¹ In this contribution we have described the assembling features of a newly developed MLE method for deposition of organic multilayered structures, which is closely connected with π -conjugation induced molecular ordering. Single crystal XRD, DSC, FTIR, UV-Vis, and PL measurement of MLE precursor and model compounds showed a strong tendency towards π -aggregation in the model compound. Both the model compounds and the MLE-derived superlattices show a new red-shifted intermolecular absorption band, suggesting an electronic cross-talk between neighboring molecules. The corresponding π -aggregation in the MLEderived multilayers is one of the fundamental driving forces for ordering and serves as a basic assembling principle. This driving force is the main methodological difference between ALE, which was applied only to the deposition of inorganic heterostructures, and the MLE method. UV-Vis and FTIR spectra of precursor and model compounds point to the formation of imide bridges, which proves the formation of covalent bridges between adjacent layers. Thermal analysis of model compounds 1 and 2 showed the existence of two polymorphic phases in the thermal range of MLE's deposition temperature. The tendency towards aggregation in the resulting MLE superlattice was confirmed by AFM imaging of the surface, while increasing the number of deposited layers led to an increase in domain size from 10 nm to 100 nm following

and a herringbone packing of compound 3 with a core-to-core distance of 5.136 Å. In conclusion, we have studied the thermal, structural and photophysical properties of model compounds that mimic the MLE structures. We find a close analogy in the properties of aggregated model compounds 1–3 with features of MLE-derived organic heterostructures. The possibility of studying aggregated model compounds opens a unique route to predicting the properties of organic quantum-confined structures and their implementation in nanometric devices.
Experimental
Vapor phase self-assembly by MLE
NTCDI-based organic superlattices with aromatic and aliphatic spacers were grown by the MLE method. An alkylamine-containing surface 3-(aminopropyl)trimethoxysilane at

NTCDI-based organic superlattices with aromatic and aliphatic spacers were grown by the MLE method. An alkylaminecontaining surface, 3-(aminopropyl)trimethoxysilane, at 200–220 °C is hit with a pulse of vaporized NTCDA precursor, forming imide linkages. Then a pulse of a vaporized diamine spacer (aromatic 4,4'-methylenedianiline (MDA) or aliphatic DAH), is used to regenerate the amine functionality on the surface that can again react with NTCDA. Cycling through these steps leads to the formation of NTCDI-based organic superlattices with covalent interplanar bonding and in-plane π -aggregation ordering. Detailed experimental conditions of the MLE vapor phase reactions and setup are given in ref. 4.

deposition of 4 bilayers. XRD analysis of single crystals of

compounds 1 and 3 allowed the verification of coplanar

packing of compound 1 with a core-to-core distance of 4.888 Å,

Photophysical characterization

UV-Vis-NIR absorption spectra were recorded on a Shimadzu UV-Vis-NIR 3101 PC scanning spectrophotometer; luminescence and PL were measured on a Shimadzu RF-5301 PC spectrofluorimeter; electroluminescence of MLE-derived thin films was observed on a homemade setup consisting of a RF-5301 PC and a Keithly 236 source measure unit. IR spectra were recorded using an IFS 113v Bruker FT-IR spectrometer, with a spectral resolution of 2 cm⁻¹. The samples contained 1% NTCDA precursor and model compounds (1–3) in pressed KBr powder pellets.

Structural investigations

DSC measurements were carried out on a Mettler TA 300 calorimeter at 10 K min⁻¹ heating/cooling rates. POM observations were performed on Zeiss Universal microscope equipped with a Mettler FP 52 heating stage. The pictures shown here were taken with transmitted light using crossed polarizers. AFM measurements of the MLE superlattices were performed on a Nanoscope Dimensions 3100 scanning probe microscope from Digital Instruments (DI) equipped with a NanoScope IV controller, in a tapping mode using a tapping etched silicon probe (TESP) tip, scanning at speeds of 1–2 Hz under ambient conditions. X-Ray diffraction data was measured on a Bruker SMART APEX CCD X-ray diffractometer system controlled by a Pentium-based PC running the SMART software package.³² The crystal was mounted on a three-circle goniometer with χ fixed at +54.76° at room temperature. The

diffracted graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) was detected on a phosphor screen held at a distance of 6.0 cm from the crystal, operating at -43 °C. A detector array of 512 × 512 pixels, with a pixel size of approximately 120 µm, was employed for data collection.

A series of 30 data frames measured at 0.3° increments of ω were collected with three different 2θ and φ values to assess the overall crystal quality and to calculate a preliminary unit cell. The measured intensities of individual reflections were plotted at 0.3° intervals of ω , and the average peak width at baseline was less than 1.5. Reflections with $I > 2\sigma(I)$ were selected from the data frames and utilized to calculate a preliminary unit cell. For the collection of the intensity data, the detector was positioned at a 2θ value of 28° and the intensity images were measured at 0.3° intervals of ω for a duration of 20 s each. The data frames were collected in four distinct shells which, when combined, measured more than 1.3 hemispheres of intensity data with a maximum 2θ of 52° . For the first shell, the crystal was positioned at $\varphi = 0^{\circ}$ and $\omega = -28^{\circ}$ and a set of 600 frames were collected. A series of 600 frames was collected in the second shell with a starting position of $\varphi = 90^{\circ}$ and $\omega =$ -28.0° . The crystal was then moved to a position of $\varphi = 180^{\circ}$ and $\omega = -28.0^{\circ}$ to measure 600 frames required for the third shell. The last 600 frames in the fourth shell were collected starting at $\varphi = 270^{\circ}$ and $\omega = -28^{\circ}$. The initial 50 frames of the first data shell were re-collected at the end of data collection to correct for any crystal decay, but none was observed.

Immediately after collection, the raw data frames were transferred to a second PC computer for integration by the SAINT program package.³³ The background frame information was updated according to the equation B' = (7B + C)/8, where B' is the updated pixel value, B is the background pixel value before updating, and C is the pixel value in the current frame. The structure was solved and refined by the SHELXTL software package.³⁴ Molecular packing images were processed on a PC using Mercury 1.4 software by the Cambridge Crystallographic Data Centre (CCDC).

Model compound synthesis

N,*N*'-**Dihexyl-NTCDI (1).** 10 g (0.037 mol) of NTCDA and 37.4 g (0.37 mol) of *n*-hexylamine with a catalytic amount of 4-(dimethylamino)pyridine (DMAP) were refluxed in DMF for 8 h. The reaction mixture was poured into water and the precipitated solid was filtered, dried and crystallized from toluene. Elemental analysis: Calculated for C, H, and N: 71.89; 6.91; 6.45; Found: 71.63; 7.02; 6.35. ¹H NMR (300 MHz, CDCl₃) δ : 0.87 (t, 6H, *J* = 7.0 Hz, CH₃); 1.36 (m, 12H, CH₂); 1.82 (m, 4H, CH₂); 4.18 (t, 4H, *J* = 7.0 Hz, N–CH₂); 8.74 (s, 4H, aromatic rings).

N,N'-Dihexadecyl-NTCDI (2). 10 g (0.037 mol) of NTCDA and 89.9 g (0.37 mol) of 1-hexadecylamine with a catalytic amount of DMAP were refluxed in DMF for 8 h. The reaction mixture was poured into water and the precipitated solid was filtered, dried and crystallized from toluene. Elemental analysis: Calculated for C, H, and N: 77.31; 9.80; 3.92; Found: 75.86; 10.16; 3.71. ¹H NMR (300 MHz, CDCl₃) δ : 8.75 (s, 4H, aromatic rings); 4.20 (t, 4H); 1.25 (s, 56H); 0.87 (t, 6H).

N,*N*'-**Diphenyl-NTCDI (3).** 10 g (0.037 mol) of NTCDA and 6.9 g (0.075 mol) of aniline were refluxed in *m*-cresol for 12 h. The reaction mixture was poured into water and the precipitated solid was filtered, dried and triturated in boiling toluene, filtered again and dried. Crystals were obtained from slow crystallization in DMF. Elemental analysis: Calculated for C, H, and N: 74.64; 3.35; 6.70; Found: 74.36; 3.54; 6.58. ¹H NMR (300 MHz, anisole-d₈) δ : 7.19 (broad singlet, 8H); 7.71 (broad singlet, 6H).

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- 27 Crystal structure of 1: $C_{26}H_{30}N_2O_4$, $M = 434.52 \text{ g mol}^{-1}$, triclinic, $P\overline{1}$, a = 8.265(2) Å, b = 14.504(3) Å, c = 4.8883(9) Å, $\alpha = 98.050(3)^{\circ}$, $\beta = 93.611(3)^{\circ}$, $\gamma = 96.27(2)^{\circ}$, V = 574.9(2) Å³, T = 293(1) K, Z = 1, $\mu = 0.085 \text{ mm}^{-1}$, total reflections = 5933, unique = 2243, $I \ge 2\sigma = 1594$, $R_{int} = 0.066$, $R_1 = 0.140$, $wR_2 = 0.178$. CCDC reference number 299524. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b601258b.
- 28 Crystal structure of **3**: C₂₆H₁₄N₂O₄, M = 418.39 g mol⁻¹, monoclinic, P_{2_1}/n , a = 5.1360(6) Å, b = 7.5227(8) Å, c = 25.623(3) Å, V = 989.81(19) Å³, T = 295(1) K, Z = 2, $\mu = 0.096$ mm⁻¹, total reflections = 10092, unique = 1952, $I \ge 2\sigma = 1116$, $R_{int} = 0.076$, $R_1 = 0.064$, $wR_2 = 0.125$. CCDC reference number 296236. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b601258b.
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