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Perylene Bisimide Dimer Aggregates: Fundamental Insights into Selfassembly by NMR and UV/Vis Spectroscopy

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Abstract: A novel perylene bisimide (PBI) dye bearing one solubilizing dialkoxybenzyl and one bulky 2,5-di-tertbutylphenyl substituent was synthesized and its aggregation behavior was analyzed by NMR and UV/Vis spectroscopy in various chloroform/methylcyclohexane (MCH) solvent mixtures. In the presence of no less than 10 vol% chloroform, exclusive self-assembly of this PBI dye into π -stacked dimers was unambiguously confirmed by means of both concentration-dependent ¹H NMR and UV/Vis spectroscopic experiments. Based on ROESY NMR, a well-defined π -stacked dimer structure was determined and further corroborated by molecular modeling studies. By varying the solvent composition of chloroform and MCH, the solvent effects on the Gibbs free energy of PBI dimerization were elucidated and

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showed a pronounced nonlinearity between lower and higher MCH contents. This observation could be related to a further growth process of dimers into larger aggregates that occurs in the absence of chloroform, which is required to solvate the aromatic π surfaces. With the help of a single-crystal structure analysis for a related PBI dye, a structural model could be derived for the extended aggregates that are still composed of defined n-n-stacked PBI dimer entities.

Introduction

Aromatic π - π interactions^[1] are one of the important noncovalent forces and exert significant influence on determining the structure and properties of supramolecular assemblies in many key biological processes.^[2] To mimic functional biological structures, aromatic stacks have recently received appreciable attention as futuristic functional nanosystems.^[3] Likewise, in thin films a great number of π - π -stacked organic materials have been employed as effective electronic and photonic molecular devices, such as organic field-effect transistors^[4] and solar cells.^[5] Among the various synthetic π conjugated molecules, pervlene bisimides (PBIs) have been shown to be excellent photofunctional building blocks for light harvesting^[6] and the most promising candidates for ntype semiconductor materials,^[7] because of their high photostability, excellent optical properties, and electron affinity.

Our group is particularly interested in controlling PBI self-assembly and elucidating the relationship between supramolecular structure and emergent optoelectronic properties.^[8,9] In solution, PBI compounds with solubilizing alkyl and alkoxy chains at the imide positions form one-dimen-

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sional infinite columnar aggregates by means of π - π interactions.^[8] The aggregation degrees may be governed primarily by three factors, that is, concentration, temperature, and solvent.^[8b] However, more detailed elucidation of the structure-property relationships are made difficult on account of their random aggregate sizes, that is, they exist as a polydisperse mixture of aggregates, such as dimers, trimers and higher oligomers. In this sense, discrete PBI dimers that are self-assembled by a single π - π interaction are strongly in demand to provide in-depth appreciation of PBI aggregation behavior. To date, it is still a challenge to trap PBI aggregation at the stage of dimer formation. Alternatively, PBI dimer aggregates have been produced in the presence of additional constraints such as covalent linkages or hydrogen bonds.^[10] The Wasielewski group synthesized a PBI dimer in which two PBI units are covalently fixed to a rigid backbone.^[10a] In this way, the PBI dimer arrangement is restricted to a reduced conformational space that facilitates good agreements between theoretical calculation and spectroscopic data.^[11] Nevertheless, the backbone-directed parallel orientation and a π - π distance of 4.5 Å are evidently not the favored arrangement of noncovalent PBI aggregates in solution or the solid state. A similar situation is encountered for calixarene-tethered PBIs synthesized by our group.^[10b] Even though the two perylene planes are restricted in a small space, their intramolecular folding process is dynamic and the spectroscopic features are strongly influenced by the electron-rich calixarene units. The first self-assembled PBI dimers were described by Schenning and Meijer.^[10c] In this case, the PBI π - π stacking appears not to be the dominant driving force for the dimer formation; instead, discrete di-

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merization is achieved with the aid of fourfold hydrogen bonding.

Very recently, our group reported discrete dimer formation of bay-substituted core-twisted PBIs comprising oligo-(ethylene glycol) bridges that surround one side of the perylene plane and therefore prevent aggregation beyond dimers.^[12] In this article, we present an alternative strategy for the uniform dimer formation of bay-unsubstituted PBIs. The discrete dimerization behavior of PBIs is realized on the basis of delicate steric control. A new PBI derivative with both rigid and flexible substituents, one at each imide position, has been designed and synthesized. Notably, Matile and co-workers have recently applied the same concept for naphthalene bisimides (NBIs). However, owing to the smaller π surface of NBIs, the π - π stacking forces are significantly reduced and no in-depth elucidation of the thermodynamics of dimerization was achieved.^[13] For our PBI systems, systematic NMR spectroscopic studies paired with molecular modeling illustrate in detail the self-assembled dimer formation process and the well-defined dimer structure. The thermodynamics of PBI dimerization were determined by variable-concentration ¹H NMR and UV/Vis spectroscopic experiments in a solvent mixture of $CDCl_3/[D_{14}]MCH$ (v:v=1:5; MCH=methylcyclohexane). Finally, the solvent effect on the Gibbs free dimerization energy is investigated by altering the solvent composition and a most interesting further self-assembly process into larger aggregates is observed upon depletion of the good solubilizing solvent chloroform.

Molecular design of the PBI building block: In order to confine the self-assembly of PBI to dimers in solution, elaborate design of the PBI substituents is a prerequisite, since parent PBIs as well as many other π systems^[14] have a strong propensity to form infinite aggregates. In the absence of baysubstituents that exert additional distortion effects,^[12] only modifications at the two imide positions may be taken into account.

In this work we chose the 2,5-di-tert-butylphenyl group as one of the imide substituents, because the ortho-positioned tert-butyl fragment is so bulky that rotation around the C-N bond is essentially impossible (rotational barrier more than 180 kJ mol⁻¹).^[15] This feature has been exploited for the design of NBI receptors for adenines^[16] and NBI oligomers with "locked-in" conformations.^[17] Since the 2,5-di-tert-butylphenyl group is fixed and unsymmetrical, the perylene plane may be distinguished into two facets. For the purpose of this discussion, the *m*- and *o*-perylene facets are defined as being on the same side as the *m*- and *o-tert*-butyl groups, respectively (Figure 1a). At the second imide nitrogen, a benzyl group was installed that may freely rotate around the C-N bond at the methylene linker. Steric repulsion between the imide carbonyls and the benzyl group drives the benzyl ring to be preferentially located above or below the perylene plane. When the benzyl ring is bent away from the opervlene facet, this conformation is assigned the open-ofacet conformation; if the benzyl ring rotates away from m-



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Figure 1. Possible equilibrium between a) open-m/o-facet monomer conformations and b) m-m, m-o, and o-o dimer combinations.

perylene facet, it is called the open-m-facet conformation. As demonstrated in Figure 1a, both open-m- and open-ofacet conformations possess only one accessible perylene facet for π - π interaction as the other facet is blocked by both the imide substituents. The open-o-facet conformation has a half-opened o-perylene facet, whereas the m-perylene facet is fully accessible in the open-m-facet conformation. In the molecularly dissolved state (nonaggregated), rotation of the benzyl group around the C-N bond serves like a "rotating door" making this molecule conformationally switchable between the open-o- and open-m-facet conformations. Both conformations can make use of the accessible perylene facet to form π - π -stacked PBI dimers, ideally in a head-to-tail manner to compensate for the spatial demands of the tertbutyl moieties. Upon dimerization, the benzyl groups will effectively be locked in a single conformation away from the aggregating facet, preventing further aggregation of the selfassembled PBI dimers.

On account of the different monomer conformations, three kinds of π - π -stacked dimers may be envisioned, namely *m*-*m* dimer (*m*-perylene facet versus *m*-perylene facet stacking of two open-m-facet conformations), m-o dimer (m-perylene facet in open-m-facet conformation versus o-perylene facet in open-o-facet conformation) and o-o dimer (o-perylene facet versus o-perylene facet stacking of two open-ofacet conformations) as shown in Figure 1b. While the o*tert*-butyl moiety points towards the π -surface of the *o*-perylene facet, the *m-tert*-butyl group extends outside the *m*-perylene facet. Therefore, m-m dimers should exhibit enhanced face-to-face contact when compared to m-o and o-o dimers. Owing to the potentially larger π - π overlap, we anticipated that the designed PBI building block would prefer m-m dimer formation to m-o and/or o-o dimers under a thermodynamically controlled self-assembly process.

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Results and Discussion

Synthesis of the desired PBI building block: The desired PBI derivative was obtained according to the synthetic route outlined in Scheme 1. Benzyl alcohol $\mathbf{1}^{[18]}$ was convert-



Scheme 1. Synthesis of PBI 6: a) CBr_4 , PPh₃, dry THF, under argon, RT, 18 h, 87%. b) NaN₃, DMF, 105 °C, 3 h, 99%. c) PPh₃, dry THF, RT, 2 h; H₂O, 3 h, 75%. d) Imidazole, 140 °C, 4 h, 50%.

ed to benzyl bromide **2** with an Appel reaction in high yield (87%). Subsequently, the bromide compound **2** was treated with sodium azide to quantitatively afford benzyl azide **3**, which was reduced to benzyl amine **4** in a Staudinger reaction over two steps. Condensation of perylene mono-imide $5^{[19]}$ with benzyl amine **4** furnished the target molecule PBI **6** in a reasonable yield of 50%.

PBI **6** was purified by using recycling HPLC and was fully characterized by ¹H and ¹³C NMR spectroscopy and ESI-TOF mass spectrometry. Although the *tert*-butyl groups provide satisfying dissolution of PBI **6** in chlorinated organic solvents like CH_2Cl_2 or $CHCl_3$,^[20] additional long alkoxy chains on the benzyl ring were introduced simply to raise its solubility in nonpolar solvents, such as MCH, that facilitate aggregation.^[21]

Concentration-dependent ¹**H NMR spectroscopic studies:** NMR spectroscopy is the preeminent method to monitor and quantify the formation of supramolecular architectures.^[22] In dilution experiments, it has been commonly observed that the proton resonance signals are shifted to a higher field upon π - π stacking^[23] and to a lower field upon hydrogen bonding.^[24] Due to the sensitivity of each proton to its magnetic environment, observation of resonance shifts provides a wealth of structural information about the self-assembled aggregates. Nevertheless, this powerful tool has been rarely employed to follow the process of PBI π - π stacking.^[12b,25] The intrinsic obstacle is the fact that PBI aggregates often suffer from extremely broadened NMR signals.^[26]

To shed light into the aggregation behavior of PBI **6**, the concentration-dependent ¹H NMR spectra were recorded at ambient temperature ranging from 0.02 to 40 mM in a solvent mixture of $CDCl_3/[D_{14}]MCH$ (v:v=1:5). This solvent

composition was selected after a series of variations to be the most suitable one to cover the major range of the aggregation process. Upon increasing concentration, the chemical shifts of perylene protons P1–P4 undergo a pronounced high-field shift as illustrated in Figure 2, reflecting the inter-

> molecular association of PBI chromophores through $\pi-\pi$ interactions. It is worthwhile noting that the two different imide substituents and their pronounced impact on the aggregate structure differentiate the perylene protons into four signals P1-P4, and they exhibit distinct concentration-dependent changes in chemical shift. Of these protons, P3 experiences the largest up-field shift $(\Delta \delta = -1.38 \text{ ppm})$, followed by P4 ($\Delta \delta = -1.10 \text{ ppm}$) and then P2 ($\Delta \delta = -0.99$ ppm), while the P1 resonance moves to high



Figure 2. Top: Molecular structure of PBI **6** with designation of its protons. Bottom: Aromatic range of concentration-dependent ¹H NMR spectra of PBI **6** from 2×10^{-5} to 4×10^{-2} M in CDCl₃/[D₁₄]MCH (v:v= 1:5) conducted with 600 MHz NMR at 20 °C. The dotted lines follow the resonance shifts of protons P1–P4 and A6 with the concentration changes.

field only by -0.40 ppm. This phenomenon indicates that the π - π stacking center of PBI **6** is not located at the center of the perylene unit, but displaced towards the P3 and P4 protons. It can be attributed to the steric demand of bulky *tert*-butyl unit, which shifts the aggregation center in the direction to the benzylimide side.

Besides the high-field shift of perylene protons, a significant down-field movement of aromatic A6 signal occurred concomitantly, indicative of hydrogen-bond formation.^[27] In this case, it is ascribed to a weak C–H…O hydrogen bond^[28]

GaA, Weinheim www.chemeurj.org _____3 These are not the final page numbers! between the aromatic A6 proton and carbonyl oxygen atom. However, the A6 proton resides outside the perylene plane and cannot interact with the carbonyl oxygen atoms of its own molecule. Accordingly, because of π - π dimer formation the A6 proton may approach the carbonyl oxygen of the neighboring PBI molecule. It is surprising and unexpected to detect the weak C-H-O interaction in solution, despite the existence of chloroform co-solvent in the system that may also act as a comparable hydrogen-bond donor.^[29] Thus, the weak C-H-O interaction cannot be regarded as a major driving force for PBI 6 self-assembly. As shown in molecular modeling studies (vide infra), the close intermolecular proximity of the A6 proton and the carbonyl oxygen is only a result of PBI 6 π - π stacking. Alternatively, the downfield shift of the A6 proton may be attributed to the magnetic anisotropy of the nearby carbonyl group, resulting in identical structural conclusions. The observation of a C-H-O interaction provides further evidence for tightly stacked PBI chromophores in solution (as close as 3.2- $3.4\;\text{\AA})^{[6b]}$ with a preferential rotational angle of approximately 30°, in accordance with the intrinsic electrostatic attraction of PBI units.^[9] Because proton A6 is positioned above the *m*-perylene facet, it can approach the intermolecular carbonyl oxygen only when PBI 6 is organized into m*m*-type dimers.

The most striking feature revealed in Figure 2, however, is the clean transition from monomers to dimer aggregates without further π - π stacking into extended oligomers, even at higher concentration. During the entire NMR dilution experiments of PBI 6, only a simple pattern of proton resonances is observed that exhibit significant broadening upon increasing concentration. This can be perceived in terms of rapid exchange between monomers and aggregates on the NMR timescale. In principle, at lower temperature the dimer species should become trapped in either M- or P-helical arrangements with concomitant splitting of each of the P1-P4 signals into two signals. Unfortunately, even at 204 K we could not observe such separated resonances (Figure S1 in the Supporting Information). Because in a fast exchange regime the observed chemical shift of a specific proton is the weighted average of chemical shifts in the native (nonexchanging) states, nonlinear least-squares analysis of the concentration-dependent chemical shift variations was performed to probe the thermodynamics of the aggregation process (Figure 3).^[14,30] All of the resonance variations of the perylene and A6 protons fit well to a model that assumes only dimer formation.^[14]

For a two-state equilibrium between monomer (M) and dimer (D) species [Eq. (1)] the equilibrium constant K_D can be characterized by Equation (2).

$$2 M \rightleftharpoons D$$
 (1)

$$K_{\rm D} = c_{\rm D}/(c_{\rm M})^2 \tag{2}$$

Herein, both $c_{\rm D}$ and $c_{\rm M}$ can be expressed by a function of the overall concentration $c_{\rm T}$ and the molar fraction of aggre-



Figure 3. Fitting of the concentration-dependent chemical shift (δ) variations of perylene protons P1–P4 and aromatic proton A6 (see Figure 2) to a dimer model by means of nonlinear least-squares analysis (correlation coefficient more than 0.998).

gated molecules α_{agg} as shown in Equations (3) and (4).

$$c_{\rm D} = c_{\rm T} \, \alpha_{\rm agg} / 2 \tag{3}$$

$$c_{\rm M} = c_{\rm T} (1 - \alpha_{\rm agg}) \tag{4}$$

Since the a_{agg} values at a certain concentration $c_{\rm T}$ can be extracted from the nonlinear least-squares analysis, both $c_{\rm D}$ and $c_{\rm M}$ are obtainable. The aggregation degree a_{agg} of PBI **6** at a concentration of 40 mm reaches nearly 90%, indicating almost complete PBI **6** dimer formation. From the fitting procedure of perylene protons, the dimerization constant $K_{\rm D}$ is generated to be 340–600 m⁻¹, whereas the best fit of A6 proton gives a somewhat higher value of $(900 \pm 50) \,\mathrm{m^{-1}}$. In spite of these deviations, all the values are in the same order of magnitude and of high reliability (correlation coefficients more than 0.998).

Concentration-dependent UV/Vis spectroscopic studies: UV/Vis spectroscopy is an alternative means applicable over a large concentration range to elucidate the thermodynamics for dyes with characteristic absorption bands in the UV/Vis range. The same PBI 6 solutions used for the NMR dilution experiments in the concentration range of 0.02 and 40 mM in $CDCl_3/[D_{14}]MCH$ (v:v=1:5) were subjected to concentration-dependent UV/Vis measurements using cuvettes with path lengths of 0.01-5 mm at ambient temperature (Figure 4). At low concentration, the absorption spectra show well-resolved vibronic bands between 400 and 550 nm for the S_0 - S_1 transition of the single PBI chromophores and can be attributed to the breathing vibration of the perylene skeleton polarized along the long molecular axis. The absorption maximum resides at 521 nm, followed by a second band at 485 nm and a third at 454 nm. The value of $A^{0\rightarrow0}/$ $A^{0 \rightarrow 1}$ at the lowest concentration is greater than 1.6, characteristic of the molecularly dissolved (nonaggregated) state of bay-unsubstituted PBIs.[25a,26a]

Upon increasing concentration, the absorption bands gradually transform, revealing strong electronic coupling between PBI chromophores due to aggregation. A new absorption maximum with a substantially smaller ε value arises

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Figure 4. Concentration-dependent absorption spectra of PBI 6 from 2× 10^{-5} to 4×10^{-2} M in CDCl₃/[D₁₄]MCH (v:v=1:5) recorded at 20 °C. The dotted lines are the calculated monomer (M) and dimer (D) absorptions from available data in terms of the dimer model. Arrows indicate the spectral changes upon increasing concentration. Notably, the spectrum labeled as D shows the absorbance of one PBI 6 dye within the dimer aggregates and the dimer spectrum therefore has a twofold intensity. Inset: Fitting of the concentration-dependent absorbance at 521 nm to a dimer model by means of nonlinear least-squares analysis (correlation coefficient 0.997). For comparison, fitting to the isodesmic model is also shown (dashed line).

at 494 nm, hypsochromically shifted by 27 nm. Such a hypsochromic shift is typical for H-type π - π stacking of parent PBIs. Simultaneously, the prominent monomer absorption at 521 nm flattens at higher concentration.

The whole set of concentration-dependent absorption spectra share several isosbestic points at 532, 505, 471, 460, and 438 nm, implying an aggregation equilibrium between only two explicit species in the system, the monomer and dimer of PBI 6. Nonlinear least-squares analysis of the concentration-dependent UV/Vis data exhibited a good fit to the dimerization model (inset of Figure 4). The resultant dimerization constant $K_{\rm D}$ calculated from the monomer absorption maximum at 521 nm is (910 ± 110) M⁻¹, in close agreement with the values from our NMR analysis.^[31] Based on the recorded absorptions (a_{agg} from 5 up to 90%), the spectra of the pure monomer and dimer species are calculated and shown as dotted lines in Figure 4. The calculated monomer spectrum exhibits an extinction coefficient of $94500 \,\mathrm{m^{-1} \, cm^{-1}}$ at 521 nm and the calculated dimer spectrum is characterized by two main bands at 496 nm ($\varepsilon =$ $39000 \,\mathrm{m}^{-1} \,\mathrm{cm}^{-1}$) and $535 \,\mathrm{nm}$ ($\varepsilon = 27800 \,\mathrm{m}^{-1} \,\mathrm{cm}^{-1}$). The presence of two allowed optical transitions in the dimer spectrum that are displaced to longer and shorter wavelengths with regard to the main transition of the monomer complies with a rotational displacement of the dyes in the π stack.^[8b,32] Remarkably, owing to the very high intensity of the PBI monomer $0 \rightarrow 0$ transition, the important lower energy absorption band of the dimer could not be experimentally obtained (solid lines), but was only revealed by our mathematical analysis of the monomer-dimer equilibrium.

To the best of our knowledge, this study is the first example in which the aggregation behavior of a PBI dye has been fully elucidated by means of concentration-dependent NMR

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and UV/Vis experiments. As the same samples prepared in the deuterated solvent mixture of $CDCl_3/[D_{14}]MCH$ (v:v= 1:5) were used, nonsystematic errors were avoided. According to our general understanding, the spectral changes in dilution experiments are attributed to the excitonic coupling^[32] of the dyes' transition dipole moments for the case of UV/ Vis absorption measurements, and to ring-current effects and hydrogen-bond formation in proton NMR spectra. Herein, the spectral changes due to the three distinct interactions could be followed simultaneously by using the two spectroscopic techniques. As demonstrated in Figures 3 and 4, the concentration-dependent NMR and UV/Vis spectra exhibit spectral changes that are attributed unambiguously to PBI 6 dimerization.

DOSY and ROESY NMR studies: To further corroborate exclusive PBI 6 dimer formation, diffusion ordered spectroscopy (DOSY) NMR experiments were carried out with the sample at a concentration of 40 mM in a $CDCl_3/[D_{14}]MCH$ (v:v=1:5) solvent mixture to evaluate the aggregate size in solution.^[33] Although the aggregation degree reaches nearly 90% at this concentration, analysis of the DOSY spectrum demonstrates a relatively large value of $2.11 \times 10^{-10} \text{ m}^2 \text{s}^{-1}$ for the translational diffusion coefficient D (Figure S2 in the Supporting Information), indicating small-sized assemblies.^[8b] By assuming a spherical shape, the hydrodynamic radius of the small PBI 6 stacks is evaluated based on the Stokes-Einstein equation: $D = k_{\rm B}T/(6\pi\eta R)$, in which $k_{\rm B}$ is the Boltzmann constant, T is the experimental temperature, η is the viscosity of the solvent mixture^[34] and R is the hydrodynamic radius of the species. According to this equation, the hydrodynamic diameter of PBI 6 aggregates was derived to be 3.2 nm. Taking into account the intramolecular distance of 2.4 nm between B2 and C4 protons in open-mfacet conformation of PBI 6 and the alkoxy chain extended length of 1 nm, the detected dimension from DOSY NMR experiment confirms the absence of assemblies larger than dimers of PBI 6.

For PBI 6 dimers, there are three potential combinations: m-m, m-o, and o-o dimers as outlined in Figure 1b. To determine if all three dimer conformations coexist or if one of them is preferred, the spatial proximity of individual protons was probed by the nuclear Overhauser effect (NOE). Cross peaks in such two-dimensional NMR spectra indicate through-space interactions at proximities of 5 Å or less and are particularly useful for determining the structure of aggregates in solution.^[35] Because the mass of dimers of PBI 6 (2074 g mol⁻¹) lies in a range for which the NOESY signal intensity may be fairly low, a ROESY technique was employed instead.

The ROESY NMR experiment was carried out with a degassed sample of PBI 6 in $CDCl_3/[D_{14}]MCH$ (v:v=1:2) at a concentration of 10 mm.^[36] Since the fixed di-tert-butylphenvl group distinguishes the pervlene plane into o- and m-perylene facets, the two distinct tert-butyl protons B1 and B2 residing above and below the perylene plane can be regard-

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Figure 5. a) Part of the ROESY NMR spectrum of PBI **6** at a concentration of 10 mM in CDCl₃/[D₁₄]MCH (v:v=1:2) conducted with 600 MHz NMR at 20 °C. Positive and negative signals are represented by blue and red contours, respectively. b) MM3* geometry-optimized m-m dimer structure of the designed PBI building block with selected intermolecular distances and red labeled protons discussed in the text.

ed as "probing protons" to detect the stacked PBI counterpart located over the o- or m-perylene facet in the dimer structure. As shown in Figure 5a, protons B2 have spatial cross correlation with protons C2 and M1 from the other imide side. Because the rigid perylene skeleton separates the two imide positions intramolecularly far away from each other, the cross signals between protons from different imide sides can be safely assigned to the dimer structure of PBI 6. The presence of cross-peaks for B2 with C2 and M1 is a strong evidence for the exclusive formation of head-totail *m*-*m* dimers. In this manner, the benzyl group is oriented away from the *m*-perylene facet and its methylene protons become spatially adjacent to the *m-tert*-butyl moiety of the nearby PBI molecule. Additionally, the cross-peak between protons A6 and M1 validates the unique m-m dimeric arrangement and also provides further evidence for the weak C-H-O interaction between the A6 proton and carbonyl oxygen as observed in NMR dilution experiments. Only in m-m dimers can the A6 protons intermolecularly approach both M1 protons and carbonyl oxygen atoms.

Furthermore, it should be especially noted that unlike protons B2 and A6, there is no cross-peak that could demonstrate the spatial approach between B1 and remote protons from the benzylimide substituent or perylene core. This finding precludes not only the existence of m-o and o-o dimers, but also the possibility of further cofacial π stacking of m-m dimers. For PBI **6** m-m dimers, the outside facing o-perylene facets are blocked by the o-tert-butyl and benzyl groups, sterically shielding the dimer from further π - π stacking beyond dimer species.

Molecular modeling of PBI dimer structure: To help visualize the structure of the PBI 6 dimer we have performed molecular modeling studies on the basis of our NMR and UV/ Vis measurements. The molecular modeling studies were accomplished with MacroModel using MM3* force-field calculations on the dimer with surrounding chloroform molecules.^[37] We began the calculation with a simple monomeric PBI building block (PBI 6 without the solubilizing long alkoxy chains) and performed an energy minimization until full convergence in search of the optimal conformation. Irrespective of the rotation of the benzyl ring along the C-C bond, only two kinds of optimized geometries bear the lowest calculated potential energy of -25 kJ mol^{-1} , corresponding to the open-m- and open-o-facet conformations (Figure 1 a). The steric repulsion between the benzyl and the carbonyl groups should be the reason why the benzyl group is prone to lie outside the perylene plane. After these two conformations were confirmed as the lowest energy states, two PBI molecules were placed in a parallel face-to-face stacked *m*-*m* dimeric arrangement and energy minimized. The dimer conformational search found a global minimum for the calculated potential energy of -125 kJ mol^{-1} , which corresponds to the *m*-*m* dimeric structure with a certain rotational angle, in accord with experimental observations. For comparison, the calculated energies of m-o and o-o dimers according to the same procedure were -117 and -114 kJ mol^{-1} , respectively. These values are approximately 10 kJ mol⁻¹ higher than that of the minimized m-m dimer. The main energy difference arises from the van der Waals term, which is attractive for π - π stacking and roughly proportional to the area of π overlap.^[1b]

In the geometry-optimized m-m dimer structure illustrated in Figure 5b, the face-to-face stacked PBIs have a π - π distance of 3.46 Å and a rotational angle of 26°. The spatial distance between B2 and C2, B2 and M1, as well as A6 and M1 are within 3 Å, accounting for the through-space correlation detected in the ROESY NMR spectrum. Since there was zero contribution of hydrogen bonds for the potential energy, the weak C-H-O hydrogen bonding was not included in the calculation. In spite of this fact, the A6 protons are directly facing the carbonyl oxygen atoms of the adjacent PBI. There is a 2.94 Å intermolecular H…O distance and the C-H-O bending angle is 152°. As observed in crystal structures and biological systems,^[28b,e] these findings corroborate the existence of the weak C-H-O hydrogen bonds in the PBI 6 m-m dimer. It is worth noting that although a starting geometry with initially parallel aligned PBI units was applied, the geometry-optimized PBI dimers display a certain rotational angle and a slight longitudinal shift, with

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the best π -overlap area close to the benzylimide side of the unsymmetrical PBI building block. This complies with the observation in NMR dilution experiments that perylene protons P3 and P4 exhibit the largest high-field shift, followed by protons P2 and then P1. Overall, the dimer structure obtained from the molecular modeling studies is strongly consistent with our robust experimental results.

Aggregation studies in pure MCH solvent: In the previous variable-concentration NMR and UV/Vis spectroscopic experiments, we employed a solvent mixture of CDCl₃/[D₁₄]MCH (v:v=1:5) to cover the largest possible range of the binding isotherm (α_{agg} from 5 up to 90%). Chloroform is a "good" solvent for PBIs, in which PBI 6 has a high solubility but quite weak aggregation property (Figures S3-S4 in the Supporting Information).^[21] In contrast, MCH is a "bad" solvent, in which PBIs bear a low solubility but very strong aggregation tendency.^[21] Indeed, unlike in the presence of at least 10 vol% chloroform (vide infra, see Figure 9), a complex pattern of proton NMR signals appears in pure MCH at higher concentration and the corresponding DOSY NMR data indicate the formation of large aggregates beyond dimers (Figure 6a and Figure S6 in the Supporting



Figure 6. a) Concentration-dependent ¹H NMR spectra of PBI **6** from 10^{-5} to 10^{-2} M in pure [D₁₄]MCH conducted with 600 MHz NMR at 20°C. b) Concentration-dependent absorption spectra of PBI **6** from 10^{-6} to 10^{-2} M in pure undeuterated MCH recorded at 20°C. Arrows indicate the spectral changes upon increasing concentration. Inset: Fraction of aggregated molecules a_{agg} plotted as a function of Kc_{T} with different $\sigma = K_2/K$ values according to the cooperative model (lines from left to right: $\sigma = 1$, 0.2, 0.1, 0.01 and 0.001), and plot of experimental absorption data of PBI **6** in MCH at 517 nm.

Information). Although these spectra show a number of reasonably defined resonances, a reliable assignment was impossible.

Accordingly, the aggregation behavior of PBI 6 in MCH was investigated by means of concentration-dependent UV/ Vis spectroscopy. Unlike the aggregation process in the solvent mixture, the self-assembly of PBI 6 in pure MCH upon increasing concentration suggests the involvement of some cooperativity.^[38] By applying the simple K_2 -K model,^[39] two equilibrium constants of $K_2 = 2800 \,\mathrm{m}^{-1}$ for dimerization and $K = 14000 \,\mathrm{m}^{-1}$ for subsequent growth were estimated (inset of Figure 6b). From the K_2 value of 2800 m^{-1} , the Gibbs dimerization energy for PBI 6 in MCH was assessed to be $-19.3 \text{ kJ} \text{ mol}^{-1}$ that agrees with the extrapolated $\Delta_{\rm D} G^{\circ}_{\rm MCH}$ value (vide infra). However, the further cooperative aggregation process is puzzling if we take into account the fact that extended PBI π - π stacking beyond *m*-*m* dimers is sterically prevented and that the UV/Vis spectra of aggregate solutions in MCH (Figure 6b) show a close resemblance to those observed for the dimer aggregates in the presence of chloroform (Figure 4). Furthermore, several isosbestic points in Figure 6b corroborate the presence of only two types of spectroscopically distinguished species, that is, monomer and dimer of PBI 6, over the whole concentration range in MCH.

Inspired by the crystal structure of a reference PBI building block 7 (Figure 7b; for further details see Supporting Information and CCDC 876014 at Cambridge Crystallographic Data Centre), we realize that the di-tert-butylphenyl group may occupy the free o-perylene facets of PBI 6 m-m dimer. Such a binding process might be strongly favored owing to a proper rigidification of the benzyl substituent in an ideal conformation for accommodation of the di-tert-butylphenyl subunit of another PBI 6 dimer. Thus, we propose a further growth process for PBI 6 self-assembly in MCH as shown in Figure 7c. In this kind of packing arrangement, the solvophobic effect^[21] and the C–H··· π interaction^[40] should play a significant role.^[41] In the absence of chloroform, which favorably solvates the PBI π surface, PBI 6 dimers need to find a way to exclude the badly solubilizing MCH molecules on top of their "naked" o-perylene facets, and the accommodation of the di-tert-butylphenyl groups just meets this demand. This evidently leads to a rather spectacular change of the self-assembly process from anti-cooperative (in the presence of "good" solvent chloroform) to cooperative (in pure MCH) upon variation of the solvent composition.

A noticeable feature of this further growth process is that it is not readily identifiable by the UV/Vis spectral changes, because they are still governed by excitonic coupling within the PBI dimer stacks, whereas excitonic coupling to neighboring PBIs is negligible owing to a large distance and improper angular relationship^[32] between the dyes' transition dipole moments.^[42] Thus, from the self-assembly process proposed in Figure 7c we are able to rationalize why the UV/Vis spectra in Figure 6b only indicate the existence of π - π -stacked PBI dimer aggregates. In many aggregation studies, similar concentration- and temperature-dependent

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Figure 7. a) Molecular structure of PBI 7. b) Packing of PBI 7 crystal structure (view along c-axis). The co-crystallized CHCl₃ molecules are also shown. c) Schematic representation of the proposed aggregation behavior of PBI 6 in MCH.

changes in the UV/Vis spectra with isosbestic points are taken as evidence for a simple dimerization equilibrium. Herein, we have shown by an in-depth analysis of the binding isotherm with the cooperative K_2 -K model and additional concentration-dependent NMR experiments that such interpretations are not necessarily correct. Indeed, we believe that many dye aggregates, if not the majority, grow into more extended aggregates in solvents with poor solubilizing capabilities for aromatic π surfaces (e.g., aliphatic solvents, protic solvents and water), although the UV/Vis spectra in these solvents are still in accordance with the presence of excitonically coupled dimers.^[9] This is explained by the pronounced distance dependence of the excitonic coupling^[32] prohibiting further insight into the location of additional neighboring molecules, the transition dipole moments of which are not as proximate as those within the π -stacked dimer units.

Solvent-dependent aggregation studies: Solvation is an important factor in controlling the self-assembly of aromatic π stacks.^[21,43] Due to the complexity of the nature of π - π interactions,^[44] the relationship between the solvent polarity and the strength of aromatic interaction is not simple.^[1,2] In recent work, we have examined the magnitude of PBI π - π interaction in water and 16 organic solvents covering the

whole polarity range.^[21] In this study, the Gibbs free binding energies were correlated with different solvent polarity scales including relative permittivity ε_r , the Kirkwood–Onsager function $(\varepsilon_r - 1)/(2\varepsilon_r + 1)$, $E_T(30)$, π^* , and χ_R . The primary conclusion from this study was that the aromatic π - π interaction is the strongest in both nonpolar aliphatic and most-polar protic solvents, and the weakest in chloroaliphatic solvents of intermediate polarity, such as dichloromethane and chloroform.^[21,43d] In a variety of cases, however, it is better to employ a binary solvent mixture to achieve the desired binding strength, particularly in studies of the folding process of oligomers and macromolecules.^[26a, 43a,d, 45] Bv mixing a "good" and a "bad" solvent, the folding degree could be modulated and a straight-line relationship between the Gibbs folding energy and solvent composition was found in the transition region.^[46]

While keeping in mind the special situation in pure MCH solvent (vide supra), we have further examined the solvent effect on the Gibbs dimerization energies of PBI **6** by using solvent titration experiments in a similar way as studied for solvent denaturation of foldamers.^[26a,45] The solvent-dependent UV/Vis absorptions with CHCl₃/MCH compositions from 100:0 to 10:90 were acquired at a fixed concentration of 10 mM and ambient temperature. Accordingly, the absorption changes shown in Figure 8a can only be attributed





Figure 8. a) Solvent-dependent UV/Vis absorption changes of PBI **6** at a concentration of 10 mM recorded at 20 °C, starting in pure CHCl₃ and increasing the volume fraction of undeuterated MCH in 10 vol% steps. Arrows indicate the spectral changes upon increasing the volume fraction of MCH. b) Plot of the $\Delta_{\rm D}G^{\rm o}$ values versus the MCH volume fraction *m*. The solid and dotted lines are the best linear fitting results of the points from m=0 to 0.6 and from m=0.6 to 0.9, respectively. The data point of $\Delta_{\rm D}G^{\rm o}=-19.3$ kJ mol⁻¹ at m=1 was deduced from the K_2 value of $2800 \, \text{m}^{-1}$ in terms of K_2 -K model.

to the solvent effect. Such absorption changes resemble those of the concentration-dependent measurements. With increasing MCH content, the monomer bands decrease gradually and the dimer bands become apparent. The aggregation degree α_{agg} , dimerization constant K_{D} , and Gibbs dimerization energy $\Delta_D G^\circ$ were calculated for each solvent composition according to Equations (5)–(7), respectively.

$$\alpha_{\rm agg} = \frac{(\varepsilon_{\rm A^{0-0}})_{\rm max} - \varepsilon_{\rm A^{0-0}}}{(\varepsilon_{\rm A^{0-0}})_{\rm max} - (\varepsilon_{\rm A^{0-0}})_{\rm min}}$$
(5)

$$K_{\rm D} = \frac{c_{\rm D}}{(c_{\rm M})^2} = \frac{\alpha_{\rm agg}}{2(1 - \alpha_{\rm agg})^2 c_{\rm T}}$$
(6)

$$\Delta_{\rm D}G^{\circ} = -RT\ln K_{\rm D} \tag{7}$$

If we neglect the possibilities of preferential solvation, the Gibbs free dimerization energies at the respective solvent composition should be proportional to their component in the solvent mixture: see Equations (8) and (9) in which *m* is the volume fraction of MCH in the solvent mixture, and $\Delta_{\rm D}G^{\rm o}_{\rm CHCl_3}$ and $\Delta_{\rm D}G^{\rm o}_{\rm MCH}$ represent the Gibbs free energy contribution for the PBI **6** dimerization in pure CHCl₃ and MCH, respectively.

$$\Delta_{\rm D}G^{\rm o} = m\Delta_{\rm D}G^{\rm o}_{\rm MCH} + (1-m)\Delta_{\rm D}G^{\rm o}_{\rm CHCl_2} \tag{8}$$

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$$\Delta_{\rm D} G^{\rm o} = m (\Delta_{\rm D} G^{\rm o}_{\rm MCH} - \Delta_{\rm D} G^{\rm o}_{\rm CHCl_3}) + \Delta_{\rm D} G^{\rm o}_{\rm CHCl_3}$$
(9)

In Figure 8b, the $\Delta_D G^o$ values were plotted against the MCH content m in the range of m=0 and 0.9. The points can be fitted to two linear relationships with the intersection at m=0.6. At low MCH contents (from m=0 to 0.6), the linear fitting can be interpreted in terms of Equation (9), giving rise to an extrapolated $\Delta_{
m D} G^{
m o}_{
m MCH}$ value of $(-16.0\pm$ 0.2) kJ mol⁻¹. In contrast, upon utilization of the data points for higher MCH contents (from m = 0.6 to 0.9), the dotted fitting line crosses the y axis at m = 1.0 for an ideal $\Delta_{\rm D} G^{\rm o}_{\rm MCH}$ value of (-19.8 ± 0.1) kJ mol⁻¹. In our opinion, this discrepancy points to a selective solvation phenomenon. In the presence of up to 60 vol % MCH in CHCl₃, PBI π faces are preferentially solvated by CHCl₃ molecules. At higher MCH contents, however, preferential solvation by the decreasing fraction of CHCl₃ molecules becomes disfavored for entropic reason (i.e., CHCl₃ molecules have to be considered like guest molecules dissolved in MCH) and PBI dimerization involving the *m*-perylene facets becomes strongly triggered by the solvophobic effect of the MCH solvent.

¹**H NMR linewidths**: Further fundamental insights into PBI aggregation can be derived from the signal broadening in NMR spectra. The widths of the ¹H NMR signals of PBI **6** exhibit a pronounced dependence on $CDCl_3/[D_{14}]MCH$ ratio (Figure 9), concentration (Figure 6a), and temperature



Figure 9. Partial ¹H NMR spectra of PBI **6** recorded with 600 MHz NMR at a concentration of 10 mM in pure CDCl₃ and $[D_{14}]$ MCH solvents as well as in solvent mixtures of CDCl₃/[D₁₄]MCH.

(Figure S1 in the Supporting Information). For a high chloroform fraction, a small PBI **6** concentration and the ambient temperature sharp signals are observed corresponding to a weighted average of monomer and dimer resonances with fast exchange between each other. For the opposite extreme (pure MCH and high PBI **6** concentration) a large number of individual ¹H NMR signals with moderate linewidths appear that can be attributed to coexisting dimers and oligomers with slow exchange resulting in individual resonances for each species. The broad NMR signals in the

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intermediate region can thus be interpreted by coalescence effects as the crossover from slow to fast exchange processes. All three types of discussed spectra (fast, intermediate, and slow exchange) can be observed by varying the solvent from pure chloroform to pure MCH at a fixed PBI **6** concentration (Figure 9). The spectral changes (chemical shifts, linewidths) upon increasing the MCH fraction from 0 to 90 vol% strongly resemble those monitored for rising concentration of PBI **6** at a constant $CDCl_3/[D_{14}]MCH$ ratio (Figure 2).

In additional investigations, we kept the dimerization degree α_{agg} constant (around 50%) and compared the ¹H linewidths under different experimental conditions, starting with a PBI **6** concentration of 2 mM in a CDCl₃/[D₁₄]MCH (v:v=1:5) mixture at 25 °C. Upon increasing the concentration of PBI **6** either the chloroform content (Figure S8 in the Supporting Information) or the temperature (Figure S9 in the Supporting Information) have to be augmented to ensure a constant α_{agg} . The narrowing of NMR signals observed for both cases can be attributed to kinetically less stable dimers at larger chloroform content or higher temperature, resulting in faster exchange rates.

These results suggest that the onset of NMR signal broadening with increasing MCH content and/or PBI **6** concentration correlates with the selective solvation phenomenon discussed in the previous paragraph. For a sufficient amount of chloroform, the PBI π faces are preferentially solvated by chloroform molecules connected with a fast exchange between monomers and dimers due to the "weakening" of π - π interactions by the "good" solvent chloroform. Below a critical chloroform content (which increases with PBI **6** concentration) the exchange rate between monomers and dimers slows down, owing to the solvophobic effect of MCH. In addition, dimers start to assemble into larger oligomers resulting in a further decrease of exchange frequencies in pure MCH solvent.

Conclusion

In this work, we reported a novel PBI building block featuring one rigid and one flexible substituent at the two imide positions. By virtue of the steric demand of these substituents, the designed PBI is prone to form discrete π - π -stacked dimers rather than extended oligomeric π stacks. The dimerization process of PBI 6 has been elucidated by means of nonlinear least-squares analysis of the concentration-dependent ¹H NMR and UV/Vis spectra in terms of a dimer model. DOSY NMR spectroscopy further confirmed the absence of aggregates larger than dimer. The observed shifts of proton resonances in NMR dilution experiments indicate the formation of a head-to-tail π stack composed of two PBIs with a certain rotational displacement. Detailed elucidation of the head-to-tail m-m dimer structure with a rotational angle of about 30° is corroborated by means of ROESY NMR spectra associated with molecular modeling studies. Consequently, we have not only programmed PBI

dimer formation driven solely by π - π interactions, but also fully described the well-defined dimer structure in solution.

Furthermore, the π - π stacking of PBI 6 was investigated in different CHCl₃/MCH solvent mixtures. Two regimes with a linear relationship of the Gibbs free energy versus the solvent composition are found between 0 and 60 vol% MCH and between 60 and 90 vol% MCH in CHCl₃ (for PBI 6 at a concentration of 10 mm), suggesting a selective solvation effect. Accordingly, preferential solvation of the π surfaces by chloroform molecules weakens the PBI π - π interaction in solvent mixtures as long as the CHCl₃ content is of sufficient magnitude (\geq 40%). In pure MCH, the free π face suffers from bad solvation, which triggers the formation of larger aggregates according to complex ¹H NMR spectra, DOSY NMR studies, and UV/Vis dilution experiments. The last set of experiments indeed revealed a cooperative selfassembly process that cannot be explained by a simple PBI dimerization process. Based on the single-crystal structure of a similar PBI building block, a packing model was elaborated for the extended aggregation that does not involve additional contacts between PBI π faces beyond those given in the dimer units, in compliance with the UV/Vis spectra of the aggregates. To the best of our knowledge, this is the first time that often observed apparent equilibria between two spectroscopically distinguished species with well-defined isosbestic points in concentration- or temperature-dependent UV/Vis experiments were analyzed not only in terms of a simple dimerization (monomer-dimer) or an isodesmic growth (monomer-oligomer). Instead, we have provided experimental evidence for the formation of larger aggregates composed of π -dimeric units. The formation of such aggregates by various types of complex self-assembly pathways^[47] might indeed be very common, but has been widely overlooked in the past. Our efforts to program discrete self-assembled PBI stacks are still in progress. Our next target is to produce uniform and kinetically stable PBI aggregates.

Experimental Section

All solvents and reagents were purchased from commercial sources and used as received without further purification, unless otherwise stated. Dry solvents were purified according to literature procedures.^[48] Benzyl alcohol 1 and perylene monoimide 5 were synthesized as described in literature.^[18,19] Thin-layer chromatography (TLC) was conducted on aluminum plates coated with silica gel (60 F254, Merck). Column chromatography was performed using silica gel (Geduran Si 60 from Merck, particle size 0.040-0.063 mm) as stationary phase. Recycling preparative HPLC was performed on a system (JAI LC-9105) equipped with a photodiode array UV/Vis detector (JAI 3702) and an RI detector (JAI RI-7 s) by use of a semipreparative NUCLEOSIL 100-5 NO2 column (Macherey&Nagel). For HPLC separation, HPLC grade solvents (CHCl₃ and MeOH) from VWR (Darmstadt, Germany) were used. High-resolution electrospray ionization (ESI) mass spectra were measured on a MicroTOF Focus instrument (Bruker Daltronik GmbH) and MALDI-TOF measurements were carried out on a Bruker Autoflex II.

UV/Vis absorption studies: The UV/Vis absorption measurements were performed on a Perkin–Elmer Lambda 35 spectrometer making use of conventional quartz cells with 0.01–10 mm path length to cover a large concentration range. The slit width and the scan speed were set to be

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1.0 nm and 120 nm min⁻¹, respectively. The temperature was controlled with a PTP-1+1 Peltier temperature programmer (Perkin-Elmer). In order to avoid nonsystematic error, all the samples having a concentration of more than 0.5 mm were individually prepared by carefully dissolving the precisely weighed compound in solvents, assuming that the volume of the compound is negligible after dissolution. The samples with a concentration less than 0.5 mm were diluted ten times from a corresponding stock solution. For a comparative study with NMR spectra. UV/Vis dilution experiments were conducted in the deuterated solvents. NMR spectroscopic studies: 1H, 13C, DEPT, COSY, HSQC, and HMBC NMR spectra were recorded in standard 5 mm NMR tubes on a Bruker Avance 400 and/or a Bruker DMX 600 spectrometer with TMS or residual undeuterated solvents as internal standard (7.26 for CHCl₃ and 77.00 ppm for CDCl₃). The 2D ROESY and DOSY data were acquired with the 600 MHz instrument, which was equipped with 5 mm $^{13}C/^{1}H$ cryoprobe with a z axis gradient coil capable of producing pulsed magnetic field gradients of 55 G cm⁻¹. For low- and high-temperature NMR measurements, the temperature was calibrated using NMR samples of 4% CH₃OH in [D₄]methanol and 80% ethylene glycol in [D₆]DMSO, respectively. Prior to 2D ROESY NMR measurements, the deuterated solvents and the NMR tubes used were degassed by bubbling with dry argon gas. Alternating-phase 180° pulses were applied during the mixing time of 200 ms for the ROESY spectra to suppress unwanted TOCSY contributions.^[49] In the DOSY experiments, the suppression of flow effects owing to temperature gradients in the coil of the cryoprobe was achieved in two different ways: 1) using the stimulated echo BPP-LED pulse sequence^[50] (longitudinal eddy current delay sequence with bipolar gradient pulse pairs for diffusion and additional spoil gradients after the second and fourth 90° pulse) in which convection in the z direction was suppressed by sample rotation^[51] and 2) by the corresponding double stimulated echo-pulse sequence^[52] (without sample rotation and with spoil gradients after the second, fourth, and sixth 90° pulse) in which the double stimulated echo results in a compensation of the flow effects. The following acquisition parameters were used for both methods: duration δ of a bipolar gradient pulse 4 or 6 ms, diffusion time Δ 50 ms, eddy current delay 5 ms. The diffusion time Δ was kept constant in each DOSY experiment while the sinusoidal diffusion gradients were incremented from 2 to 95% of maximum gradient strength in 32 linear steps.

3,5-Bis(dodecyloxy)benzyl bromide (2): A mixture of compound 1 (1.52 g, 3.2 mmol), carbon tetrabromide (1.60 g, 4.8 mmol, 1.5 equiv), and triphenylphosphine (1.26 g, 4.8 mmol, 1.5 equiv) in anhydrous THF (16 mL) was stirred under an argon atmosphere at room temperature overnight (ca. 16 h). The solvent was removed under reduced pressure and the residue was washed with MeOH (3×10 mL). After that, the crude product was purified by column chromatography on silica gel with CH_2Cl_2/n -hexane (v:v=1:1) as eluent. Yield: 1.49 g (2.76 mmol, 87%) as a white solid; TLC (CH₂Cl₂/*n*-hexane=1:1): $R_f = 0.83$; m.p. 48–49°C; ¹H NMR (400 MHz, CDCl₃): $\delta = 6.51$ (d, J = 2.0 Hz, 2H; Ph-H), 6.38 (t, J=2.0 Hz, 1H; Ph-H), 4.40 (s, 2H; PhCH₂Br), 3.93 (t, J=6.8 Hz, 4H; OCH₂CH₂), 1.76 (quint, J=6.8 Hz, 4H; OCH₂CH₂), 1.41-1.48 (m, 4H; OCH₂CH₂CH₂CH₂), 1.27 (brs, 32H; alkoxy-H), 0.89 ppm (t, J=7.0 Hz, 6H; CH₂CH₃); HRMS (ESI-TOF, pos. mode): m/z calcd for C₃₁H₅₆BrO₂: 539.34582 [M+H]+; found 539.34587; elemental analysis calcd (%) for C₃₁H₅₅BrO₂: C 68.99, H 10.27; found: C 68.72, H 10.42.

3,5-Bis(dodecyloxy)benzyl azide (3): A mixture of compound **2** (1.08 g, 2.0 mmol) and sodium azide (390 mg, 6.0 mmol, 3.0 equiv) in anhydrous DMF (20 mL) was heated to 105 °C for 3 h. After cooling, the DMF solvent was removed under reduced pressure. The residue was dissolved in ethyl ether (20 mL) and washed with H₂O (3×20 mL) and brine (3× 20 mL). The aqueous layer was extracted with ethyl ether (3×20 mL) and the combined organic layers were concentrated in vacuum and purified by column chromatography on silica gel with CH₂Cl₂/*n*-hexane (v:v=1:1) as eluent. Yield: 0.99 g (2.0 mmol, 99%) as a white solid; TLC (CH₂Cl₂/*n*-hexane=1:1): R_1 =0.76; m.p. 36–37 °C; ¹H NMR (400 MHz, CDCl₃): δ =6.43 (d, J=2.4 Hz, 2H; Ph-H), 6.41 (t, J=2.4 Hz, 1H; Ph-H), 4.25 (s, 2H; PhCH₂N₃), 3.94 (t, J=6.4 Hz, 4H; OCH₂CH₂), 1.77 (quint, J=6.4 Hz, 4H; OCH₂CH₂), 1.41–1.48 (m, 4H; OCH₂CH₂), 1.27 (brs, 32 H; alkoxy-H), 0.88 ppm (t, J=6.8 Hz, 6H; CH₂CH₃). HRMS

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(ESI-TOF, pos. mode): m/z calcd for $C_{31}H_{56}N_3O_2$: 502.43670 $[M+H]^+$; found: 502.43631; elemental analysis calcd (%) for $C_{31}H_{55}N_3O_2$: C 74.20, H 11.05, N 8.37; found: C 74.26, H 11.21, N 8.35.

3.5-Bis(dodecyloxy)benzyl amine (4): Triphenylphosphine (0.65 g, 2.5 mmol) was added to a solution of compound 3 (0.61 g, 1.2 mmol) in THF (10 mL). After the reaction mixture was stirred for 2 h at room temperature, distilled H₂O (0.2 mL, 11.1 mmol) was added and resulting mixture was stirred for another 3 h. After reaction, the solvent was removed under reduced pressure. The residue was dissolved in CH2Cl2 (20 mL) and washed with 5% NaOH solution (3×20 mL). The aqueous layer was extracted with CH2Cl2 (3×20 mL) and the combined organic layers were concentrated in vacuum and purified by a short column chromatography on silica gel with CH2Cl2/MeOH (v:v=97:3) as eluent. The ¹H NMR and MS indicate a mixture of benzyl amine product and triphenylphosphine oxide byproduct (molar ratio about 1:1), which was used for next step without further purification. Yield: 0.43 g (0.9 mmol, 75%) as a white solid; TLC (CH₂Cl₂/MeOH=9:1): R_f =0.47; ¹H NMR (400 MHz, CDCl₃): $\delta = 6.45$ (d, J = 2.4 Hz, 2H; Ph-H), 6.34 (t, J = 2.4 Hz, 1H; Ph-H), 3.92 (t, J=6.6 Hz, 4H; OCH₂CH₂), 3.80 (s, 2H; PhCH₂NH₂), 1.77 (quint, J=6.6 Hz, 4H; OCH₂CH₂), 1.40–1.47 (m, 4H; OCH₂CH₂CH₂), 1.27 (brs, 32H; alkoxy-H), 0.88 ppm (t, J=6.8 Hz, 6H; CH₂CH₃); HRMS (ESI-TOF, pos. mode): m/z calcd for C₃₁H₅₈N₁O₂: 476.44621 [*M*+H]⁺; found: 476.44612.

N-[3,5-Bis(dodecyloxy)benzyl]-N'-(2,5-di-tert-butylphenyl)perylene-

3,4:9,10-tetracarboxylic acid bisimide (6): A mixture of compounds 5 (116 mg, 0.20 mmol), 4 (240 mg, 0.75 mmol), and imidazole (10 g) was stirred under an argon atmosphere at 140 °C for 4 h. Before cooling, the reaction was directly quenched with 2.0 M HCl (50 mL) and stirred for another 1 h. The resulting precipitate was separated by filtration and washed with MeOH (3×10 mL). After drying in vacuum, the crude product was purified first by silica gel chromatography (CH2Cl2 as eluent) and then by using recycling HPLC (CHCl₃ as eluent). Yield: 102 mg (0.10 mmol, 50%) as a deep red solid; TLC (CH₂Cl₂): $R_{\rm f}$ =0.34; m.p. 168–169 °C; ¹H NMR (400 MHz, CDCl₃): $\delta = 8.24-8.68$ (m, 8H; perylene protons), 7.61 (d, J=8.8 Hz, 1 H; Ph-H), 7.49 (dd, J¹=8.8 Hz, J²=2.4 Hz, 1H; Ph-H), 7.30 (t, J=2.4 Hz, 1H; Ph-H), 6.66 (d, J=2.4 Hz, 2H; Bn-H), 6.36 (t, J=2.4 Hz, 1 H; Bn-H), 5.29 (s, 2 H; NCH₂), 3.93 (t, J=6.4 Hz, 4H; OCH₂CH₂), 1.74 (quint, J=6.4 Hz, 4H; OCH₂CH₂), 1.40-1.45 (m, 4H; OCH₂CH₂CH₂), 1.37 (s, 9H; tBu-H), 1.31 (s, 9H; tBu-H), 1.24 (brs, 32H; alkoxy-H), 0.87 ppm (t, J=6.8 Hz, 6H; CH₂CH₃); ¹³C NMR $(100 \text{ MHz}, \text{ CDCl}_3): \delta = 164.2, 162.9, 160.3, 150.3, 143.7, 139.0, 134.4,$ 134.1, 132.6, 131.5, 131.1, 129.6, 128.9, 128.7, 128.0, 126.3, 126.2, 125.9, 123.7, 123.0, 122.9, 122.8, 107.3, 100.3, 68.0, 43.7, 35.5, 34.3, 31.9, 31.7, 31.3, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 26.0, 22.7, 14.1 ppm; HRMS (ESI-TOF, pos. mode): m/z calcd for C₆₉H₈₅N₂O₆: 1037.64021 [M+H]+; found 1037.64073; elemental analysis calcd (%) for C₆₉H₈₄N₂O₆: C 79.88, H 8.16, N 2.70; found: C 79.39, H 8.13, N 2.90.

N-(4-Iodobenzyl)-N'-(2,5-di-tert-butylphenyl)perylene-3,4:9,10-tetracar-

boxylic acid bisimide (7): A mixture of compound 5 (100 mg, 0.17 mmol), 4-iodobenzyl amine (100 mg, 0.43 mmol), and imidazole (10 g) was stirred under an argon atmosphere at 140 °C for 4 h. Before cooling, the reaction was directly quenched with 2.0 M HCl (50 mL) and stirred for another 1 h. The resulting precipitate was separated by filtration and washed with MeOH (3×10 mL). After drying in vacuum, the crude product was purified by silica gel chromatography (CH2Cl2 as eluent) and reprecipitated between CH₂Cl₂/MeOH. Yield: 90 mg (0.11 mmol, 64%) as a red solid; TLC (CH₂Cl₂): R_f=0.10; m.p. 388–389°C; ¹H NMR (400 MHz, CDCl₃): $\delta = 8.54 - 8.74$ (m, 8H; perylene protons), 7.65 (dt, $J^1 = 8.8$ Hz, $J^2 = 2.0$ Hz, 2H; Bn-H), 7.61 (d, J=8.8 Hz, 1H; Ph-H), 7.48 (dd, $J^1=8.8$ Hz, $J^2=$ 2.4 Hz, 1H; Ph-H), 7.33 (dt, $J^1 = 8.8$ Hz, $J^2 = 2.0$ Hz, 2H; Bn-H), 7.13 (d, J=2.4 Hz, 1H; Ph-H), 5.34 (s, 2H; NCH₂), 1.35 (s, 9H; tBu-H), 1.29 ppm (s, 9H; *t*Bu-*H*). ¹³C NMR (100 MHz, CDCl₃): $\delta = 164.3$, 163.3, 150.2, 143.7, 137.6, 136.7, 134.8, 134.7, 132.6, 131.8, 131.6, 131.2, 129.8, 129.3, 128.8, 127.8, 126.6, 126.4, 126.3, 123.8, 123.2, 123.1, 123.0, 93.3, 43.3, 35.5, 34.3, 31.7, 31.2 ppm; HRMS (ESI-TOF, pos. mode): m/z calcd for C₄₅H₃₆IN₂O₄: 795.17143 [*M*+H]⁺; found: 795.17179; elemental analysis calcd (%) for $C_{45}H_{35}IN_2O_4$: C 68.01, H 4.44, N 3.53; found: C 68.00, H 4.52, N 3.58.

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Supporting Information). All of the three ROESY spectra exhibit the same and reproducible cross signals.

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FULL PAPER

CHEMISTRY

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Perylene Bisimides -

C. Shao, M. Grüne, M. Stolte, F. Würthner*.....

Perylene Bisimide Dimer Aggregates: Fundamental Insights into Selfassembly by NMR and UV/Vis Spectroscopy



Self-assembly control: Proper steric control can program the formation of well-defined perylene bisimide (PBI) dimer aggregates (see figure) in chloroform ("good" solvent). The further growth of PBIs into extended aggregates can be triggered by the addition of methylcyclohexane ("bad" solvent). These processes have been investigated in great detail and may serve as a guideline for an in-depth characterization of dye aggregates.

Widely applied automotive color pigments...

...based on perylene bisimide have hitherto been utilized by many groups to create extended onedimensional π stacks by selfassembly. In their Full Paper on page **I** ff., Würthner et al. report on the application of sterically demanding groups to terminate self-assembly at the dimer stage. Only in highly nonpolar aliphatic solvents is a rather unusual growth into larger selfassembled structures observed.

