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Controlling the π -Stacking Behavior of Pyrene Derivatives: Influence of H-Bonding and Steric Effects in Different States of Aggregation

Andreas T. Haedler,^[a] Holger Misslitz,^[a] Christian Buehlmeyer,^[b] Rodrigo Q. Albuquerque,^[c] Anna Köhler,^[b] and Hans-Werner Schmidt^{*[a]}

The performance of opto-electronic devices built from low-molecular-weight dye molecules depends crucially on the stacking properties and the resulting coupling of the chromophoric systems. Herein we investigate the influence of H-bonding amide and bulky substituents on the π -stacking of pyrene-containing small molecules in dilute solution, as supramolecular aggregates, and in the solid state. A set of four pyrene derivatives was synthesized in which benzene or 4-tert-butyl benzene was linked to the pyrene unit either through an ester or an amide. All four molecules form supramolecular H-aggregates in THF solution at concentrations above 1×10^{-4} mol L⁻¹. These aggregates were transferred on a solid support and crystallized. We investigate: the excimer formation rates within supramolecular aggregates; the formation of H-bonds as well as the optical changes during the transition from the amorphous to the crystalline state; and the excimer to monomer fluorescence ratio in crystalline films at low temperatures. We reveal that in solution supramolecular aggregation depends predominantly on the pyrene chromophores. In the crystalline state, however, the pyrene stacking can be controlled gradually by H-bonding and steric effects. These results are further confirmed by molecular modeling. This work bears fundamental information for tailoring the solid state of functional optoelectronic materials.

1. Introduction

Supramolecular chromophoric or multichromophoric systems are envisioned to serve as active materials in opto-electronic devices, in particular for organic photovoltaics (OPVs).^[1] For those applications π -conjugated aromatic systems are promising candidates. They can transfer charge and energy, and their absorption and photoluminescence wavelength can be tuned comparatively easily.^[2] Transport as well as the optical properties and thus the device performance depend largely on the

[a]	A. T. Haedler, ⁺⁺ H. Misslitz, ⁺⁺ Prof. Dr. HW. Schmidt Macromolecular Chemistry I and
	Bayreuther Institut für Makromolekülforschung (BIMF) and Bayreuth Zentrum für Kolloide und Grenzflächen (BZKG)
	University of Bayreuth
	95447 Bayreuth (Germany)
	Fax: (+ 49) 921-55-3206
	E-mail: hans-werner.schmidt@uni-bayreuth.de
[b]	C. Buehlmeyer, Prof. Dr. A. Köhler
	Experimental Physics II and
	Bayreuther Institut für Makromolekülforschung (BIMF)
	University of Bayreuth
	95447 Bayreuth (Germany)
[c]	Prof. Dr. R. Q. Albuquerque ⁺
	Experimental Physics II
	University of Bayreuth
	95447 Bayreuth (Germany)
[+]	Current address:
	Institute of Chemistry of São Carlos
	University of São Paulo (USP)
	13560-970 São Carlos-SP (Brazil)
[++]	Both authors contributed equally
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electronic coupling of the π -conjugated systems.^[3] Therefore, the distance between and the relative orientation of the chromophores are crucial and need to be adjusted thoroughly by fine-tuning the molecular structure.^[4] To solve this difficult task, tools and concepts of supramolecular chemistry are utilized. However, a good understanding of the interplay of non-covalent intermolecular interactions like ionic, dipole or Van der Waals interactions and combinations thereof is needed.^[5] Especially H-bonding, hydrophilic–hydrophobic interactions, and steric repulsion are widely used in this context.^[6] Furthermore, the influence of those intermolecular interactions on the π - π stacking of the active chromophoric system depends also on the state of matter and aggregation.

A well-established chromophore is needed to investigate the complex relationship between the molecular structure, the relative orientation of the π -conjugated systems and the resulting optic and electronic properties. Pyrene is a suitable candidate as its optical behavior is well understood in solution, the aggregated and the solid state.^[7] Förster assigned the quenching of fluorescence in pyrenes to the formation of excimers already in 1955, and Birks later investigated this excimer formation in detail.^[8] An excimer may be considered as a pair of molecules that, in the ground state, are bound together only weakly (e.g. in the solid) or not at all (e.g. in solution), and that absorb light as monomers, but that reorient in the excited state and then fluoresce as dimers.^[9,10] The excited dimer (= excimer) fluorescence is broad, unstructured and bathochromically shifted from the monomer fluorescence, and it leads to the two monomers in their ground state.^[11-13] The strong ten-

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dency of pyrene to form excimers prevails both in solution and in condensed matter such as amorphous films, liquid crystals and crystals.^[9,14] Note that in the condensed phase, the pyrene chromophores are usually already in close proximity and often, for example, in the crystal, arranged in sandwich-type pairs. However, for the excimer formation, a displacement leading to closer and/or differently oriented arrangement is still needed.

This excimer emission can also be used indirectly to detect the aggregation process of pyrene derivatives.^[10,15,16] These characteristic properties have been employed in the investigation of pyrene-based tweezer molecules^[17] and multimolecular aggregates of micelles and membranes,^[18] the gelation detection of organic low-molecular-weight compounds,^[19] the inspection of the active sites of enzymes,^[20] the molecular recognition process of artificial receptors^[21] and DNA sequences^[22] and, in the detection of nitroaromatic explosives.^[23]

Herein, we use pyrene derivatives to study the influence of H-bonding and steric effects on the coupling behaviour of the chromophores in different phases. For that purpose a set of four compounds was synthesized consisting of a benzene or a 4-*tert*-butyl benzene group connected to the pyrene through a methylene-ester or -amide linker (Figure 1). The methylene



Figure 1. Pyrene derivatives consisting of different linker and substituents separated by a methylene group from the chromophore.

group breaks the conjugation between the dye and the rest of the molecule, hence, the optical properties of the pyrene is not directly influenced by the linker and the benzene substituent. However, indirect influence is possible due to the potential formation of H-bonds in the case of the amide compounds and due to steric effects arising from the additional *tert*-butyl group.

2. Results and Discussion

2.1. Synthesis and Thermal Properties

The synthetic routes to pyrene-based ester derivatives **1***a*,**b** and their corresponding amide derivatives **2***a*,**b** are shown in Scheme 1. (1-Pyrenyl) methanol was reacted with benzoic acid chloride or *p*-(*tert*-butyl) benzoic acid chloride in chloroform and triethylamine as base to obtain the two ester compounds **1***a*,**b**. For the amide compounds **2***a*,**b** the same acid chlorides were reacted with (1-pyrenyl) methylamine in dry *N*-methyl-2-pyrrolidone (NMP) and pyridine as base. All products are in-



Scheme 1. Synthesis of pyrene derivatives with ester linker 1 a,b and amide linker 2 a,b. i) chloroform, triethylamine, DMAP, 60 °C; ii) NMP, pyridine, 80 °C.

soluble in apolar solvents and show moderate solubility in THF, chloroform, dioxane and DMSO.

The thermal properties of compounds **1a,b** and **2a,b** were determined by differential scanning calorimetry (DSC) and are shown in Table 1. Upon first heating, the ester compounds **1a**

Table 1. Thermal properties of amide and ester compounds determined from DSC measurements (Heating and cooling rate: 20 °C min ⁻¹ under N ₂)							
	T _m [°C] (first/second heating)	T _{cryst} [°C] (cooling)	T _{recryst} [°C] (second heating)	T _g [°C] (on heating)			
1a	133/130	-	70	4 ^[a]			
1b	140/-	-	-	23 ^[a]			
2a	199/196	123	114	54 ^[a]			
2b	248/245	178	-	77 ^[b]			
[a] Determined from second heating. [b] Determined upon first heating of a previously quenched sample.							

and **1b** exhibit melting points (T_m) at 133 °C and 140 °C, respectively. Both compounds do not crystallize upon cooling forming a vitrified supercooled liquid. Consequently, upon second heating 1a and 1b feature glass transitions with temperatures (T_{a}) at 4 °C and 23 °C. On further heating, only **1 a** recrystallizes at 70 °C and subsequently melts at 130 °C. As expected, the glass transition temperature is shifted to higher temperatures for compound 1b due to the bulky tert-butylgroup. In contrast, the amide compounds 2a and 2b possess more pronounced crystalline behavior. Upon first heating the melting points were detected at 199°C and 248°C, respectively, while upon cooling both compounds crystallize at 123 °C and 178°C. Upon second heating 2a features a glass transition at 54°C and recrystallizes at 114°C indicating incomplete crystallization upon cooling. In contrast, compound 2b exhibits complete crystallization upon cooling. Hence, to determine its glass transition temperature, an amorphous sample was prepared by rapid quenching from the molten state. The first heating curve reveals the T_{α} at 77 °C. Similar to the ester compounds, the $T_{\rm q}$ and the $T_{\rm m}$ increase with the introduction of the tert-butyl group. A significant difference between the ester and the amide compounds are higher $T_{\rm m}$ (70 °C to 100 °C) and

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 $T_{\rm g}$ (50 °C) values for the latter. This result is a consequence of the formation of intermolecular H-bonds by the amide units. A similar shift of $T_{\rm g}$ and $T_{\rm m}$ to higher temperatures by substituting ester with amide linkages was recently also reported for trisazobenzene derivatives.^[24]

2.2. Structural Influences on the Pyrene Interaction in Diluted to Concentrated THF Solution

In this section we first focus on discussing the photophysical properties inherent to all four pyrene-derivatives before then considering the differences resulting from the substitutents. The UV/Vis absorption spectra were recorded at different concentrations in THF solution and are shown in Figure 2 for **1a**



Figure 2. UV/Vis absorption spectra of compound **1 a** at different concentrations from 1×10^{-4} to 1×10^{-3} molL⁻¹ in THF normalized to the (0–1) transition at 326 nm; the enlargement shows the 10 times magnified transition to the first electronically excited state for the concentration of 1×10^{-4} molL⁻¹.

as an example and for all compounds in the Supporting Information, Figure S1. For all absorption measurements 1 mm cuvettes were used to account for the high concentrations at which the measurements were performed keeping the maximum OD values below 3. All four compounds show almost identical absorption characteristics (1a,b; 2a,b), which proves the electronic decoupling of the chromophore from the substituent by the methylene spacer. The absorption closely resembles that of pyrene. It shows a very weak feature at about 375 nm and two intense bands, one in the 350-300 nm range and one from 280-240 nm. By comparison with the pyrene spectrum these features can be readily assigned. The weak 375 nm feature is the symmetry-forbidden $S_0 \rightarrow S_1$ transition in pyrene, the first intense band with a (0-0) peak at 344 nm and vibronic replicas at 326 nm, 313 nm and 301 nm corresponds to the pyrene $S_0 \rightarrow S_2$ transition and the peak at 278 nm is due to the pyrene $S_0 \rightarrow S_3$ (0–0) transition, with vibronic replicas at shorter wavelength.^[25] Those characteristics are likewise reported in literature for similar pyrene derivatives.[15]

An interesting detail concerns the relative intensities of the vibrational peaks at different concentrations. The curves in

Figure 2 are normalized to the peak maximum of the (0-1) transition of S₂ at 326 nm, which enables a comparison of the absorption intensities originating from the different vibrational transitions A₍₀₋₀₎, A₍₀₋₁₎, A₍₀₋₂₎, and so forth. With increasing concentration, $A_{\scriptscriptstyle (0-0)}\!/A_{\scriptscriptstyle (0-1)}$ decreases while the ratio of the (0–1) transition to higher transitions is almost identical. Similar behavior is also seen for the vibrational structure of the third electronic excitation. This is unusual. A relative reduction of the 0-0 peak intensity compared to the 0-1 has been reported for the S₁ state of perylene bisimide dyes and of the polymer P3HT. In both cases, it has been taken as indication for the formation of weakly interacting H-aggregates.[26,27] Higher electronic excitations have not been considered explicitly so far in this framework. To the best of our knowledge, this is the first experimental report explicitly describing such behavior in the excitation of two higher electronic states. We note, though, that Winnik, in a review article, also noticed a reduction in relative 0-0 peak height with increasing degree of pyrene association.^[10] Winnik assessed this by considering the 0-0 peak height and comparing it to the intensity of the minimum between the 0-0 and the 0-1 vibrational peak. In view of today's knowledge of electronic interactions between molecules,^[26,28] we consider that the reduction of the 0–0 peak in S_2 and S_3 in the pyrene derivatives may be taken to indicate the formation of such a weakly interacting H-aggregate, that is, associations of pyrene molecules that electronically interact already in the ground state.

In the same concentration range $(1 \times 10^{-4} \text{ mol L}^{-1} - 1 \times$ 10⁻³ mol L⁻¹), dynamic light scattering (DLS) measurements were conducted to obtain an indication for the size of the aggregates. We used a laser beam of 632.8 nm wavelength to avoid the excitation of the pyrene units during the measurements. For all compounds (1 a,b; 2 a,b) the obtained scattering signal implies that at a concentration of 1×10^{-4} mol L⁻¹ in THF, the size of any supramolecular aggregates is below the detection threshold, whereas particles of at least a few tens of nm in size are detected at concentrations above 1×10^{-3} mol L⁻¹. From the DLS measurements we cannot give a reliable size distribution of the particles as the supramolecular aggregates are non-spherical in all cases. The morphology of the supramolecular aggregates at concentrations of $1 \times 10^{-2} \text{ mol L}^{-1}$ was visualized by (SEM) using freeze-dried samples from dioxane (Figures S2.1 and S2.2).

The steady-state photoluminescence (PL) spectra of the compounds in THF were investigated at different concentrations, ranging from 6×10^{-6} to 6×10^{-2} molL⁻¹. The spectra are displayed in Figure 3. The evolution of the monomer fluorescence intensity and the relative $A_{(0-0)}/A_{(0-1)}$ absorption peak height with concentration is shown in Figure 4. All compounds (**1a,b**; **2a,b**) show the same concentration-dependent PL properties. At low concentrations, the PL spectrum shows a vibrational structure that is characteristic for the $S_1 \rightarrow S_0$ fluorescence of molecularly dissolved pyrenes.^[29] With increasing concentration, a broad unstructured emission appears, centered at around 470 nm, that is typical for the excimer fluorescence of pyrene. All four compounds (**1a,b**; **2a,b**) show an identical excimer fluorescence at a concentration of $6 \times 10^{-2} \text{ mol L}^{-1}$, which

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Figure 3. Photoluminescence spectra of compound **2b** at different concentrations from 6×10^{-6} to 6×10^{-2} mol L⁻¹ normalized at 434 nm.



Figure 4. Photoluminescence intensities of the (0–0) transition at 375 nm (left) and the ratio of $A_{(0-0)}/A_{(1-0)}$ (right) of compounds **1a** and **2a** at different concentrations. The shaded area depicts the concentration range in which the formation of aggregates starts to occur.

confirms the formation of the same excimer species in all cases (Figure S3). This excimer fluorescence is first barely discernible at a concentration of 6×10^{-4} mol L⁻¹ (and more clearly visible at 1×10^{-3} mol L⁻¹) and then increases in intensity with concentration. In contrast, when considering the intensity of the monomer fluorescence, the intensity increases with concentration until, at 2×10^{-5} mol L⁻¹, it reaches its maximum and then reduces drastically. The ratio of $A_{(0-0)}/A_{(0-1)}$ in absorption remains constant up to a concentration of 3×10^{-4} mol L⁻¹ and then drops steeply.

For the interpretation of this data it is important to recall that the three spectroscopic signatures, that is, the monomer fluorescence, the excimer fluorescence and the $A_{(0-0)}/A_{(0-1)}$ absorption peak height indicate distinct photophysical processes. 1) The sudden decrease of the $A_{(0-0)}/A_{(0-1)}$ ratio in absorption gives the concentration at which ground-state association begins to occur. In Figure 4, this is shaded gray. In contrast, 2) the fluorescence quenching at a much lower concentration marks the regime where some interaction takes place in the excited state of the molecule, leading to a non-emissive spe-

cies. This species cannot be the sandwich-type pyrene excimer identified by Birks,^[11] because the guantum yield of emission of the pyrene monomer and the pyrene excimer observed by Birks are comparable. For example, in cyclohexane solution it is at 0.65 for the monomer and 0.75 for the excimer and in toluene solution the values are 0.52 and 0.55, respectively.^[25] If the excited monomer were to result in an excimer, according to the reaction $M + M^* \rightarrow E^*$ (E* denotes the excimer $(M + M)^*$), the reduction of monomer fluorescence should be accompanied by a concomitant growth of excimer fluorescence. In the experiment, this is however not the case. We therefore come to the conclusion that the quenching of monomer fluorescence in the intermediate concentration regime (1× 10^{-5} mol L⁻¹–3×10⁻⁴ mol L⁻¹) indicates the formation of a nonemissive precursor-type species. At this stage, we can only speculate on the nature of this species. It is conceivable that the molecular approach and orientation required for the formation of an emissive excimer is impeded in compounds 1 and 2 by the substituents, so that only a non-emissive precursor can be formed. 3) We now focus our attention on the experimental observation that excimer fluorescence is only observable at concentrations in excess of 6×10^{-4} mol L⁻¹, yet not at lower concentration. From the $A_{(0-0)}/A_{(0-1)}$ ratio we know that ground-state associates prevail in this regime, and the DSL measurements tell us these evolve into supramolecular aggregates of a few tens of nm for concentrations above 1× 10^{-4} mol L⁻¹. This implies that for the pyrene-derivatives **1** and 2, the formation of emissive excimers requires a kind of ground-state stabilization that is only available in the environment provided by supramolecular aggregates.

While the decay of the monomer fluorescence with increasing concentration is almost identical for all compounds, a small variation in the ratio of monomer-to-excimer fluorescence intensity can be observed for the different substituents. In order to evaluate how the excimer formation is affected by chemical modification, we have determined the excimer formation rates using time-resolved photoluminescence measurements and analyzing the associated rate equations analogous to the approach taken by Birks et al. in 1963. Birks and coworkers described excimer formation as a process of the type M+ $M^* \rightleftharpoons E^*$ that takes place with a concentration-dependent rate $k_{\rm FM}$ [M] for the forward reaction (excimer formation) and a concentration-independent rate $k_{\rm ME}$ for the reverse reaction (excimer dissociation).^[12] Here, [M] is the concentration of monomers. In addition, the deactivation processes $M^* \rightarrow M$ and $E^* \rightarrow$ M+M are considered with rates k_M and k_E , respectively. After pulsed excitation, the decay of M* and E* is then described by the rate equations $d[M^*]/dt = -(k_M + k_{EM}[M])[M^*] + k_{ME}[E^*]$ and $d[E^*]/dt = -(k_E + k_{ME})[E^*] + k_{EM}[M^*]$. These two coupled differential equations can be solved to give two concentration-dependent decay constants λ_1 and λ_2 from which the excimer formation rate $k_{\rm EM}$ can be extracted by a linear fit to the concentration dependence since $\lambda_1 + \lambda_2 = k_M + k_E + k_{ME} + k_{EM}$ [M].^[12]

For the pyrene derivatives investigated here, we need to consider that the excimer is evidently not formed by the association of two monomers but that it is preceded by the formation of ground-state associates. As we have no experimental

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information on the number of electronically interacting molecules in these associates, we take the heuristic approach of considering dimers. The excimer formation is then described as $D+D^* \rightleftharpoons E^*+D$ with $k_{ED}[D]$ and k_{DE} being the forward and back reaction rate. The deactivation processes are $\mathsf{D}^*\!\!\rightarrow\!\!\mathsf{D}$ and $(E^*+D) \rightarrow (D+D)$ with rates k_D and k_E , respectively. The decay rates can be formulated and analyzed analogously to the Birks-1963 model, $d[D^*]/dt = -(k_D + k_{ED}[D])[D^*] + k_E[(E^*+D)]$ and $d[(E^*+D)]/dt = -(k_E+k_{DE})[(E^*+D)] + k_E[D^*]$. The signals to monitor as function of concentration are then the fluorescence of the (dimer stabilized) excimer (E^* + D) at 470 nm and the fluorescence of the excited dimer D*. What is the spectral signature of the dimer fluorescence? Since the dimer is of a weakly interacting H-aggregate type, as suggested by the absorption spectra, the emission is at the same spectral position than the monomer emission, albeit of a different, that is, weaker oscillator strength. The signal to monitor is therefore the emission at 400 nm.

We have thus measured the photoluminescence decay of the compounds in THF at different concentrations ranging from 2×10^{-4} mol L⁻¹ to 6×10^{-2} mol L⁻¹ using a time-correlated single-photon counting (TCSPC) setup. The chromophores were excited with a 375 nm laser and the time-dependent spectra were recorded at 400 nm and at 485 nm. The typical change in the fluorescence decays with increasing concentration is shown in Figure 5 for compound 2a, along with the concentration dependence obtained for the decay constants λ_1 and λ_2 . The decay curves show a buildup of the excimer emission (gray curve) at short times, for example, below 50 ns at 5.7×10^{-4} mol L⁻¹ and below 10 ns at 6×10^{-2} mol L⁻¹, followed by mono-exponential decay. The dimer emission at 400 nm (black curve) also decays mono-exponentially. The decay of the dimer fluorescence (black curve) becomes faster with increasing concentration as the formation of excimers gets more likely. The excimer fluorescence (gray curve) increases in the beginning due to the time-delayed formation of the excimer species after the initial excitation of the monomer. The excimer fluorescence reaches, as expected, its maximum more quickly with increasing concentration. From those curves, the decay constants λ_1 and λ_2 can be determined and can be plotted against the concentration of monomers (=twice the dimer concentration) (Figure 5). The dependence of their sum on the concentration agrees well with the linear relationship suggested by the kinetic model and gives, a posteriori, further support to the heuristic approach taken. Fitting the data with the equations from Birks et al. yields the relevant values of $k_{\rm ED}$ (Table 2). The entire approach is portrayed in more detail in the supporting information (Figures S4, S5).^[12]

The excimer formation rates (k_{ED}) found in this way for all four compounds (**1 a,b**; **2 a,b**) for the formation of excimers



Figure 5. Time-resolved photoluminescence transients of compound **2a** at $5.7 \times 10^{-4} \text{ mol L}^{-1}$ (left) and $6 \times 10^{-2} \text{ mol L}^{-1}$ (middle) showing the fall-off of the emission at 400 nm (black) and at 485 nm (gray). Right top: Decay rates λ_1 and λ_2 of the emission at 485 nm (\Box) and at 400 nm (**a**) at different concentrations for compound **1a** fitted according to Birks.⁽¹²⁾ Right bottom: Sum of λ_1 and λ_2 plotted against the concentration yielding the expected linear dependency.

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Table 2. Excimer formation rates for pyrene and the four compounds1 a,b and 2 a,b determined from the TCSPC measurements.								
	Pyrene ^[a]	1a	2 a	1 b				
$k_{\rm ED} [10^9 {\rm L s^{-1} mol^{-1}}]$	6.7	6.88 ± 0.7	5.34 ± 0.5	3.96 ± 0.4				
[a] Value was determined by Birks et al. ^[12]								

from pre-existing dimers are between 6.9×10^9 and $3.9 \times 10 \text{ Ls}^{-1} \text{ mol}^{-1}$. This agrees well with the value of $6.7 \times 10^9 \text{ Ls}^{-1} \text{ mol}^{-1}$ determined by Birks et al. for the formation of excimers from individual monomers in the unaltered pyrene.^[12] Within the four compounds the ones with the bulky *tert*-butyl group, **1b** and **2b**, show the lowest excimer formation rates of approximately $3.9 \times 10^9 \text{ Ls}^{-1} \text{ mol}^{-1}$. We attribute this to sterical hindrance. For both the -H- and the -tBu-substituted compounds the ones with the ester linker (**1a** and **1b**) show higher excimer formation rates than the corresponding amide compounds **2a** or **2b**. Hence, the amide linker does not favor the formation of an excimer, but rather hinders it.

We now summarize the insight gained from the spectroscopic investigations in solution. At low concentrations, that is, below 1×10^{-5} mol L⁻¹, the four compounds (**1 a,b**; **2 a,b**) are molecularly dissolved in THF. In an intermediate concentration range (about 1×10^{-5} mol L⁻¹-3 × 10⁻⁴ mol L⁻¹), non-emissive intermediate species are formed. They quench the monomer fluorescence yet do not impinge on the absorption spectra, implying that they may be viewed as a non-emissive precursor to an excimer state. At increased concentrations, that is, above 3×10^{-4} mol L⁻¹ weakly interacting ground state H-aggregates are formed. In contrast to unaltered pyrene, in the compounds (1 a,b; 2 a,b) with the comparatively large side chains, the formation of emissive excimers requires stabilization provided by the aggregate. A significant influence of the structural variations, namely the linker moiety (ester or amide) and the sterical hindrance of the substituted benzene unit on the optical and aggregation properties in THF cannot be observed. Therefore, we conclude that the pyrene chromophores, which are coherently present in all compounds, are the crucial and determining part of the compounds in this concentration regime. Only a closer look at the excimer fluorescence and the excimer formation rates reveal the influence of the variable substitutions on the pyrene chromophore. The ester compound 1 a is most feasible to form excimers. The introduction of the tert-butyl group strongly hinders the excimer formation. The same effect is observed much weaker when the ester group is replaced with an amide linker. The influence of the linker and the bulky tert-butyl group on the pyrene chromophore is just secondary and only observable at concentrations where supramolecular aggregates are present.

2.3. Structural Influences on the Pyrene Interaction in Thin Films

Thin films were prepared as detailed below and investigated in two morphologies, an optically isotropic one and a crystalline one, by using polarized optical microscopy (POM), absorption and fluorescence spectroscopy, and in the case of the amide compounds also by FT-IR spectroscopy. The POM images of the crystalline films are presented in the Supporting Information (Figure S7).

Optically Isotropic Films

All compounds (1a,b; 2a,b) were spin-coated from THF solution at a concentration of 5×10^{-2} mol L⁻¹. At this concentration supramolecular aggregates are present in solution as previously demonstrated in DLS experiments. The fresh films were optically transparent and no crystalline structure could be observed by POM. The absorption spectra are similar for all compounds (Figure S6) and closely resemble that observed in concentrated solution, except for a slight red-shift. Interestingly, the $A_{\scriptscriptstyle (0-0)}/A_{\scriptscriptstyle (0-1)}$ ratio is slightly lower in concentrated solution (about 1.0 for concentrations of $1 \times 10^{-3} \text{ mol L}^{-1}$ and above) than in the thin film (about 1.1). This implies that electronic coupling within aggregates is slightly stronger in solution than in the film, presumably because the local geometry can be optimized more in solution as compared to film. The room-temperature photoluminescence spectra of the fresh films of all investigated compounds do not show any monomer fluorescence. Instead, they show only the same excimer fluorescence that was already observed in concentrated solution, except that the center wavelength shifts from 470 nm in solution to 500 nm in the film due to the different dielectric constant (Figure S8).

From the solution measurements we know that, in contrast to unsubsitituted pyrene, the substituted derivatives (**1a,b**; **2a,b**) only show excimer emission when the excimer geometry is stabilized within a ground state associate. Thus we can interpret the thin film PL data such as to indicate the presence of aggregates in the film. This is not surprising. For example, for the polymers poly(9,9'-dioctyl-fluorene) (PFO) and poly(3-hexylthiophene) (P3HT), it is well known that aggregate formation is enhanced in thin films upon spin-coating when aggregates already existed in the solution used.^[30] The absence of any monomer fluorescence suggests that either no monomers are present, or, any excited monomer state is quenched by energy transfer either to non-emissive states such as the states observed in solution at intermediate concentration or to emissive excimers.

Crystalline Films

The PL spectra are different when the films are processed such as to obtain a crystalline structure. To induce crystallization, the fresh films of amide **2a** and amide **2b** were annealed above T_g at 80 °C and 130 °C. The observation of light transmission under crossed polarizers in an optical microscope confirms the presence of crystalline structures in the film (Figure S7). To obtain further insight into the structural changes associated with the crystallization process, FT-IR studies were performed on the films of the amide compounds (**2 a–b**) in the isotropic and crystalline state. For both compounds, a shift in

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the N–H and the carbonyl stretching vibration to lower wave numbers as well as an increase in the IR absorption intensity is observed during the crystallization process. Both changes in the FT-IR spectra strongly indicate the formation of strong hydrogen bonds.^[31] The shift of the N–H and carbonyl stretching vibration from 3312 cm⁻¹ to 3281 cm⁻¹ and from 1637 cm⁻¹ to 1629 cm⁻¹, respectively, is shown for compound **2a** in Figure 6. Amide **2b** exhibits the same trend but much less pro-



Figure 6. Enlargements of the relevant parts of the FT-IR spectra of a thin film of compound **2a** during the aging process resembling different degrees of crystallization; the N-H stretching vibration (left: around 3300 cm⁻¹) and the carbonyl stretching vibration (right: around 1630 cm⁻¹) are represented.

nounced. This indicates weaker hydrogen bonds due to the steric hindrance of the *tert*-butyl group (Figure S10).

For the ester compounds, a different approach was needed to obtain crystalline films. Unlike the amide compounds, the fresh films of the ester compounds exhibited dewetting at elevated temperatures. Therefore, they were aged at room temperature in the dark for several months to induce crystallization, as confirmed by POM. Hence, in all cases we were able to convert the optically isotropic fresh film into one containing crystallites. The aging and annealing processes were conducted until a stable state was achieved and no further changes could be observed in the POM, FT-IR and photoluminescence spectra at room temperature.

For all compounds except **1b**, the photoluminescence spectra change upon crystallization. During this process, the excimer emission is reduced and simultaneously a structured higher-energy emission rises. This is shown in Figure 7 for ester **1a**.

For a clearer understanding of the molecular behavior in the crystalline state, the thin film photoluminescence was investigated as a function of temperature upon heating from 5 K to 295 K. The spectra at selected temperatures are shown in Figure 8. For all compounds except **1b**, the excimer fluorescence vanishes gradually upon decreasing the temperature, while simultaneously the structured higher energy fluorescence intensity rises. At 5 K, only the structured higher energy emission prevails. In contrast, compound **1b** shows exclusively



Figure 7. Absorption (right) of an amorphous thin film of compound **1a** directly after spin coating and photoluminescence spectra (left) of a thin film of compound **1a** during the aging process resembling different degrees of crystallization.

excimer fluorescence even at 5 K. In general, the relative fraction of excimer emission compared to the higher energy emission is higher in compounds **1b** and **2b** containing the sterically demanding *tert*-butyl group compared to compounds **1a** and **2a**, that only contain a –H atom instead. The relative amount of excimer emission is also higher in the ester-containing compounds (**1a** and **1b**) compared to the amide-containing compounds (**2a** and **2b**).

To understand the changes that take place in the electronic structure upon crystallization, let us first recall that compound **2a** allows for the most ordered structure due to the effect of the H-bonding amide moieties. On the other hand, the sterically demanding *tert*-butyl group and the absence of the stabilizing amide group implies that compound **1b** is likely to have the least ordered structure. This correlates with the fact that compound **2a** shows the lowest relative amount of excimer emission while **1b** exhibits purely excimer emission. Evidently, excimer formation is prevented upon crystallization, while it is promoted by aggregates. This is different to the situation in unsubstituted pyrene, where excimers form in the crystalline state. In fact, in pyrene crystals, the basis of the unit cell is formed by sandwich-type dimer pairs of pyrene molecules that slip horizontally upon photoexcitation to form an excimer.^(9, 25)

How can we understand the absence of excimer emission in crystallites of the substituted pyrene-derivatives? The aggregates prevailing in the optically isotropic film and the crystallites in the films evidenced by the POM patterns differ in the degree of structural order. We propose that the aggregates that are formed in solution or in the non-equilibrium structure of a spin-cast film will be subject to a certain amount of structural variation with regard to molecular orientation or distance. Further, intermolecular distance between two pyrenes may vary at the interface between the ends of two aggregates. Some of these local geometries may be suitable for excimer formation after photoexcitation. As mentioned above, the fact that in freshly spun films only excimer fluorescence is observed

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Figure 8. Photoluminescence spectra at different temperatures from room temperature to 5 K of the four compounds 1 a (A), 1 b, (B), 2 a (C), and 2 b (D) in crystallized thin films. For a comprehensive representation, graph A was normalized at 2.73 eV, graph B at the maximum intensity, graph C at 2.78 eV and, graph D at 2.93 eV. For compound 1 a the decrease of the excimer fluorescence and the increase in monomer fluorescence with reduced temperature are indicated with arrows. This is also commonly observed for compounds 2 a and 2 b.

implies that there is an excimer-site within the exciton diffusion range of any photoexcited chromophore. In contrast, the structure within the crystallites is, by definition, more regular and, as experiment tells us, of a kind that does not allow for excimer formation. It seems that the horizontal slip movement that results in excimers in unsubstituted crystalline pyrene is impeded by the large side chain in substituted crystallized pyrene. Thus, upon crystallization, the number of sites that allow for excimer formation therefore reduces, as manifested in Figure 7.

In this framework, we can interpret the results of Figure 8. For compound **1 b**, which is structurally most disordered, excimer emission is observed at all temperatures even when the light transmission in the POM indicates that crystallites have been formed. This leads to two conclusions. First, in this compound, the remaining structural inhomogeneity is sufficient to result in sites for excimer formation and/or monomer quenching within the exciton diffusion range of each chromophore. Second, since excimer emission occurs at 5 K, it does not require any activation energy. This confirms that sites with mole-

cules already in the excimer geometries must be pre-existing. In passing we point out that the increasing blue-shift of the high-energy emission tail with increasing temperature is an exceptionally nice example for the increase in thermal equilibrium energy in a Gaussian density of states.^[32] We now turn to compounds 1a, 2a and 2b. At 5 K, these compounds show a structured emission with a 0-0 peak at 400 nm and a 0-1 peak at about 425 nm. The relative intensity of the vibrational peaks varies between the compounds. This emission can be attributed to the pyrene monomer unit, possibly slightly modified by weak H-type interaction. (Since the $S_1 \rightarrow S_0$ transition in pyrene is symmetry-forbidden, one cannot distinguish whether the 0-0 peak height is modified due to symmetry-selection rules or due to weak H-type interaction). At 5 K, spectral diffusion of singlet excitons is reduced. Evidently, structural order in the crystalline compounds 1a, 2a and 2b is increased such that there are no sites with excimer geometry within reach at 5 K. At elevated temperatures, the exciton diffusion range increases so that some excimer sites can be populated and

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a spectrum showing both, monomer and excimer fluorescence results.

2.4. Structural Influences on the Pyrene Interaction: Molecular Modeling

CHEMPHYSCHEM

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The conclusions drawn so far on the basis of spectroscopic data are well supported by molecular modeling of the crystallite structure. In order to assess, how the molecules pack, the geometry of the monomers of the esters **1a**, **1b** and the amides **2a**, **2b** were optimized using the B3LYP functional and basis set 6-31G. The optimized structures, together with the predicted partial charges, were used to build and optimize the



Figure 9. Molecular mechanics geometry optimization of hexamer aggregates of the esters **1 a** (A) and **1 b** (B) and the amides **2 a** (C) and **2 b** (D) with the corresponding top views of two stacked molecules. The two orange lines represent the twist of two adjacent pyrene chromophores. Additionally, the distance between two pyrene chromophores and in the case of the amide compounds **2 a-b** the O–H distance of the H-bonding amide moieties are stated. The geometry of the monomers was optimized with DFT.

structure of the aggregates by means of molecular mechanics (MM), from which qualitative results could be obtained (Figure 9).

As expected, the π - π stacking of the pyrene moieties is the dominant driving force towards self-aggregation. This can be seen from the almost parallel orientation of the chromophores in all cases. The distance between the pyrene units is approximately 3.50 Å in the calculated hexamer aggregates, which is in good agreement with crystal structure data of stacked pyrenes featuring a distance of 3.53 Å.^[29] In the case of the amide compounds **2a** and **2b** additional H-bonds are observed in the MM calculations with O–H distances of 1.92 Å and 2.17 Å, respectively. The longer O–H distance of compound **2a** which

can be attributed to the additional bulky *tert*-butyl group. This is in perfect agreement with the previous results from the FT-IR measurements. Furthermore, the sterically demanding *tert*-butyl group of compound **2b** enforces a slight twist in the molecular structure within the calculated hexamer aggregate.

Although in general π - π stacking of the pyrene moieties is present in all calculated hexamer aggregates, slight differences can be observed in the relative orientation of the chromophores. While ester compound **1a** features an almost perfect π - π stacking of the pyrene units an increasing parallel offset is observed for compound **2a** and **2b**. Additionally, in the hexamer aggregate of compound **1b** a rotational twist of adjacent pyrene units is present (orange lines, Figure 9). In compound

> **1 a** the π - π stacking of the pyrene chromophores is the only intermolecular interaction. The columnar stacking is increasingly disturbed by the introduction of the amide and the tert-butyl moiety. The results from the molecular modeling calculations are in good agreement with the previous discussion on thin film properties, whereas the solution properties differ. In the film the steric demand and disorder introduced by the tert-butyl group (Figure 9B,D) correlates well with the enhanced propensity to form excimers which was already observed in the low temperphotoluminescence measurements ature (Fiaure 8B,D). Compound 1b, which has, as already assumed previously, the least ordered structure is unique in two ways-it exhibits a strong rotational twist of adjacent pyrene chromophores and shows exclusively excimer fluorescence even after crystallization and at very low temperatures. On the other hand, H-bonding amide groups as well as the lack of the sterically demanding tert-butyl group promote a more ordered structure reducing the propensity to form excimers in the crystalline state. Note that in the crystalline state, unlike the unchanged pyrene, the investigated molecules (1a,b; 2a,b) do not arrange in a sandwich-type structure but seem to exhibit equidistance.

3. Conclusions

We were able to understand the influence of H-bonding amide linkers and sterically demanding *tert*-butyl groups on the π -stacking of pyrene chromophores in different states of matter. This was achieved by carefully studying a set of four pyrene derivatives exhibiting either an ester or amide linker and with or without a bulky *tert*-butyl substituent. The four compounds were investigated from molecularly dissolved solutions up to concentrations where supramolecular aggregates are formed, as well as in spin-cast films in a virgin and in a crystallized state.

The influence of the linker and the steric hindrance on the pyrene stacking gets more significant the closer the molecules are forced together. In dilute solution up to the threshold concentration for the formation of aggregates the molecular behavior is independent of the variable groups, as all four com-

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pounds show identical spectra and behavior. The four compounds differ, however, from unsubsituted pyrene. Whereas unsubstituted pyrene readily forms excimers in solution from monomers, in the substituted derivatives excimer formation requires additional stabilization within aggregates. The rate of excimer formation depends on the nature of the sidechain. While the excimer formation rate in the ester compound **1a** is comparable to that of unsubstituted pyrene, excimer formation proceeds slower with the amide linker of compound **2a**, and is reduced even more by the bulky substituents of **1b** and **2b**.

In thin films we find that excimers are readily formed within the supramolecular aggregates present in freshly spin-cast films, yet that excimer formation is suppressed by crystallization. Such crystallization can be induced by heating the amidecontaining compounds, which develop intermolecular Hbonds, as well as by aging at room temperature in the case of the ester compounds. The amount of structural order in the crystalline state is strongly dependent on the variable groups. H-bonding amide groups in contrast to ester groups promote a more ordered structure, while the sterically demanding tertbutyl substituent hinders a highly ordered packing of the molecules. In the case of compound 1 b this leads to a strong rotational twist of adjacent pyrene moieties and an enhanced propensity to form excimers in the crystalline structure. Compound 2a on the other hand favors a highly ordered packing resulting in the least amount of excimer fluorescence of all compounds.

With this variety of experiments we were able to understand the molecular behavior and the influence of the variable groups on the pyrene stacking in different states of matter in great detail. This study clearly points out how crucially the molecular design can affect the performance of chromophoric systems.

Experimental Section

Materials and Methods

Solvents were distilled and when necessary dried according to standard procedures. All starting materials were obtained from Aldrich, Alfa Aesar, Fluka or Riedel-de Haën and used without further purification. ¹H NMR spectra were recorded on a Bruker Avance 300 spectrometer. Mass spectra were recorded on a Finnigan MAT 8500 apparatus (EI, 70 eV) using direct injection mode. Elemental analysis (C, H, N) was carried out with an EA 3000 instrument (HE-KAtech).

General Synthetic Route to Pyrenyl-Substituted Esters 1 a,b

1-Pyrenyl-methanol (2.5 g, 10.8 mmol) were dissolved in chloroform in a Schlenk tube under inert gas. Triethylamine (1.8 mL) and 4-dimethylaminopyridine (DMAP) (50 mg) were added. The solution was cooled to 0 °C and benzoic acid chloride (12.0 mmol) was added dropwise. The reaction mixture was boiled for 15 h. After cooling to room temperature, the yellow mixture was filtered (Alox N) and washed with chloroform. The solvent was evaporated and the raw product was dissolved in dichloromethane and extracted subsequently with aqueous HCI (2 m), aqueous NaHCO₃ (5%) and water. The solution was dried over $\rm Na_2SO_4$ and the solvent was evaporated in vacuum.

1 a: Yield 2.9 g of a yellow powder (92%, 8.9 mmol); $R_{\rm f}$ =0.76 (Hexane/THF 2:1); m.p. 133 °C; 1H NMR (300 MHz, [D₆]DMSO, 25 °C, TMS): δ =6.11 (s, 2H), 7.50 (m, 1H), 7.64 (m, 1H), 7.98 (m, 1H), 8.08–8.49 ppm (m, 9H); IR: $\tilde{\nu}$ =1709 cm⁻¹ (C=O); UV/Vis (THF): $\lambda_{\rm max}$ (ε) = 344 nm (31924 mol⁻¹ m³ cm⁻¹); elemental analysis calcd (%) for C₂₄H₁₆O₂ C 85.69, H 4.79, O 9.51; found: C 85.55, H 5.07, O 9.17. **1b**: Compound **1b** was recrystallized from toluene. Yield 1.8 g of a yellowish powder (43%, 4.6 mmol); $R_{\rm f}$ =0.83 (Hexane/THF 2:1); m.p. 140 °C; 1H NMR (300 MHz, [D₆]DMSO, 25 °C, TMS): δ =1.52 (s, 9 H), 6.09 (s, 2H), 7.50 (d, J=8.4 Hz, 1H), 7.90 (d, J=8.4 Hz, 1H), 8.08–8.46 ppm (m, 9H); IR: $\tilde{\nu}$ =1717 cm⁻¹ (C=O); UV/Vis (THF): $\lambda_{\rm max}$ (ε) = 344 nm (32819 mol⁻¹ m³ cm⁻¹); elemental analysis calc (%) for C₂₈H₂₄O₂: C 85.68, H 6.16, O 8.15; found: C 85.66, H 5.95, O 8.39.

General Synthetic Procedure to Pyrenyl-Substituted Amides 2 a,b

1-Pyrenyl-methyl-amine-hydrochloride (2.5 g, 9.4 mmol) was suspended in *N*-methyl-2-pyrrolidone (NMP) in a Schlenk tube under inert gas. Dry pyridine (20 mL) and LiCl (0.05 g) was added and the mixture was stirred for 30 min. The solution was cooled to 0 °C and benzoic acid chloride (9.4 mmol) was added dropwise and the reaction mixture was stirred for 2 h at 70 °C to yield a yellowish solution. After cooling to room temperature, the mixture was precipitated in ice water (600 mL). The mixtures were filtered to retrieve the solid, which was washed with water and dried under vacuum at 80 °C.

2a: Compound 2a was recrystallized from ethyl acetate/hexane mixture (1:1). Yield 3.1 g of a white powder (98%, 9.2 mmol); $R_{\rm f} =$ 0.22 (THF/Toluene 1:20); m.p. 199 °C; 1H NMR (300 MHz, [D₆]DMSO, 25 °C, TMS): $\delta = 5.24$ (d, J = 5.6 Hz, 2 H), 7.45–7.54 (m, 3 H), 7.93– 7.96 (m, 2 H), 8.04–8.54 (m, 9 H), 9.25 ppm (t, J = 5.6 Hz, 1 H); IR: $\tilde{\nu} =$ 1625 (C=O), 3266 cm⁻¹ (N-H); UV/Vis (THF): λ_{max} (ϵ) = 344 nm (29098 mol⁻¹ m³ cm⁻¹); elemental analysis calcd (%) for $C_{24}H_{17}NO: C$ 85.95, H 5.18, N 4.18, O 4.77; found: C 85.91, H 5.07, N 3.79, O 5.04. 2b: Compound 2b was recrystallized from toluene. Yield 2.6 g of a white powder (71 %, 6.6 mmol); $R_{\rm f}$ = 0.31 (THF/Toluene 1:20); m.p. 248 °C; 1H NMR (300 MHz, [D₆]DMSO, 25 °C, TMS): δ = 1.29 (s, 9H), 5.24 (d, J=5.7 Hz, 2H), 7.49 (d, J=8.2 Hz, 2H), 7.89 (d, J=8.2 Hz, 2 H), 8.06–8.53 (m, 9 H), 9.18 ppm (t, J=5.7 Hz, 1 H); IR: $\tilde{\nu}$ =1633 (C=O), 3311 cm⁻¹ (N-H); UV/Vis (THF): λ_{max} (ε) = 344 nm (31 324 mol⁻¹ m³ cm⁻¹); elemental analysis calcd (%) for $C_{28}H_{25}NO: C$ 85.90, H 6.44, N 3.58, O 4.09; found: C 85.51, H 6.07, N 3.70, O 4.76.

Differential Scanning Calorimetry (DSC)

The thermal properties were investigated by DSC measurements with a PERKIN-ELMER DSC7 (standard heating rate: 20 Kmin^{-1}) utilizing 10 mg of the compounds.

Dynamic Light Scattering (DLS)

DLS was performed on an ALV DLS/SLS-SP 5022F compact goniometer system with an ALV 5000/E cross-correlator and a He-Ne laser (632.8 nm). All measurements were performed at concentrations of 1×10^{-4} molL⁻¹, 1×10^{-3} molL⁻¹, and 1×10^{-2} molL⁻¹ of the four compounds **1 a-b** and **2 a-b** in THF.

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Thin Film Preparation

THF solutions (concentration: 5×10^{-2} mol L⁻¹) of the four compounds were spin coated on spectrosil or silicon wafer substrates (30 s, 1020 rpm).

UV/Vis Spectroscopy

UV/Vis spectra on solution and thin film samples were recorded on a JASCO V-670 spectrophotometer. For the measurements in THF the path length of the cuvettes was 1 mm. The extinction coefficient of the 0–0 transition to the S₂ state was for all compounds about 5×10^4 molL⁻¹ in the molecularly dissolved state at $1 \times$ 10^{-4} molL⁻¹ which results in an OD of 0.5. The further increase of the concentration aggregation occurs and the extinction coefficient is substantially reduced so that the OD values are still below 3. Note also that only the extinction coefficients of the two 0–0 transitions to the S₂ and S₃ states are reduced due to aggregation at higher concentrations, while the others remain unchanged.

Photoluminescence Spectroscopy in Solution

For the photoluminescence study THF solutions of the compounds were prepared and investigated with a FluoroMax 3 spectrometer at an excitation wavelength of 344 nm.

Photoluminescence Spectroscopy on Thin Films

The photoluminescence measurements of the thin films were performed on a home-built setup. An argon laser (Coherent Innova 300C) with wavelengths of 354 nm and 361 nm was used for the excitation and a CCD-camera (Andor iDus DU420) was used as detector.

Time-Correlated Single-Photon-Counting (TCSPC) Measurements

The TCSPC measurements were conducted on a FluoTime 200 setup from PicoQuant. The samples were excited with 375 nm laser pulses and the resulting fluorescence was detected with a MCP-PMT detector from Hamamatsu.

Optical Microscopy

The spin coated thin films were investigated between crossed polarizers on an optical microscope (Leica DMRX) equipped with a hot-stage (Mettler, model FP82TM).

Preparation of Freeze-Dried Samples

Supramolecular aggregates of the four compounds were prepared in dioxane (concentration: $1 \times 10^{-2} \text{ mol L}^{-1}$) by heating to dissolution and subsequent cooling to room temperature. One drop of the mixture was given on a DSC pan, frozen in liquid nitrogen/pentane mixture and subsequently dried at high vacuum (0.007 mbar).

Scanning Electron Microscopy (SEM)

The samples were coated using platinum (about 1.4 nm) in a Cressington sputter coater 208HR. The SEM micrographs were recorded on a LEO 1530 FE-SEM (Zeiss, Jena) with a Schottky-field-emission cathode and an in-lens detector.

FT-IR Spectroscopy

The infrared measurements were performed on a PerkinElmer FT-IR Spectrum 100 spectrometer. The solution measurements were conducted in THF solutions at 1×10^{-2} mol L⁻¹ using a NaCl cell of 0.5 mm diameter. For the measurements on thin films, the films had to be spin coated on silica wavers (30 s, 1020 rpm). The resulting films were measured at the ATR unit of the spectrometer.

Modeling

Initially a conformational search was carried out to know the most probable conformation of the molecules **1a**, **1b**, **2a** and **2b**. DFT calculations were carried out for those compounds using the functional B3LYP and basis set 6-31G for all atoms and the program Gaussian 03 was used. No constraints in the geometry optimizations were applied. The optimized geometries were checked by calculation of the vibrational spectra, where no negative frequencies were found. The optimized geometries and the partial charges obtained from the DFT calculations were used in order to build aggregates containing six monomers each. The geometries of the aggregates were then optimized using the Molecular Mechanics and considering explicitly the atomic charges (MM+force field, Hyperchem 7.5 program).

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ARTICLES



The Influence of H-bonding and steric hindrance on the optical properties and the π -stacking of pyrene derivatives is

investigated and described in dilute solution, as supramolecular aggregates and in the crystalline state. A. T. Haedler, H. Misslitz, C. Buehlmeyer, R. Q. Albuquerque, A. Köhler, H.-W. Schmidt*



Controlling the π -Stacking Behavior of \square Pyrene Derivatives: Influence of H-Bonding and Steric Effects in Different States of Aggregation