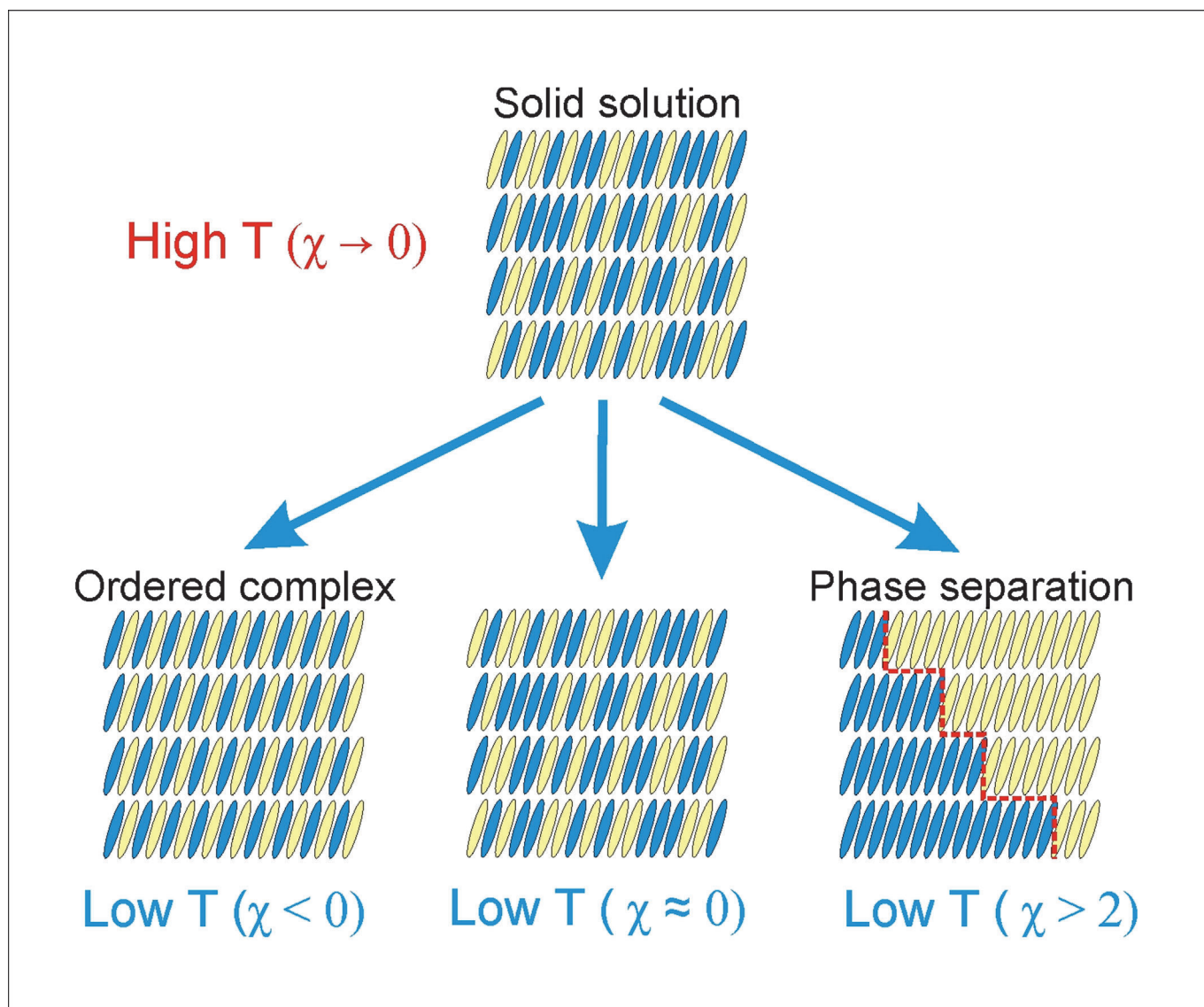


# Organic–Organic Heterostructures: Concepts and Applications

Alexander Hinderhofer and Frank Schreiber<sup>\*,[a]</sup>



We review basic concepts as well as recent examples and applications of organic–organic heterostructures. We organize the different types of heterostructures according to material A deposited on material B (A/B), A co-deposited with B (A:B), heterostructures in the monolayer regime including nanostructuring concepts and systems involving self-assembled monolayers,

as well as various other architectures, including superlattices. While most examples are related to small-molecule organic semiconductors, many of the ideas can be applied to other systems. The central theme is growth and structure as well as optical and electronic properties. Finally, we comment on implications for device applications.

## 1. Introduction

Organic materials exhibit a wide variety of structures and associated properties, mechanical as well as optical and electrical. The constituents can be diverse, from small molecules to polymers, as can be the structures composing the materials.

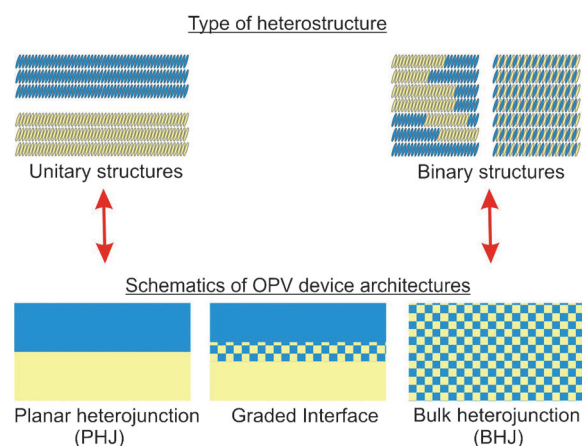
Generally, growth and structure of organic heterostructures are a substantial challenge. In fact, growth is an inherently complex subject.<sup>[1,2]</sup> Compared to their inorganic (elemental) counterparts, organic systems exhibit additional complications in their growth behavior associated with their additional degrees of freedom related to orientation and internal molecular structure.<sup>[3–7]</sup> Thus, already the growth and structure of single-component organic films can be challenging. For growth of organic–organic heterostructures, that is, systems with at least two components, there are further complexities, such as issues related to the compositional homogeneity and the structure and its quality as well as to the evolution of the top surface known from single-component films. The structure of course has an impact on optical and electronic properties, which are of interest both from a fundamental as well as from an applications perspective.

A model class of compounds for organic–organic heterostructures are small-molecule organic semiconductors (OSCs). Recent years have witnessed spectacular progress in their device applications.<sup>[8–14]</sup> Many device architectures feature actually rather complex structures, involving frequently at least two different compounds (“donor” and “acceptor” or more precisely electron and hole conduction layer) forming a heterojunction, as in the case of organic photovoltaics (OPV) and organic light emitting diodes (OLEDs).

This review tries to provide an overview of the current status of the field and indicate trends and concepts. Most examples are drawn from the area of small molecule OSCs prepared by organic molecular beam deposition (OMBD), that is, by evaporation in vacuum. For the background of OMBD, with emphasis on single-component systems, we refer to the literature.<sup>[3,4,15–25]</sup> Importantly, many of the concepts discussed here for heterostructures of OSCs are rather general and can be applied also to heterostructures of other organic compounds. In addition to growth and structure we discuss optical and electronic properties of these systems and their implications for devices, without reviewing complete device architectures. For basic concepts of devices we refer to dedicated references.<sup>[8–13,26,239]</sup> We discuss thin films (and indeed rather thick ones, that is, 3D) as well as monolayers, that is, 2D systems. The area of multi-component monolayers offers exciting opportunities for structure formation and their direct observation.

We include some heterostructure work related to self-assembled monolayers (SAMs) and also their combination with OSCs. We omit polymer-based heterostructures. These are of course interesting in their own right, but in their structure formation they follow somewhat different mechanisms with entropy and disorder playing a more important role.<sup>[27–32]</sup>

Figure 1 shows schematically different types of organic–organic heterostructures and, as one possible example for applications, compares these to prototype OPV device geometries.



**Figure 1.** Top: A/B and A:B heterostructures. Bottom: Translation of these limiting cases into prototype device architectures, namely planar heterojunctions (PHJ) and bulk heterojunctions (BHJ) as used in OPV. BHJs can exhibit different mixing/demixing scenarios. Generally, of course, intermediate scenarios are possible, for example a graded interface.

A/B systems are layers of A and B deposited one after the other. Here, the interface between the two organic compounds A and B is the key to the functioning of the device, and at the same time it is probably the least understood. In OPV, A/B heterostructures are referred to as planar heterojunctions (PHJ). A:B heterostructures are prepared by simultaneous deposition of A and B. For OPV devices, these are referred to as mixed or bulk heterojunctions (BHJs). For BHJs the interface formation between both materials is obviously closely related to the mixing behavior of the two compounds, that is, whether the compounds phase separate or mix efficiently. Heterostructures

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combining both concepts can also be realized (e.g. a graded interface), and generally there is a large variety of schemes for preparation and resulting functional properties.

Note that implicitly the schematics in Figure 1 are side views or cross sections of thin films and thus their vertical structure, but in principle they may also be considered as top views and thus their lateral structure. This is valid in particular for monolayer systems, where similar issues of intermixing versus phase separation are discussed in 2D.

In the following sections, we discuss the major classes of organic–organic heterostructures, for which we try to provide a dedicated overview and an up-to-date collection of references. For each case, we first outline the basic concepts followed by typical case studies.

We focus on four types of heterostructures in separate sections and address the following key questions:

1. A/B: To which degree is the growth and structure of the top layer influenced by the structural properties of the bottom layer? For which material combinations do we find specific growth effects like organic–organic heteroepitaxy or templating?
2. A/B: For which molecular mixtures do we find phase separation or mixing or even ordered superstructures? In this context, it is a rather fundamental question whether or not for example, the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), and the associated energy gap etc. change continuously or step-wise and what the structural length scale for the required intermixing is if the system should exhibit *common* energy levels of A and B and thus features characteristic for coupling in their spectrum.
3. Monolayer-based heterostructures: How can the structure formation of B be influenced by depositing first a monolayer A on the substrate? How can the interface energetics be tailored? How can lateral heterostructures be grown?
4. More complex heterostructures, such as superlattices or other sophisticated structures will be addressed, as well as the implications for device performance.

Obviously, the selection of examples can never be absolutely unbiased and complete, but we hope to cover most of the published work and the relevant aspects and ideas. At the same time we apologize for possible omissions.

## 2. Types of Organic–Organic Heterostructures and Case Studies

### 2.1. A/B-type Heterostructures

Generally, one possible approach to predict or rationalize the structural behavior of material A on B is the concept of interface energies similar to the prediction of wetting angles.<sup>[33]</sup> The wetting or non-wetting morphologies are then related to layer-by-layer growth (Frank–van-der-Merwe), islanding (Volmer–Weber) or a combination of both (Stransky–Krastanov). However, this can at best be a reference scenario, since

growth, which is by definition a non-equilibrium phenomenon cannot be explained solely based on equilibrium energy considerations. The full picture has to incorporate non-equilibrium, that is, kinetic aspects.<sup>[1,2,6,7,34–36]</sup>

The systems under consideration are of course frequently highly anisotropic. In addition, orientational degrees of freedom of the molecules are important, which are not included in conventional growth theories.<sup>[1,2,34]</sup>

In this section we focus on A-on-B type structures, which in device terminology correspond to planar hetero-junctions. Already these apparently simple heterostructures can exhibit complex growth behavior. Related to the complex growth scenarios are, *inter alia*, internal degrees of freedom, which lead to anisotropic diffusion coefficients<sup>[37]</sup> and anisotropic capturing potentials.<sup>[38]</sup> In addition, high step edge barriers are frequently observed for growth of organics.<sup>[39–41]</sup> Obviously, in organic heterostructure growth, crystal structure and morphology of the bottom layer influence the growth of the top layer. We may categorize growth effects of A/B type organic heterostructures as follows.

#### 2.1.1. Organic–Organic Heteroepitaxy

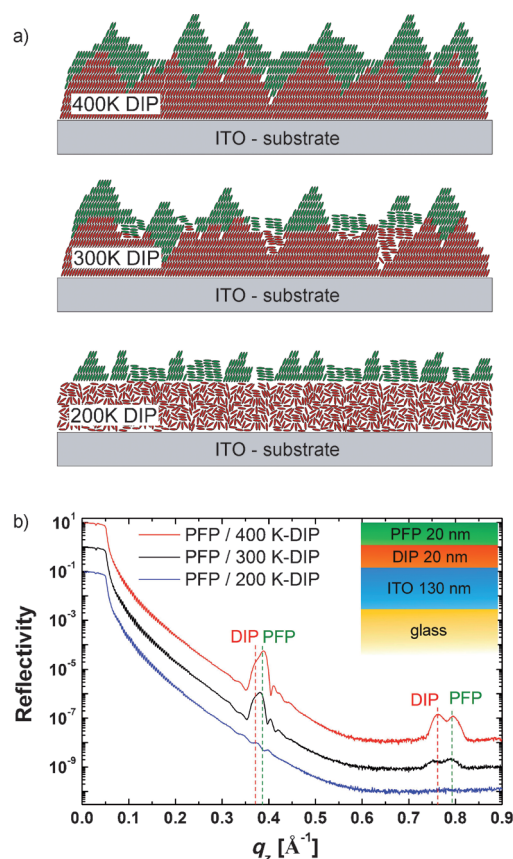
The question of epitaxy at the organic–organic interface has been addressed quite early in refs. [15,23,42–45]. More recent work is reviewed, for example, in ref. [46]. Organic–organic heteroepitaxy implies there is a well-defined crystallographic relationship of two molecular layers (note that the epitaxy of stacked *monolayers* is discussed in Section 2.3.5). In some fortunate cases, the surface unit cells and the corresponding corrugation of the surface potential of the two materials involved are suitable. An interesting case, which has been studied in some detail, including modeling, is  $\alpha$ -quaterthiophene ( $\alpha$ -4T) on tetracene.<sup>[47–49]</sup> Generally, for organic–organic A/B systems discussed here epitaxy is slightly less crucial than for conventional semiconductors because of only weak intermolecular van der Waals interactions, however, the structural compatibility of A and B at the interface can certainly be of importance. Although the unit cells of the two materials are in general not identical, the preferential orientation of organic crystallites on oriented organic thin films due to the anisotropic potential surface of the bottom layer is commonly observed for a variety of compounds (note in this context that here we count azimuthal alignment as a form of epitaxy). Other examples, which do not all exhibit a similarly well-defined structure as the  $\alpha$ -4T/tetracene example, include the growth of  $\alpha$ -4T on rubrene<sup>[50]</sup> and several phthalocyanines grown on 3,4,9,10-perylene-teracarboxylic-dianhydride (PTCDA)<sup>[51]</sup> or other phthalocyanines.<sup>[52,53]</sup> Similar weak epitaxy was shown for the combination of  $\alpha$ -sexithiophene ( $\alpha$ -6T) and *para*-sexiphenyl (*p*-6P)<sup>[54]</sup> and several other materials.<sup>[53,55–61]</sup> This azimuthal templating, that is, a pre-defined in-plane orientation, is also accomplished by epitaxy on an inorganic stepped substrate.<sup>[23,62]</sup>

### 2.1.2. Orientational Templating (Lying-Down versus Standing-Up)

An important question concerns the molecular orientation (in particular lying-down vs. standing-up for rod-like molecules) at the interface or induced by the interface. In this context, one may observe orientational templating, that is, the orientation of the molecules in the top layer adopt the orientation of the bottom layer.<sup>[64,67]</sup> The orientation may be changed (compared to single-component film growth on, for example, SiO<sub>2</sub>) by an underlying organic layer, for example, by the balance of the interface energies. For example for perfluoropentacene (PFP) growth on diindenoperylene (DIP, Figure 2a), the PFP orientation is changed by tuning the growth behavior of the DIP bottom layer.<sup>[63]</sup> The molecular orientation may also be influenced by a specific step pattern or their height,<sup>[68,69]</sup> which for organics is obviously greater than for typical inorganic substrates.

### 2.1.3. Crystal Nucleation and Growth

Dependent on the structural characteristics of the bottom layer a change in crystalline grain size may be observed. This was shown for example for PFP/DIP heterostructures (Figure 2a).<sup>[63]</sup> Here the crystalline quality of the PFP layer correlates with that of the DIP layer underneath in terms of the coherent in-plane and out-of-plane crystallite size. The latter can



**Figure 2.** a) Three different PFP/DIP heterostructures on an indium tin oxide (ITO) substrate. DIP layers were grown at three different temperatures ( $T = \{200\text{ K}, 300\text{ K}, 400\text{ K}\}$ ) to control the crystalline quality and orientation of DIP. PFP layers were grown at  $T = 300\text{ K}$  and exhibit a structure and morphology dependent on the structural properties of the DIP bottom layer. b) XRR data from the three PFP/DIP heterostructures. The intensity of the PFP Bragg reflections varies with the intensity of the DIP reflections. Reprinted with permission from ref. [63].

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be extracted from X-ray reflectivity (XRR) data shown in (Figure 2b).

Another growth effect is a change in mosaicity for growth on different organic thin films. For example C<sub>60</sub>, which grows with large out-of-plane mosaicity (random distribution of crystal orientations) on SiO<sub>2</sub><sup>[70]</sup> and CuPc,<sup>[71]</sup> has a strongly reduced mosaicity for growth on PEN (pentacene)<sup>[37,72,73]</sup> or DIP.<sup>[26,74]</sup>

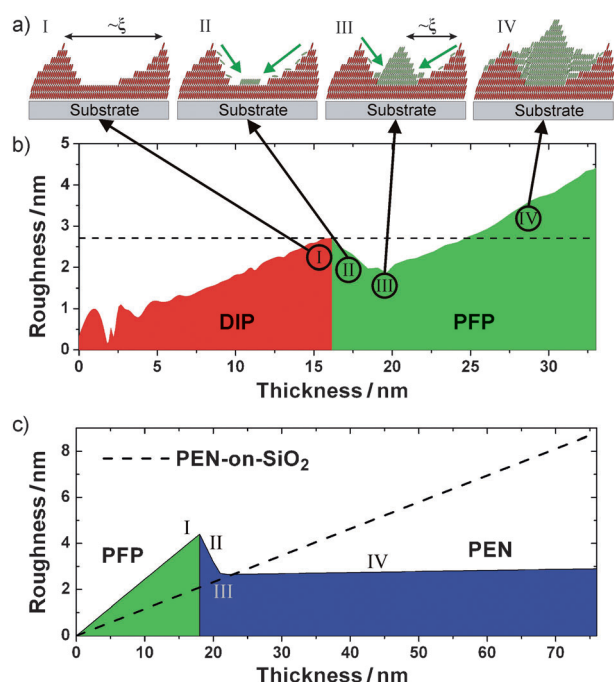
For one system (perfluorinated cobalt-phthalocyanine, or F<sub>16</sub>CoPc, on DIP) it was shown that as long as the diffusion length of the top layer compound is smaller than the typical terrace of the bottom layer, the nucleation density is independent of the bottom layer morphology.<sup>[75]</sup>

### 2.1.4. Roughening for A/B-Type Heterostructures

Several studies show the formation of mound growth on top of organic thin films due to dewetting<sup>[76–78]</sup> or preferred nucleation at step edges.<sup>[68,69]</sup> In contrast to the scenario of fast roughening also roughening nearly independent of the bottom layer was shown<sup>[75]</sup> underlining that, of course, the growth scenario depends on the specific system.

### 2.1.5. Smoothing for A/B-Type Heterostructures

Another interesting effect is smoothing (Figure 3), which was observed for growth of PFP on DIP and PEN on PFP.<sup>[79]</sup> For both systems, surface smoothing during thermal evaporation



**Figure 3.** Roughness evolution of organic-organic heterostructure growth determined with real-time XRR: a) Growth scenario of PFP islands on DIP b) Roughness evolution of a PFP-on-DIP heterostructure. c) Roughness evolution of a PEN-on-PFP heterostructure. For comparison the roughness evolution for growth of PEN on SiO<sub>2</sub> is indicated. Reprinted with permission from ref. [79].

of the second material on top of the first is observed. The smoothing mechanism is sketched in Figure 3a. Islands of the top material are nucleating between grains of the bottom material leading to reduction of roughness of the top surface. After this filling of valleys is completed, the roughness increases again (Figures 3b,c). The smoothing may be rationalized by, compared to homoepitaxy, a lowered step edge barrier for one species diffusing on the other, but the details have yet to be explored.

### 2.1.6. Interface and Thermal Stability

The interface between two materials may exhibit a reconstruction during deposition<sup>[80]</sup> or the two compounds may partially intermix at the interface, which is referred to as graded interface<sup>[81]</sup> (see also Section 2.4.2).

Interface stability effects may also be exploited in interrupted growth. An interesting study to tune the growth mode in organic molecular-beam epitaxy employing interrupted growth for 4T/potassium acid phthalate was presented in ref. [82].

The oxidation dynamics of rubrene/tetracene heterostructures were studied in ref. [83].

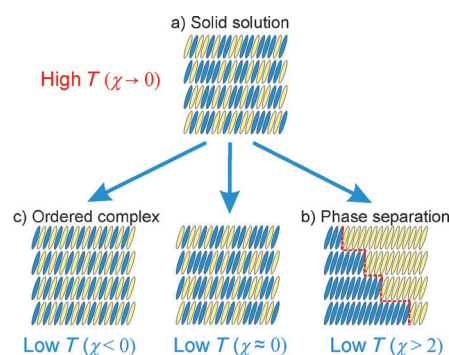
The post-growth stability of the organic-organic interface and the interdiffusion behavior was studied in refs. [84,85]. Other studies on the temperature dependence are discussed in Section 2.3.2, where enhanced thermal stability was found due to an organic capping layer.<sup>[86]</sup> Generally, the thermal stability can also be enhanced using (inorganic) capping layers.<sup>[87]</sup>

## 2.2. A:B-Type Heterostructures

A key question for a binary molecular mixture is whether the two materials are phase separating or mixing on the molecular level. Complete or partial intermixing of two molecular species might be possible, if a mixed crystal energetically more favorable than two pure crystals exists. Of importance in this regard is the isostructural compatibility of both compounds, which is in many cases a prerequisite for efficient mixing.<sup>[88]</sup>

Organic binary mixtures (A:B), which correspond to bulk hetero-junctions (BHJs) in OPV, are widely used in organic thin film devices, for example, for improvement of conductivity<sup>[89]</sup> or for efficient charge carrier separation.<sup>[90]</sup>

Following ref. [88] we classify binary mixtures in the categories phase separation, solid solution and molecular complex formation (Figure 4).



**Figure 4.** Simplified schematic of different mixing scenarios for molecular crystals dependent on  $\chi$ : a) Solid solution. b) Molecular complex due to strong interaction between A and B ( $W_{AB}$  large) c) Phase separation. Broken lines are highlighting phase boundaries. Note that the temperatures necessary to activate the phase transition between the low  $T$  scenarios and the high  $T$  solid solution may be well above the melting or sublimation point of the organic mixture.

The mechanisms behind the formation of the different mixing scenarios can be viewed from different perspectives including steric considerations as well as thermodynamics and interactions. Steric compatibility of the two components may be seen as a precondition for good intermixing. From the point of equilibrium thermodynamics and minimizing the free energy, there is first the entropy contribution, which always favors mixing. Second, the different interaction energies ( $W_{AA}$ ,  $W_{BB}$ ,  $W_{AB}$ ) between the two species A and B entering the free energy can either favor or disfavor mixing. The classical approach in the simplest version would be based on the regular solution model, a mean-field approach. The free energy of mixing is then written as Equation (1):

$$\frac{F_{\text{mix}}}{k_{\text{B}}T} = x_{\text{A}} \ln x_{\text{A}} + x_{\text{B}} \ln x_{\text{B}} + \chi x_{\text{A}} x_{\text{B}} \quad (1)$$

with the dimensionless interaction parameter [Eq. (2)]:

$$\chi = \frac{1}{k_{\text{B}}T} [W_{\text{AA}} + W_{\text{BB}} - 2W_{\text{AB}}] = \frac{1}{k_{\text{B}}T} W \quad (2)$$

playing the key role and  $x_{\text{A}}$  and  $x_{\text{B}}$  being the concentrations. At high  $T$  the entropy (the two  $\ln$  terms) will dominate  $F_{\text{mix}}$  leading to statistical intermixing, which we call here a *solid solution* (Figure 4a). The sign of  $\chi$  can serve as a guide for the behavior of the mixture in the low  $T$  limit, when the interaction term becomes larger. Note that this simple model does not explicitly include molecular shape, that is, lattice distortions and strain are not explicitly considered.

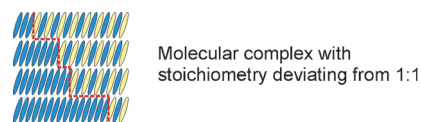
**a. Solid Solution ( $\chi \simeq 0$ ).** For  $\chi \simeq 0$  the mixture remains a *solid solution* at low  $T$ , since the attraction between compound A and B ( $2W_{\text{AB}}$ ) is similar to the attraction of the pure systems ( $W_{\text{AA}} + W_{\text{BB}}$ ). A solid solution is a mixed crystal where guest molecules can randomly replace host molecules. This phenomenon is also known as mixing by substitution,<sup>[88]</sup> illustrated in Figure 4a. A necessary condition for the formation of solid solution crystals by two organic substances is similarity in shapes and sizes of the compounds to allow close packing in a crystal. If these conditions are satisfied, the substitution of host molecules by guest molecules does not lead to a large increase in free energy and a continuous series of solid solutions with different mixing ratios might be possible. In general solid solutions exhibit weak long range order since random inclusion of guest molecules in a host crystal leads to lattice distortions.<sup>[88]</sup> For a more detailed discussion on short and long range order in solid solutions we refer to ref. [88].

**b. Phase Separation ( $\chi > 2$ ):** If the above conditions are not satisfied, that is, if sufficiently unfavorable interaction or steric incompatibility between species A and B is found, the solubility of one compound in a crystal of the second compound is strongly reduced, and we observe phase separation in the low  $T$  limit (Figure 4b).<sup>[91]</sup>

**c. Ordered Molecular Complex Formation ( $\chi < 0$ ):** For  $\chi < 0$  the mixture becomes ordered upon cooling, as the attraction between compound A and B ( $W_{\text{AB}}$ ) is stronger than the attraction in the pure systems ( $W_{\text{AA}} + W_{\text{BB}}$ ). We refer to such an ordered mixture, where sufficiently strong bonds between A and B can be formed, as a *molecular complex* (Figure 4c). In case of formation of such a strong bond, for instance a hydrogen bond, the free energy can no longer be considered as determined mainly by van der Waals forces and entropy. Instead we expect a specific *ordered* molecular arrangement of the complex in respect to the stronger intermolecular interactions present. We note that for the purpose of this review the term *molecular complex* does not necessarily imply a partial or complete charge transfer in the ground state between compound A and B. The strong attraction may also be driven by induced or permanent dipole or quadrupole interaction.

**d. Non-Stoichiometric Complexes:** Many molecular complexes exhibit preferentially a simple stoichiometry such as 1:1

or 1:2. We note that in molecular complexes the crystal structure of the complex may be very different from the pure materials crystal structures. The incorporation of additional guest molecules of either species into a molecular complex would necessarily deform the complex, which would lead to a rapid increase of lattice energy. Due to this, excess molecules of either species are expected to phase separate from the molecular complex crystal (Figure 5).



**Figure 5.** Simplified schematic of phase separation of the non-stoichiometric parts of a molecular complex. Broken lines highlight phase boundaries.

The key difference between solid solutions and molecular complexes is the difference in the solubility curve, which is continuous for solid solutions and discontinuous (in extreme cases a step function) for molecular complexes. In contrast to, for example, alloys of conventional metals, the bulk phase diagram of mixtures of organics is frequently not known, so that the bulk (and equilibrium) reference for the thin films is not available. For typical phase diagrams of bulk solid solutions see ref. [88].

Furthermore, we wish to point out the following on mixed systems:

1. We also mention here inclusion, or clathrate complexes, in which the host compounds form a crystal structure with a framework of large cavities due to strong interaction, for example, hydrogen bonds or other dipole interactions. These cavities are occupied by guest molecules. Some metal-organic frameworks<sup>[92–94]</sup> may appear like this, but since these materials are seen normally in a somewhat different category and they are not further discussed here, we refer to refs. [88, 95, 96].
2. For inorganic atomic systems phase transitions between solid solutions with special mixing ratios (mostly 1:1, 1:2, 1:3) to ordered crystals with long-range order at low  $T$  were frequently observed. For example in metallic alloys  $\text{Cu}_3\text{Au}$  forms an ordered structure.<sup>[97]</sup> A phase transition between a molecular complex or phase separated system at low  $T$  to a solid solution at high  $T$  may be difficult to observe for some systems, since large molecules may not easily exchange lattice sites with their neighbors due to their size. Therefore, the high  $T$  necessary to activate the phase transition may be above the melting or sublimation point of the organic mixture.
3. The above considerations are based on an equilibrium scenario, which serves as a reference framework. In contrast to mixing properties in thermal equilibrium, which are described by minimization of the free energy, for mixing in thin film growth one also has to take kinetic effects into consideration. Kinetic effects can and usually will prevent

the true equilibrium structure to occur, which means that systems tending to solid solutions or tending to ordered complexes are *not* completely mixed as expected in equilibrium and, reversely, systems tending to phase segregation are *more* mixed than expected in equilibrium. Note that an ordered complex is in an equilibrium picture obtained for low  $T$ . Growing the film in the ordered complex structure is potentially difficult, since from the growth perspective frequently some elevated temperature is preferred to obtain a good structure. It may be speculated that true long-range order of a superstructure is probably difficult to achieve by co-evaporation.

- Note that many functional properties depend on concentration in a non-trivial way, which is known already from binary alloys, among others. See for example ref. [98].
- Interactions from a more chemical perspective are reviewed in refs. [240,241].

In the following, we discuss the structure formation for several organic–organic mixed films. An overview of mixing scenarios for some material combinations is shown in Figure 6.

Donor \ Acceptor	PEN	DIP	H <sub>16</sub> CuPc
PFP			
C <sub>60</sub>			
F <sub>16</sub> CuPc			

**Figure 6.** Selected material combinations organized into acceptor materials and donor materials. For each material combination the mixing scenario is depicted as a sketch.

### 2.2.1. Solid Solutions in A:B Systems

As solid solutions in thin films we consider mixtures with continuous or nearly continuous mixing behavior. For a solid solution we expect therefore also a more or less continuous change in lattice parameters dependent on the mixing ratio, if compound A and B have a slightly different shape/size.

Solid solutions have been reported in blends of different phthalocyanines.<sup>[71,99,100]</sup> Phthalocyanines are particularly suitable

for mixtures, since, as long as the central ion is not too big, the molecule retains its flat structure and thus different phthalocyanines are structurally compatible and should intermix well. In ref. [100] it is shown that the change in optical transmission spectra of thin films does not follow a regular pattern for solid solutions of different phthalocyanines. This behavior shows the importance of spectroscopic properties, which are of course also interesting in their own right.

Also mixtures of  $\alpha$ -6T and  $\alpha$ -6P with dihexylsexithiophene seem to exhibit continuous solubility and can therefore be classified as solid solutions.<sup>[101]</sup> In ref. [102] the mixing behavior of conjugated rod-like molecules is systematically studied. In agreement with the concept of structural compatibility in solid solutions explained above, molecules of similar length are forming solid solutions. In contrast, compounds with very different length exhibit phase separation.

### 2.2.2. Phase Separation in A:B Systems

For several combinations of compounds, which are structural/sterically apparently incompatible (e.g. platelet vs. sphere),

for instance for mixtures of C<sub>60</sub> and CuPc<sup>[71,103]</sup> or C<sub>60</sub> and PEN,<sup>[73,104]</sup> pronounced phase separation was observed. For mixtures of DIP and C<sub>60</sub> the coherent domain size of separated material patches increases at elevated growth temperatures.<sup>[26]</sup> Due to kinetic growth effects the heterostructure is, in this case, more mixed than the equilibrium structure, which corresponds to phase separation. With elevated substrate temperatures a structure closer to the equilibrium structure can be realized. Similar behavior was observed for oligothiophene:C<sub>60</sub> mixtures.<sup>[242]</sup> Post-growth heat treatment may also be a route for obtaining an increased domain size and crystal order in phase separated bulk heterostructures.<sup>[90,104]</sup>

Phase separation in thin films was also demonstrated for mixtures of PEN:PEN-quinone.<sup>[105,106]</sup>

### 2.2.3. Arene:Perfluoroarene Molecular Complexes

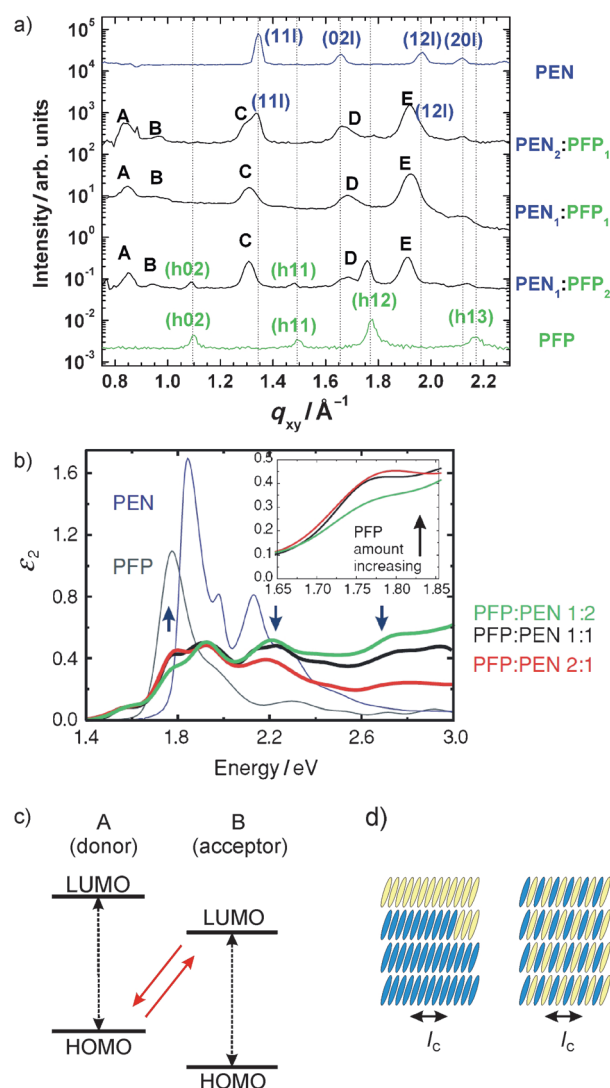
Molecular complexes in thin films have not yet been studied extensively in the literature. An exception are 2D molecular complexes formed in the monolayer region (see Section 2.3.3).

One famous example for complex formation in the bulk is the equimolar benzene:hexafluorobenzene mixture. The melting point of this complex at 23.7 °C, which is significantly

higher than the melting points of the pure components (5.0 °C and 5.4 °C, respectively),<sup>[107]</sup> is evidence for the strong arene:perfluoroarene interaction. Molecular complexes formed due to arene:perfluoroarene interaction are commonly observed<sup>[108]</sup> and explained to be formed by quadrupole interaction.<sup>[109]</sup> The crystal structure of the benzene:hexafluorobenzene complex exhibits displaced face-to-face stacking,<sup>[110]</sup> which is not present in the crystal structures of the pure materials.<sup>[111,112]</sup> This kind of stacking was also observed for other arene:perfluoroarene complexes.<sup>[113,114]</sup> The interaction is strong enough to enable formation of complexes with two structurally very different compounds.<sup>[115]</sup> The pronounced face-to-face stacking was also described as dimerization in the crystal,<sup>[116]</sup> although also arene:perfluoroarene mixtures with a 2:1 ratio were found.<sup>[114]</sup> The arene:perfluoroarene interaction was discussed to exhibit charge transfer characteristics in the ground state for some complexes.<sup>[117]</sup> Studies on other complexes concluded that charge transfer is not present for many arene:perfluoroarene complexes in the ground state.<sup>[116,115]</sup>

The arene:perfluoroarene interaction was also studied in mixed thin films with the combination of PEN and PFP, which was only synthesized recently. These compounds are sterically compatible, since both are derived from the same molecular structure. The system PEN:PFP was studied structurally<sup>[118,119]</sup> as well as spectroscopically<sup>[120,121]</sup> and was shown to exhibit molecular complex formation. With grazing incidence X-ray diffraction (GIXD) data from different mixing ratios (Figure 7a), it is shown that PEN:PFP forms its own structure with 1:1 stoichiometry.<sup>[119]</sup> For mixing ratios deviating from 1:1 the equimolar mixed structure is found, in addition to the pure crystal structure of the respective excess compound. For a detailed discussion of the subtleties of X-ray diffraction on this system, see ref. [119]. Aspects related to the microstructure studied by X-ray microscopy and micro-NEXAFS (near-edge X-ray absorption fine structure) of PEN:PFP mixtures including dichroism are discussed in ref. [122]. Recently, it was shown that a molecular complex is also formed in mixed PFP:DIP thin films.<sup>[123]</sup>

Importantly, upon mixing PEN and PFP, in optical absorption spectra a new transition arises at 1.6 eV (Figure 7b), which is not present in either of the spectra of the pure materials and indeed also below both of the respective gaps.<sup>[121]</sup> Detailed analysis shows that the absorption spectrum of PEN:PFP cannot be explained by a superposition of the spectra of the pure substances. This and in particular the new transition are taken as evidence for coupling between the two components, which is another hint that both compounds form a molecular complex. These findings are further corroborated by photoluminescence spectra, which exhibit a new transition at 1.4 eV related to the one in absorption at 1.6 eV.<sup>[124]</sup> The new excitation might be related to a charge transfer state on the PEN-PFP complex (see schematic in Figure 7c). Note that the optical data (photoluminescence as well as absorption) depend crucially on the respective mixing scenario and the associated coupling length (Figure 7d). Note also that for coupled A:B systems with charge transfer between materials A and B in the excited state one expects the infrared oscillator strength to differ from that of the individual compounds so that the rela-



**Figure 7.** a) GIXD of several PEN:PFP mixtures with different mixing ratio. Reprinted with permission from ref. [119]. b)  $\epsilon_2$  of several PEN:PFP mixtures. The inset shows a close-up of a transition which appears only in a PEN:PFP mixture and not in the pure compounds. Reprinted with permission from ref. [121]. c) Possible charge-transfer excitation on a pair of materials A (donor) and B (acceptor) in a molecular complex. Broken lines indicate transitions of the uncoupled system. d) Mixing scenario may influence the coupling in a thin film. Within the coupling length  $l_c$  may be molecules from only one compound (phase separation) or from two compounds (molecular complex and solid solution).

tive intensities of the different modes are changed. Furthermore, in ref. [120] it is reported that the coupling of neighboring molecules in PEN:PFP mixtures results in a significant shift of the ionization potential in respect to the pure materials.

#### 2.2.4. Charge Transfer Complexes (CTCs)

A further class of systems are charge transfer complexes (CTCs), which exhibit a rather specific A–B interaction and are not the focus of this review. They represent a strong limiting case of complex formation with strong ordering tendency driven by a strong favorable  $W_{AB}$  interaction. The reader is re-

ferred to refs. [125–128] and references therein. CTCs enjoy also a certain popularity in monolayer-based structures and in device-related studies, which is discussed in Section 2.3.3.

### 2.2.5. Doping of A by B versus A:B Mixtures

In conventional semiconductors dopants are employed for increasing conductivity of semiconductors. The concentration of host atoms to dopants is then typically in the range  $10^7$ – $10^4$ :1. Doping for organic semiconductors is also successfully applied, but the conductivity improvement follows a different mechanism. Typically, the host molecule:dopant ratios in organic devices are in the range of  $10^3$ – $1$ :1.<sup>[89, 129–132]</sup> Considering these high concentrations, doped organic semiconductor thin films can essentially be considered as binary mixtures and regarding structural issues follow the mechanisms outlined above to a large extent.

## 2.3. Monolayer-Based Heterostructures

In monolayers evidently the molecular interactions of the two (or more) different compounds composing the monolayer enter *only laterally*. The mechanisms leading to intermixing or phase separation described in Section 2.2 are also relevant for monolayer systems, but they have to be viewed in two dimensions instead of three, which changes the dynamics of diffusion pathways.

For monolayers the relative contribution of the (vertical) interactions with the substrate is commonly more important than for thicker films, which can and usually will contribute to the structure formation with quite interesting phenomena.<sup>[133]</sup> We note that the vertical adsorption distance has been determined for several archetypical organic semiconductors on metal single crystals with high precision using X-ray standing waves.<sup>[134–136]</sup>

This is quite important in the context of understanding the type of interaction (van der Waals contribution as well as nature of the interaction of the  $\pi$ -electron system of the molecule with the metal electrons). Among other things, significant intermolecular distortions upon adsorption have been identified, which have implications for the associated interface dipoles<sup>[11, 137–140]</sup> and in some cases for the growth of subsequent layers.

There are several different types of monolayers, which may be categorized according to their interactions:

1. Van der Waals dominated systems similar to, for example, PEN and DIP as discussed above, deposited by OMBD, with usually comparatively weak interactions (both laterally and vertically). We should note that the interaction with the substrate is not necessarily only van der Waals-like.
2. Self-assembled monolayers (SAMs) in their conventional definition,<sup>[141, 142]</sup> which exhibit a strong and specific interaction of the molecular headgroup with the substrate (e.g. an S–Au bond) and typically hydrocarbon chains attached to the headgroup with non-specific chain–chain interactions laterally.

3. Monolayers with specific in-plane interactions such as H-bonding networks.
4. Monolayers based on charge transfer complex (CTC) compounds.

Furthermore, mixed Langmuir–Blodgett films<sup>[143, 144]</sup> have been studied, however, these are beyond the scope of this review.

In the following, we discuss these systems and their combinations. We shall include in this context work on two monolayers stacked on top of each other, although this may also be seen in the A/B context of Section 2.1 with obvious relevance of *vertical* interactions. The character of these studies is related to true monolayer work and typical methods of surface science, including most notably scanning tunneling microscopy (STM), play a more important role than for thicker films. Moreover, the choice of the substrate tends to be leaning more towards metals and in particular metal single crystals (and some HOPG work) but less than, for example, silicon oxide. Note that surface-mediated (catalyzed) reactions of binary mixtures have been studied as well.<sup>[145, 146]</sup>

### 2.3.1. Mixed Self-Assembled Monolayers (SAMs)

The use of mixed SAMs is a popular approach to tailor the surface energy and the associated wetting properties of the thus functionalized surface, for example, with a selected ratio of hydrophobic and hydrophilic terminations. Other applications concern, for example, the tailoring of the electronic properties or the adsorption behavior. For the background on SAMs and these issues we refer to specialized reviews.<sup>[141, 142, 147]</sup>

A fundamental question for mixed SAMs, in particular in the context of this review, concerns intermixing. Of course, this is a purely 2D issue, and the energetics is also different from that described in Section 2.2. We should point out that despite the rather strong and specific interaction of the headgroup with the substrate, the barrier against lateral diffusion is not necessarily very high, since for diffusion not the absolute absorption energy but the *corrugation*, that is, the energy *difference* between different sites is relevant. The lateral diffusion is thus expected to be higher for, for example, thiols on Au(111) than for silanes on siliconoxide, since the latter are supposed to exhibit a more localized bond. The strength of the driving force for phase separation versus intermixing of course depends also on the nature of the components (including the respective chains and endgroups) involved.

Mixed SAMs have already been employed in the early days of thiol on gold SAMs<sup>[148]</sup> and continue to be employed for various applications. For more recent examples see, for example, refs. [149–153].

### 2.3.2. OMBD on Self-Assembled Monolayers

Self-assembled monolayers (SAMs) coatings are a rather universal approach to engineer surface properties, and they also enjoy enormous popularity for tailoring OMBD growth. Initially PTCDA on SAMs as well-defined organic model surfaces has

been studied mostly with respect to structure-related issues such as the question of epitaxy at the organic–organic interface.<sup>[86, 154, 155, 156]</sup>

As an interesting side-effect it was found that the melting point of the alkanethiol-SAM on Au(111) was substantially enhanced under the PTCDA capping layer compared to the uncovered SAM. We note that a similar (and indeed much stronger) effect of shift of the melting/sublimation point was also observed for organic semiconductors (DIP), but under an aluminiumoxide (i.e. inorganic) capping layer,<sup>[87]</sup> which might be used in applications to enhance the temperature stability.

The deposition on SAMs has later become a rather common strategy for the growth of organic semiconductors such as PEN on silicon oxide surfaces, and it has been found that in many cases prior modification of these surfaces by SAMs improves the performance in terms of, for example, charge carrier mobility.<sup>[157–161]</sup> The role of the SAM in this latter context is to improve the growth of pentacene (by secondary effects, such as changing the interface energy, etc.) rather than to be an active component of an organic–organic heterostructure. Detailed studies of the growth of PEN on SAMs can be found in ref. [162]. The case of PFP on different types of SAMs has been studied by Desai et al.<sup>[38]</sup> Trapping dynamics of DIP on different SAMs were calculated in ref. [163].

Furthermore, the energy alignment, workfunction changes and barrier formation for PEN on benzenethiols on Cu(100) was studied in ref. [164].

### 2.3.3. Mixed OMBD Including CTCs

If van der Waals-type systems are co-evaporated in conventional OMBD, in 2D similar issues arise related to phase separation versus intermixing and possible superstructure formation as in 3D (Section 2.2). A preferred A–B interaction, such as expected for donor–acceptor pairs, would favor intermixing. There might also be an interaction mediated by the substrate. It should be noted that the two components have to be sterically compatible.

Molecular complex formation in the monolayer region, mostly on single crystalline metal substrates or highly oriented pyrolytic graphite, are observed for a variety of combinations of compounds. Most systems are composed of only planar molecules like DIP, perfluorinated copper-phthalocyanine ( $F_{16}CuPc$ ), protonated copper-phthalocyanine ( $H_{16}CuPc$ ),<sup>[165–174]</sup> but  $C_{60}$  was also employed.<sup>[175]</sup> Supramolecular 2D complexes may also exhibit chirality, for example mixtures of PEN and PTCDA.<sup>[176]</sup> The formation of superstructures in some of these systems has been discussed as driven by weak hydrogen bonding ( $C-F\cdots H-C$ ).<sup>[165, 108]</sup> Nevertheless, similar structures were also observed for systems, which do not seem to exhibit a strong specific interaction.<sup>[170, 171, 175]</sup>

In the next section we discuss systems with stronger and more specific binding between the two components, which can lead to still more complex and also open 2D network structures on the surface.

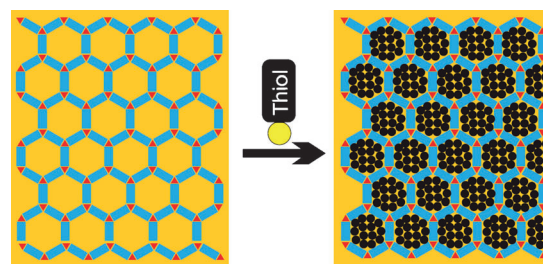
A number of CTCs have also been studied in the monolayer regime, in some cases to modify the charge injection proper-

ties at the interface.<sup>[138, 177]</sup> In these cases, in particular for device structures, this is a (sub)monolayer underneath a multilayer, which serves as the main active layer. It can thus also be seen as an A/B structure, but with A being a (sub)monolayer. Examples for CTCs as true complexes in 2D (i.e. A:B in the monolayer) can be found, for example, in refs. [178, 179]. These may also be seen as part of Section 2.3.4 due to their rather specific interactions.

### 2.3.4. Mixed Monolayers Involving (Potentially Open) Networks with Specific Binding

A different case arises if the adsorbate exhibits more specific lateral interactions, such as H-bonding. This can be exploited for certain compounds to form 2D networks. Recent reviews of the underlying concepts can be found in refs. [180, 181]. Typical examples include refs. [182–187]. An example of a transition from 2D to 1D coordination networks is shown in ref. [188].

If the molecular architecture with its geometry and docking sites for H-bonding is suitable, this can result in a relatively open 2D network on the surface, which may be filled with a second molecular species, thus forming a 2D heterostructure. For an example see Figure 8.<sup>[189]</sup> After generating a 2D network



**Figure 8.** Example of a 2D heterostructure. First a PTCDI-melamine network is formed on Au. In a second step the open cells are filled by thiols. Reprinted with permission from ref. [189].

of PTCDI and melamine on Au(111), the resulting voids could be filled with thiols conventionally employed for the formation of SAMs. Moreover, the resulting three-compound architectures turned out to be sufficiently stable to be used in (patterned) electrochemical deposition of Cu in the underpotential region. More complex 2D nanostructures with four components were prepared with a different approach in ref. [190].

There are further unique opportunities for templating and directed synthesis on the surface with the help of these nanostructures, as for example, shown in ref. [191], but a detailed discussion of these is beyond the scope of the present review.

### 2.3.5. Stacked Monolayers (A/B-Type)

There are of course similarities with the examples presented in Section 2.1, but for monolayers the influence of the substrate is more important, which is why we discuss them separately. Similar to the above sections on monolayer-based systems,

here systems are mostly studied where the compounds are lying down relative to the substrate.

For stacked monolayers a possible epitaxial relationship between A and B can be characterized in detail, since the interface is directly observable. Organic–organic epitaxy for stacked monolayers was found for PTCDA on hexa-peri-hexabenzocoronene (HBC) on HOPG<sup>[192]</sup> and on Au(111).<sup>[193]</sup> One of these studies revealed a new type of epitaxy (line-on-line) so far only observed for organic–organic heterostructures.<sup>[45]</sup> Other examples are quaterylene on HBC heteroepitaxy<sup>[194]</sup> and C<sub>60</sub> on mixed monolayers.<sup>[174]</sup> A stacked system of C<sub>60</sub> on acridine-9-carboxylic acid was shown to exhibit a chiral supramolecular structure.<sup>[195]</sup>

An interesting question concerns the stability of A/B stacked monolayer structures. Remarkably, for certain systems an exchange of stacking sequence of A and B was observed, if the structure with B directly on the substrate was more stable. This type of layer inversion has been observed for PEN/p-6P/Cu(110).<sup>[196]</sup>

Spectroscopic issues were studied, for example, for SnPc on PTCDA on Ag(111).<sup>[197,198]</sup> The authors find that the molecules are lying flat and that the bonding at the SnPc/PTCDA interface is weak. Moreover, the evolution of the interface dipole in this bilayer system was discussed.<sup>[198]</sup> Optical properties of bilayers were also studied. It was found that 1 ML of HBC completely decouples the on-top grown QT electronically from the metal substrate.<sup>[199]</sup>

These monolayer-based A/B systems are expected to be studied further in the future as model systems for both structural relationship as well as the electronic structure at the organic–organic interface.

## 2.4. Other Architectures

Various other architectures are conceivable. We will present two of these here. In particular in the context of device applications, also others have been tested, which is briefly discussed in the next section. We note that of course specific nanostructuring concepts used for single-component films can also be employed for organic–organic heterostructures. As an example, we mention the nanocolumns grown by glancing-angle deposition,<sup>[200,201]</sup> which may be used to grow intentionally rough or otherwise structured A/B structures.

### 2.4.1. Superlattices

Superlattices are essentially *n* periodic repetitions of A/B heterostructures, which can then be denoted as (A/B)<sub>*n*</sub>. One of the ideas behind these is to enhance a (volume-related) signal by the larger amount of material, while at the same time trying to maintain thin film/interface-dominated properties in the individual (thin) layers. This concept is used successfully also in other areas, such as for ferromagnetic multilayers used in magnetic storage technology.

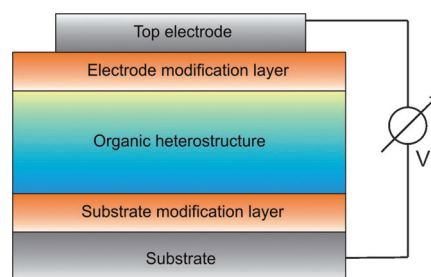
Generally, for organic materials the controlled growth of an ordered multilayer appears to be still more challenging than for most inorganic materials, presumably due to the additional

sources of disorder. In addition, the requirements for lattice compatibility of the materials are different. Some early work on organic–organic superlattices and bilayers can be found, for example, in refs. [23,44,202–204]. More recent efforts are, for example, ref. [58], where for > 5 pairs of NTCD/DB-TCNQ layers sustained azimuthal crystalline alignment was reported.

Kowarik et al. studied PEN/PFP superlattices.<sup>[205]</sup> Using anomalous (soft) XRR near the F(1s) edge, good contrast for XRR was found. Zhu et al. reported on crystalline organic superlattices of H<sub>2</sub>Pc and F<sub>16</sub>CuPc and studied their electronic transport.<sup>[52]</sup>

### 2.4.2. Graded and Other Non-Trivial Concentration Profiles

In particular in the context of device applications such as OPV (Figure 9), in addition to A/B (corresponding to PHJ) and A:B (corresponding to BHJ), other (intermediate) architectures have



**Figure 9.** Example of a typical simplified OPV device structure consisting of an organic heterostructure and additional layers. The organic heterostructure may be a BHJ or PHJ or based on another concept discussed in the preceding sections.

been studied, such as mixed layers sandwiched between pure layers (planar-mixed heterojunction, PM-HJ).<sup>[26,206,207]</sup> A further concept is a graded concentration profile.<sup>[208]</sup> The impact of these different architectures on the device performance has been studied in refs. [13,209].

## 3. Implications for Spectroscopic and Device Properties—and Concluding Remarks

In the preceding sections we outlined the concepts, opportunities, and limitations for growth and structure formation as well as the spectroscopic properties of organic–organic heterostructures. In addition to thick 3D films we have also discussed opportunities related to nano-structuring in 2D, where the interaction with the substrate is particularly important.

As explained in the introduction, in addition to rather fundamental issues such as phase separation versus intermixing or spectroscopic coupling, a strong driving force for research in this area is related to the possible application in devices. These issues can be connected to the local structure and environment on the molecular level or to the somewhat larger-scale morphology (as shown schematically in Figure 1) or to some intermediate length scale (Figure 7 d).

### 3.1. Spectroscopy: Optics, UPS, and Related

Motivated also by the relevance for devices, there have been efforts to determine the energy levels in general and in particular the HOMO and the LUMO using photoelectron spectroscopy and inverse photoemission. In multicomponent systems the relative position has to be determined for a given system individually and cannot be derived directly from the data for single-component systems.

A detailed discussion of energy alignment and so forth at the organic–organic interface, which directly influences charge injection,<sup>[210,211]</sup> is beyond the scope of this review, but we wish to point out that there are efforts to understand it experimentally as well as theoretically mostly at A/B type interfaces (i.e. PHJs). For dedicated reviews we refer to refs. [11,132,137,212–217]. In addition we refer to several examples for the energy-level alignment at the organic–organic interface in the literature.<sup>[67,218–223]</sup> For a further up-to-date collection of energy levels, see ref. [224].

The properties probed by optical spectroscopy as explained in Section 2.2 and ref. [121] are presumably related to possible coupling on a molecular, that is, local scale. This has been observed in several systems and is considered strong evidence for intermixing on a local scale, or, in turn, the structural intermixing is considered a precondition for efficient optical coupling.

We should emphasize that the length scale of coupling is not a binary issue, of course. While for certain properties<sup>[225]</sup> only the immediate environment appears to matter, since the relevant coherence length is on the molecular scale, for others longer range coupling may be found. For instance, for charge carrier transport the coherence length has to exceed molecular length scales if the picture of band transport is approached (Figure 7 d).

In addition, the morphology may also strongly influence the spectroscopic and transport properties; see, for example, refs. [226–228] and references therein.

### 3.2. Implications for Devices

The implications of structure and morphology for device performance are doubtlessly severe, but not easy to cast into one parameter. In fact, it may happen that one device-relevant performance parameter is improved at the expense of another, and it may be extremely difficult to determine the optimum.

Already for organic field-effect transistors (OFETs) this is not trivial<sup>[9,14,57]</sup> for OLEDs and OPV (Figure 9) in addition to transport the optical properties enter, and changes in the structure and morphology affect the various aspects differently. Finally, a complete device features, in addition to an organic heterostructure, further layers, for example, electrodes, layers for improving conductivity, passivation layers, blocking layers and so forth (Figure 9). These add further challenges such as the controlled growth of metals on organic materials,<sup>[229,230]</sup> but a detailed discussion of these issues is beyond the scope of this review.

OPV devices may serve as an example to illustrate the following interrelated issues and their different scales as well as response to structure and growth.<sup>[8,10,231]</sup>

1. Spectroscopic properties, such as coupling of electronic states, absorption and possible (re)emission spectra.
2. Exciton diffusion, affected by structural quality and grain boundaries.
3. Interface optimization for charge separation in OPV.
4. Charge carrier transport (also affected by structural quality and grain boundaries)

These issues have been discussed recently for OPV cells using the rather promising new donor–acceptor pair of DIP and C<sub>60</sub> as PHJ versus BHJ versus PM-HJ geometry, together with XRR, GIXD, atomic force microscopy (AFM), optical and electronic characterization.<sup>[26]</sup> We also refer to various other device studies.<sup>[232–234]</sup> For other work on organic–organic heterostructures combining structural as well as spectroscopic characterization with transport or other device performance parameters we refer to refs. [13,71,99,235] and references therein.

### 3.3. Concluding Remarks

To conclude, we have reviewed basic concepts and recent examples of organic–organic heterostructures, with emphasis on small-molecule organic semiconductors, organized according to A on B (A/B), A co-deposited with B (A:B), heterostructures in the monolayer regime including self-assembled monolayers, and various other architectures including superlattices.

A wide range of scenarios is possible, depending on equilibrium interactions (the balance between internal energy and entropic contributions) including the interactions with the substrate, which are particularly important for monolayers. It should be emphasized that even the bulk equilibrium structure of many organic mixed systems is not yet known. Thus the understanding of mixed films almost inevitably is limited at this stage, since of course the kinetic parameters of the preparation process of thin films increase the complexity of structure formation. Nevertheless, PEN:PPF and PEN/PPF as a model system may help to address these issues more thoroughly and systematically, which has already been exploited partly. The resulting heterostructures have direct consequences for the spectroscopic properties and the question, to which extent *common* energy levels, that is, a spectrum which is not a linear superposition of the respective pure compounds spectra, arises. The formation of excited charge transfer states is intriguing and fundamental in its own right, and is studied of course not only in absorption but also in emission and with time resolution. Spatially resolved experiments on not perfectly homogeneous samples (e.g. with phase boundaries at some variable spacing) will help to elucidate these points further.<sup>[236–238]</sup>

The anisotropy of the interactions offers an enormous potential for nano-structuring in the monolayer regime (2D) as well as for thicker films (3D). While the relevance of both the molecular-scale structure as well as the larger-scale morphology, for the performance of devices and their different architec-

tures is clear, it appears difficult to quantify it in a simple way. Nevertheless, we are at the beginning of understanding the connections, and we expect that progress in the understanding of structure formation and elementary spectroscopic properties will go hand in hand with a systematic understanding and improvement of device architectures.

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