Supramolecular Chemistry |Hot Paper|

Exciton-Vibrational Couplings in Homo- and Heterodimer Stacks of Perylene Bisimide Dyes within Cyclophanes: Studies on Absorption Properties and Theoretical Analysis

David Bialas,^[a] Christoph Brüning,^[b] Felix Schlosser,^[a] Benjamin Fimmel,^[a] Johannes Thein,^[a] Volker Engel,^{*[b]} and Frank Würthner^{*[a]}

Dedicated to Professor Gerhard Bringmann on the occasion of his 65th birthday

Abstract: The optical properties of a series of three cyclophanes comprising either identical or different perylene bisimide (PBI) chromophores were studied by UV/Vis absorption spectroscopy and their distinctive spectral features were analyzed. All the investigated cyclophanes show significantly different absorption features with respect to the corresponding constituent PBI monomers indicating strong coupling interactions between the PBI units within the cyclophanes. DFT calculations suggest a π -stacked arrangement of the PBI units at close van der Waals distance in the cyclophanes

Introduction

Exciton coupling is among the most vividly discussed properties of molecular materials because of its fundamental importance for the understanding of coherent energy transport in natural light-harvesting systems^[1] as well as its relevance for various functional properties of organic dyes and semiconductors with relevance for (opto-)electronic and photovoltaic applications.^[2] Moreover, the molecular exciton theory as introduced by Davydov and Kasha^[3] fifty years ago constitutes the basic concept to derive structural insights into supramolecular arrangements in dye aggregates, for example, H- and J-aggregates.^[4] Accordingly, plenty of research has been carried out on exciton coupling to obtain structural information as well as insight into functional properties of dye aggregates. Interestingly, however, all this research has focused for half of a century on molecular aggregates obtained from identical dye or organic semiconductor molecules, that is, homoaggregates. For het-

[a]	D. Bialas, Dr. F. Schlosser, Dr. B. Fimmel, J. Thein, Prof. Dr. F. Würthner Universität Würzburg
	Institut für Organische Chemie and Center for Nanosystems Chemistry
	Am Hubland, 97074 Würzburg (Germany)
	E-mail: wuerthner@chemie.uni-wuerzburg.de
[b]	C. Brüning, Prof. Dr. V. Engel
	Universität Würzburg
	Institut für Physikalische und Theoretische Chemie
	Emil-Fischer-Str. 42, 97074 Würzburg (Germany)
	E-mail: volker.engel@uni-wuerzburg.de
	Supporting information for this article can be found under http://

Supporting information for this article can be found under http:// dx.doi.org/10.1002/chem.201603205. spectra based on time-dependent quantum mechanics properly reproduced the experimental spectra, revealing excitonvibrational coupling between the chromophores both in homo- and heterodimer stacks. The PBI cyclophane comprising two different PBI chromophores represents the first example of a PBI heterodimer stack for which the exciton coupling has been investigated. The quantum dynamics analysis reveals that exciton coupling in heteroaggregates is indeed of similar strength as for homoaggregates.

with rotational displacement. Simulations of the absorption

eroaggregates as present in, for example, bulk heterojunction solar cells, exciton coupling between dyes with differing absorption energies is considered to be negligible. This view was also expressed in the still quite limited number of structurally defined synthetic heteroaggregate systems bearing π -stacks of different dyes,^[5] albeit a close look on some of the absorption spectra reveal deviations with regard to the simple addition of the spectra of the monomeric building blocks. These deviations were related to conformational distortions, solvent effects, or charge-transfer interactions. In this regard, our recent study on a merocyanine foldamer bearing two different merocyanine dyes with distinct absorption maxima at ~540 and ~650 nm provided a so-far unique showcase example, revealing strong exciton coupling in the closely π -stacked conformation despite an energetic offset of $> 3000 \text{ cm}^{-1}$ between the absorption energies of the two dyes. As a result, significantly different absorption spectra were recorded for this heterodimer system compared to the addition of the spectra of the two monomeric dyes.[6]

This, so far, unique example constituted the starting point for our current study on the exciton coupling in perylene bisimide based homo- and heteroaggregates. Perylene-3,4:9,10bis(dicarboximides) (in short perylene bisimides; PBIs) represent a privileged class of chromophores for various applications owing to their outstanding optical and electronic features. They exhibit high photostability,^[7] easily tunable absorption, fluorescence, and redox properties,^[8] and thus comply with the basic requirements for applications in organic electronics^[9] and photovoltaics.^[10] In addition, their unique self-as-

Chem. Eur. J. **2016**, 22, 1–9

Wiley Online Library

These are not the final page numbers! 77



sembly behavior based on π - π -stacking and hydrogen-bonding interactions makes them highly versatile building blocks for the construction of functional supramolecular assemblies.^[11] The optical properties of PBI assemblies not only depend on the structural features of the constituent monomeric chromophores, but also very decisively on the molecular arrangement in the assembly, leading to exciton coupling regimes that cover the whole range from H- to J-type.^[11,12] For PBIs the situation is, however, more challenging than for the above-mentioned merocyanine dyes because the optical excitation of PBIs is accompanied by a strong coupling to aromatic carboncarbon stretching vibrations. The resultant complex exciton-vibrational coupling in PBI aggregates requires accordingly a more elaborate quantum dynamical treatment that we and others have pursued in work on PBI π -stacks of various size but always comprised of the same type of PBI chromophores.[13, 14]

Since supramolecular aggregates consisting of different types of chromophores can provide functionalities that cannot be realized with homoaggregates,^[5] gaining insight into the exciton coupling of PBI hetero- π -stacks should be a rewarding task. Therefore, we elucidate here the absorption properties of a first example of a structurally well-defined PBI heterodimer π -stack by quantum dynamical analysis, along with two homodimer π -stacks for comparison.

For the detailed study of interchromophore interactions, model systems with distinct orientations of the chromophores are required.^[15] For this purpose, PBI cyclophanes^[16] bearing two PBI chromophores positioned by a spacer in a fixed geometry are properly suited. Recently, we have reported the synthesis of cyclophane **r2-CP** (in the notation of the cyclophanes



(**CP**) "**o**" and "**r**" indicate the parent orange-colored and the tetraphenoxy-substituted red-colored PBI chromophores, respectively) which comprises two identical PBI chromophores bearing *tert*-butylphenoxy substituents in the bay positions ("red PBI", rPBI), leading to intense emission in the red spectral range.^[17] This cyclophane affords co-facially stacked PBI chromophores, thus the phenylene butadiynylene spacer unit of **r2-CP** allows a perfect preorganization of the PBI chromophores in a π -stacked arrangement. To investigate PBI heterodimer stacks in terms of exciton coupling, we have newly synthesized, by employing the same spacer, the cyclophane **or-CP** consisting of two different PBI chromophores, one bearing *tert*-butylphenoxy groups in the bay positions ("red PBI", rPBI)

and the other one without any bay substituents ("orange PBI", oPBI). For comparison, cyclophane **o2-CP** containing two bayunsubstituted PBI chromophores with orange color ("orange PBI") has also been investigated.

Herein we report that the hetero-PBI cyclophane **or-CP** exhibits quite different UV/Vis absorption spectral features than those calculated from the absorption spectra of the individual dyes or those of the homo-PBI cyclophanes **o2-CP** and **r2-CP**. Our theoretical studies based on time-dependent quantum mechanics reveals exciton-vibrational coupling between the chromophore units not only in the homo-PBI cyclophanes but also in the hetero-PBI cyclophane, explaining the distinctive absorption features of these π -stacked dimers.

Results and Discussion

Synthesis

Cyclophane **o2-CP** comprising two orange PBIs and cyclophane **or-CP** bearing one orange and one red PBI chromophore were synthesized according to the routes depicted in Scheme 1. Starting from commercially available perylene-3,4:9,10-tetracarboxylic bisanhydride 1, cyclophane **o2-CP** was synthesized in four steps (Scheme 1, route a). The imidization of 1 with 4-iodoaniline, followed by Sonogashira coupling reaction with triisopropylsilyl (TIPS)-functionalized phenylene acetylene derivative $3^{[17]}$ and subsequent deprotection of the silyl group with tetrabutylammonium fluoride afforded the PBI precursor **5** for the final step in good overall yield. Pd-catalyzed homocoupling of **5** with [PdCl₂(PPh₃)₂] as the catalyst and copper(I) iodide as co-catalyst afforded the desired cyclophane **o2-CP** bearing two identical PBI chromophores (Scheme 1, route a).

The target cyclophane **or-CP** comprising two different PBI chromophores was synthesized in two-steps, one-pot reaction by deprotection of the TIPS groups in literature-known PBI derivative **6**^[17] and newly synthesized PBI **4** (Scheme 1, route a) with tetrabutylammonium fluoride and a subsequent Pd-catalyzed heterocoupling reaction of the in situ generated terminally acetylene-substituted orange and red PBI derivatives in 3.4% isolated yield (Scheme 1, route b). The low yield of this hetero PBI cyclophane is caused by the formation of undesired polymeric byproducts and homocoupled cyclophanes **o2-CP** and **r2-CP**. The latter PBI cyclophane has been previously reported.^[17] For the detailed synthetic procedures and characterization data of new compounds, see the Supporting Information.

UV/Vis absorption spectroscopy

Exciton-vibrational couplings manifest in the UV/Vis absorption bands of the respective optical transitions. Accordingly, the PBI cyclophanes **o2-CP**, **r2-CP**, and **or-CP** were studied in comparison with the respective monochromophoric PBI references by UV/Vis spectroscopy in high permittivity (ε_r =9.0) solvent dichloromethane for dilute solutions to ensure the absence of any intermolecular aggregates formed by self-association. The

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Scheme 1. Synthetic route to a) cyclophane o2-CP bearing two bay-unsubstituted orange PBI chromophores and b) cyclophane or-CP consisting of one orange and one red PBI chromophore.

monochromophoric reference PBI 4 shows the typical absorption bands of a core-unsubstituted PBI chromophore with pronounced vibronic fine structure (Figure 1a, dash-dotted line).^[11] The 0-0 transition with the highest absorption is located at 528 nm and exhibits a vibronic progression with less intense absorption bands at 491, 459, and 431 nm. In contrast, the spectrum of cyclophane o2-CP containing two identical coreunsubstituted oPBI chromophores shows a reversal of the band intensities compared to the reference PBI 4 at around 530 and 490 nm (Figure 1a, solid line). This phenomenon is characteristic for helically π -stacked oPBI chromophores and arises from exciton-vibrational coupling.^[13] The spectra indeed resemble those of self-assembled closely stacked oPBI dyes,^[18] for which our analysis yielded a value of 524 cm⁻¹ for the exciton coupling strength, that is, a situation called the intermediate coupling regime.^[13] A similar situation is given for the red cyclophane r2-CP (Figure 1b, solid line). Here the monochromophoric rPBI reference 6 bearing four tert-butylphenoxy substituents in bay positions shows a bathochromic shift to 583 nm compared to the core-unsubstituted oPBI reference 4 with broader absorption bands and a loss of vibronic fine structure (Figure 1 b, dash-dotted line). These less defined vibronic progresses are caused by the bulky tert-butylphenoxy substituents, which induce a rotational twist of the two naphthalene-imide subunits thereby reducing the rigidity of the scaffold and enabling a broader conformational distribution. $^{\left[19,20\right] }$ The absorption band at 541 nm belongs to the vibronic progression of the S_0-S_1 absorption band, while the weak absorption band at 454 nm arises from the S₀-S₂ transition.^[21] As in the case of cyclophane **o2-CP**, the absorption spectrum of cyclophane **r2-CP** bearing two identical core-tetraphenoxy-substituted rPBI chromophores shows a reversal of the band intensities at around 580 and 540 nm with respect to the corresponding reference PBI derivative **6**, indicating a similar π -stacked arrangement with exciton-vibrational coupling of the rPBI chromophores in this cyclophane as well (Figure 1 b, solid line).^[17]

As immediately apparent from Figure 1c, the situation for cyclophane or-CP bearing one core-unsubstituted and one core-tetraphenoxy-substituted PBI chromophore is more complex. Thus, the absorption spectrum of or-CP (solid line) does neither equal the sum of the spectra of the respective reference compounds 4 and 6 (situation without exciton coupling, dash-dotted line) nor resemble the spectra of o2-CP and r2-CP. However, a clearly visible redistribution of oscillator strength among the dyes is indicative for an exciton coupling interaction between the different types of chromophores within this cyclophane. The shift of the 0-0 absorption band of the constituent PBIs is, however, very modest for cyclophane or-CP with a small bathochromic shift of the absorption band of the core-tetraphenoxy-substituted PBI chromophore from 583 to 586 nm and a smaller modulation of the absorption of the core-unsubstituted PBI compared to o2-CP. As for the homodimers o2-CP and r2-CP, additional bands at 500 and 469 nm are observed, which are of higher intensity and show a bathochromic shift compared to the absorption bands of the vibronic progression of reference PBI 4. Taken together, these spectroscopic observations clearly indicate an exciton coupling be-

Lhem. Eur. J. 2016 , 22, 1–9	www.chemeurj.org
These are not the	final page numbers! 77





Figure 1. UV/Vis absorption spectra of a) reference **4** (----) and cyclophane **o2-CP** (——), b) reference **6** (----) and cyclophane **r2-CP** (——), and c) sum of the spectra of **4** and **6** (----) as well as the spectrum of cyclophane **or-CP** (——) in dichloromethane ($c \approx 10^{-5}$ M) at room temperature.

tween the two different PBI chromophores within cyclophane **or-CP** leading to distinctive changes in the optical absorption properties.

The absorption spectra of all three cyclophanes in the less polar solvent toluene are very similar to the ones measured in dichloromethane (Figure S1, Supporting Information). Besides a hypsochromic shift for cyclophanes **r2-CP** and **or-CP**, which is known as positive solvatochromism of PBI chromophores,^[22] the shape of the spectra is not affected by the solvent polarity. This indicates similar coupling strengths in toluene and dichloromethane for all three cyclophanes revealing the same arrangements of the chromophores in both solvents.

The subsequent theoretical studies are devoted to establish a proper understanding of this exciton coupling in heterodimers in the presence of strong vibronic coupling as given for PBI dyes and the majority of other common chromophores.

Quantum chemical studies

According to CPK models, the π -conjugated phenylene butadiynylene tethers are supposed to preorganize the PBI units in a rather stiff or even compressed co-facial π -stacking arrangement. Nevertheless, due to the different geometries of the two utilized PBI cores—oPBI being planar and rPBI having a twisted π -core (rotational twist of 25-30° between the two naphthalene imide subunits)^[19]—and the sterical demands of the tetraphenoxy substituents, a deeper insight into the specific molecular arrangement of the PBI chromophores within the cyclophanes is required. Therefore, DFT calculations were performed by employing B97D3^[23] as a functional and def2-SVP^[24] as a basis set. The functional includes a dispersion correction that is required to describe π - π -interactions between the PBI chromophores in an adequate way.^[25] The geometry-optimized structures of the PBI cyclophanes are shown in Figure 2. All



Figure 2. Geometry-optimized structures of PBI cyclophanes a) **o2-CP**, b) **r2-CP**, and c) **or-CP** (B97D3, def2-SVP, hexyl groups were replaced by methyl groups). Hydrogen atoms were omitted for clarity. α represents the rotational displacement and *r* the distance between the chromophores in the respective cyclophanes as depicted in Figure 2 a.

three cyclophanes show π - π -stacking between the PBI chromophores with distances (*r*) of 3.24–3.84 Å and rotational displacements (*a*) of 10.6–28.6° between the chromophores. The molecular arrangement of the chromophores in cyclophane **o2-CP** (r=3.24 Å, α =28.6°) represents the ideal ground-state geometry of two co-facially stacked core-unsubstituted oPBI chromophores,^[25] corroborating our molecular design for a spacer unit that supports the desired preorganization of these chromophores in the cyclophanes. While the core-unsubstituted oPBI chromophores in **o2-CP** are almost perfectly planar, the naphthalene imide units of the core-tetraphenoxysubstituted red PBI in **r2-CP** are twisted by 27° due to the sterical constraints in the bay area imposed by the bulky *tert*-bu-

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

4



tylphenoxy substituents.^[19,26] Notably, also this value is in accordance with crystallographic data for monomeric tetraphenoxy-substituted PBIs.^[19,27] The phenoxy substituents prevent, however, a close contact of the PBI chromophores in twisted conformation, resulting in a larger distance of 3.84 Å between the π -scaffolds in **r2-CP**. As our calculation shows, the phenylene butadiynylene tether enforced helical displacement of 24.5° enables all eight phenoxy substituents to accommodate without sterical congestions as a homochiral dye pair (both dyes exhibit the same plane chirality, that is, PP or MM). For or-CP, the situation is obviously more demanding because a planar and a nonplanar dye have to interact by co-facial π - π -stacking. According to our calculations, the interchromophore distance in or-CP is smaller compared to that of r2-CP and indeed close to o2-CP despite the fact that one PBI contains bulky substituents and a twisted π -core. Remarkably, to enable such a close contact, the planarity of the core-unsubstituted oPBI chromophore is lost in cyclophane or-CP leading to a rotational twist of approximately 11° caused by a templating effect of the core-twisted (26°) at bay positions tetrasubstituted rPBI chromophore. Accordingly, the utilized phenylene butadiynylene bridging unit indeed acts as a bracket that compresses the two dyes on top of each other.

Quantum dynamics studies

The absorption properties of dye aggregates consisting of identical chromophores can be easily rationalized with Kasha's exciton theory assuming an interaction between the oscillating transition dipole moments of the constituent chromophores.^[3b] Exciton coupling between two chromophores results in a Davydov splitting^[3a] of the excited states with a splitting energy of 2J, in which J is the exciton coupling energy, as illustrated in the exciton state diagram for a dimer stack of two identical PBI chromophores in a hypothetical perfectly collinear arrangement in Figure 3a. The two nondegenerate excited states S₁' and S_1'' differ in the phase relation between the oscillating transition dipole moments. The excitation to the highest excited state (S1") is allowed due to the in-phase oscillation of the transition dipole moments, while the transition to the lower excited state is forbidden since the transition dipole moments are oscillating out of phase. Hence, the absorption spectrum of a H-dimer exhibits a hypsochromically shifted absorption band with respect to the monomer absorption band (Figure 3a). As shown in our previous work on a merocyanine heterodimer composed of two chromophores with different excited state energies, a splitting of the excited states occurs as well in this case.^[6] In a heterodimer, the splitting energy amounts to $\sqrt{\Delta E_{o,r}^2 + 4J^2}$ with $\Delta E_{o,r}$ as the energy difference between the excited states of the different PBI chromophores $S_{1,o}$ and $S_{1,r}$ respectively (Figure 3 b).^[28] Importantly, in contrast to the homodimer, the transition to the lowest excited state becomes partially allowed in such a heterodimer, even for a perfect collinearly stacked H-type dimer. This effect may be attributed to different magnitudes of the resp. transition dipole moments of the chromophores or simply to differences in the excited-state energies of the two coupled chromophores. Based on these in-



Figure 3. Schematic exciton state diagram for H-type PBI dimer stack composed of a) identical and b) different chromophores in a hypothetical collinear arrangement and neglecting vibronic coupling. The orange and red arrows illustrate the relationship between the oscillating transition dipole moments. $S_{1,o}$ and $S_{1,r}$ denote the excited states of orange and red PBI, respectively. ΔE_{or} is the energy difference between the excited states $S_{1,o}$ and $S_{1,r}$ and $S_{1,r}$ denotes the excited states $S_{1,o}$ and $S_{1,r}$ denotes the excited states $S_{1,o}$ and $S_{1,r}$ and $S_{1,r}$ denotes the excited states $S_{1,o}$ and $S_{1,r}$ denotes the excited states $S_{1,o}$ and $S_{1,r}$ and $S_{1,r}$ denotes the excited states $S_{1,o}$ and $S_{1,r}$ denotes the excited states $S_{1,r}$ denotes the excited sta

sights, we can expect two absorption bands in the UV/Vis spectrum with a hypsochromic and a bathochromic shift with regard to the absorption bands of the involved monomeric chromophores and a redistribution of oscillator strength, that is, an increase of absorbance for the higher energy and a decrease of absorbance for the lower energy band.

For the given PBI cyclophanes, the situation is, however, more complex due to the strong coupling of the PBI $S_0 \rightarrow S_1$ transition to aromatic CC-stretching modes and a rotational displacement of the chromophores. In the case of a rotational displacement of the chromophores, the transition to the lower excited states becomes partially allowed,^[3b] resulting in the presence of a second less intense absorption band with a bathochromic shift ("J-band") even for identical chromophores. Due to the fact that for the PBI $S_0 \rightarrow S_1$ transition the vibrational coupling with about 1400 cm⁻¹ is stronger than the exciton coupling with about 500 cm⁻¹ (so-called intermediate coupling regime) the main signature of the exciton coupling is indeed not a pronounced shift of the absorption band but the reversal

Chem. Eur. J. 2016 , 22, 1–9	www.chemeurj.org
These are not the	final page numbers! 77



CHEMISTRY A European Journal Full Paper

of the intensity of the two lowest energy bands^[13,14] as observed for **o2-CP** and **r2-CP** homodimers in Figure 1a,b. Accordingly, the simple model described above has to be extended by considering rotational displacements as well as vibrational coupling between the chromophores. Following our earlier work on homoaggregates of PBIs^[13] we can be confident to obtain a conclusive understanding of the absorption bands of **o2-CP** and **r2-CP** homodimers and novel insights into the hitherto unexplored impact of exciton-vibrational couplings on the spectra of hetero-PBI cyclophane **or-CP**.

Towards this goal we have performed time-dependent quantum mechanical simulations. We solve the time-dependent Schrödinger equation for a Hamiltonian of Holstein type,^[29,30] which in many cases gives an excellent description of vibronic spectra^[4a,31] and has been applied to self-assembled PBI aggregates before.^[13] The absorption spectra are then obtained by a Fourier transform of the calculated time-dependent autocorrelation function.^[32] A more detailed description of the procedure and the model Hamiltonian can be found in the Supporting Information.

In Figure 4, we compare calculated and measured spectra for the monochromophoric reference PBIs **4** and **6** (panels a,c) and the **o2-CP** and **r2-CP** homodimers (panels b,d). We use the monomer spectra to fix the parameters that enter the model Hamiltonian. These are the frequencies ω , Huang–Rhys-factors ξ , and excitation energies ΔE . Best agreement with experiment is achieved for the sets: $\omega = 1411 \text{ cm}^{-1}$, $\xi = 0.79$, $\Delta E =$ 18954 cm⁻¹ for the orange monomer and $\omega = 1331 \text{ cm}^{-1}$, $\xi =$ 0.78 and $\Delta E = 17164 \text{ cm}^{-1}$ for the red monomer. The very simi-



lar values for the vibrational frequency and the Huang–Rhys factor indicate that the substituents attached to the red PBI monomer do not influence the vibrational motion significantly.

Turning to the homodimers, we fix the angle α between the transition dipole moments to 28.6° for **o2-CP** and 24.5° for **r2-CP**, respectively (see Figure 2). The absolute values of the transition dipole moments result, at least in the case of homodimers, only in a global prefactor in the spectrum, and is therefore set equal to one. We find best agreement for the simulated spectra with experiment for an exciton coupling energy of J= 613 cm⁻¹ for **o2-CP** and 500 cm⁻¹ for **r2-CP**. These values are comparable to the coupling strength of 524 cm⁻¹ found for self-assembled homodimers of core-unsubstituted PBI molecules.^[13]

The two exciton states illustrated in Figure 3a overlap, because the coupling strength is small compared to the vibrational frequency. Since the $S_0 \rightarrow S_1$ ' transition is only weakly allowed for angles of roughly 25°, we attribute the line-shape mostly to vibrational levels in the S_1'' exciton state. There, the intensities of the peaks marked with an asterisk in the figure are strongly dependent on the exciton coupling energy.^[31,33] We note that the Huang–Rhys factors are increased to $\xi = 0.88$ (orange) and 0.83 (red) to achieve a better agreement with the experiment. This may indicate that in the dimers a strain acts on the PBI scaffold, and thus changes the excited-state equilibrium geometry of the monomer units. Such possible geometry deformations are not the focus of this work, and more extended electronic structure calculations involving excited-state geometry optimizations would have to be conducted in the future.

We now apply the same model to the or-CP heterodimer. The calculated spectra for the sum of the monomers and the heterodimer are shown in Figure 5. In contrast to the homodimers, the relative strength of the transition dipole moments is important here. Their absolute values will, however, still result in a global factor. We will therefore only give the ratio $\bar{\mu} = \mu(\mathbf{r})/\mu(\mathbf{o})$ of the individual absolute values. The sum of the monomer spectra is best matched by a model spectrum for an uncoupled dimer (J=0) when we set the dipole moment ratio $\bar{\mu} = 0.69$. This, however, most probably underestimates the value of $\mu(\mathbf{r})$ because the oscillator strength corresponds to the total area of the spectral band and the spectrum for the red monomer is broader for reasons discussed above. All other parameters have been kept at the values determined from the individual monomer spectra. For the spectrum of the **or-CP** heterodimer, we fix the angle α between the transition dipole moments to a value of 10.6° as indicated in Figure 2 c and the Huang-Rhys factors at the values determined from the homodimer spectra. From the comparison of calculated and measured spectra, we arrive at a dipole moment ratio of $\bar{\mu} = 0.81$ and an exciton coupling energy of J = 427 cm⁻¹. It is somewhat smaller than that found for the homodimers, but still comparable in its numerical value. Again, the coupling strength has a large effect on the intensity of the 0,0 transition peak of the oPBI chromophore (marked with an asterisk in Figure 5 b). The ratio of the dipole moments further determines the intensity of the low-energy band originating mainly from

www.chemeurj.org

6

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Figure 5. Comparison of experimental (----, measured in dichloromethane) and calculated spectra (-----): a) Sum of measured spectra of reference PBI dyes 4 (oPBI) and 6 (rPBI) and calculated uncoupled or-CP heterodimer. Also shown is the theoretical spectrum of reference PBI 6. b) Coupled heterodimer. Values for the exciton coupling energy J and the ratio of the magnitudes of the dipole moments are indicated.

the rPBI chromophore and explains why the intensity is markedly decreased compared to the monomeric rPBI chromophore (see also Figure 1 c).

Overall, the calculated absorption spectra of the studied monomers, homodimers, and heterodimers are in very good agreement with the experimental ones, while the parameters that enter the model differ only little from those found for selfassembled PBI aggregates.^[13, 14] It should be clear that the simple model of exciton states as illustrated in Figure 3 is insufficient to explain the spectral lineshapes. Because of the rather weak exciton coupling, the appearance of the spectra is dominated by vibronic progressions for both homo- and hetero-PBI aggregates.

Conclusion

In a comparative study of two PBI cyclophanes each bearing two identical chromophores and one PBI cyclophane comprising two different chromophores, we were able to observe pronounced changes in the absorption properties and to relate those to substantial exciton coupling between the PBI units within the cyclophanes. Most importantly, by comparing calculated and measured absorption spectra, we were able to quantify the exciton-vibrational coupling in these cyclophanes. These couplings lead to the emergence of quite different absorption properties compared to the corresponding monomeric PBI chromophores not only for homo- but similarly for heterodimer aggregates. To the best of our knowledge, our guantum mechanical analysis on the cyclophane bearing two different PBI chromophores represents the first example of PBI hetero- π -stacks for which exciton-vibrational coupling has been explored. The new insights derived from our work justify further efforts toward an understanding of optical properties of larger PBI hetero-*π*-stacks. Based on those studies tailored dye aggregate systems should become accessible for functional materials with desired properties.

Experimental Section

Detailed information can be found in the Supporting Information. The document includes experimental procedures, details of the synthetic procedures, characterization of all new compounds (NMR, mass spectrometry), details of the quantum chemical calculations, and graphical accounts of the NMR and mass spectra.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (DFG) for support of this project in the framework of the research group FOR 1809 on "Light-induced dynamics in molecular aggregates" at the Universität Würzburg. D. B. thanks the Fonds der Chemische Industrie for a PhD fellowship.

Keywords: cyclophanes · dyes · exciton coupling · vibronic coupling $\cdot \pi - \pi$ stacking

- [1] a) T. Brixner, J. Stenger, H. M. Vaswani, M. Cho, R. E. Blankenship, G. R. Fleming, Nature 2005, 434, 625-628; b) R. J. Cogdell, A. Gall, J. Köhler, Q. Rev. Biophys. 2006, 39, 227-324.
- [2] G. D. Scholes, G. Rumbles, Nat. Mater. 2006, 5, 683-696.
- [3] a) A. S. Davydov, Sov. Phys. Usp. 1964, 7, 145-178; b) M. Kasha, H. R. Rawls, M. A. El-Bayoumi, Pure Appl. Chem. 1965, 11, 371-392.
- [4] a) F. C. Spano, Acc. Chem. Res. 2010, 43, 429-439; b) F. Würthner, T. E. Kaiser, C. R. Saha-Möller, Angew. Chem. Int. Ed. 2011, 50, 3376-3410; Angew. Chem. 2011, 123, 3436-3473.
- [5] a) A. L. Sisson, N. Sakai, N. Banerji, A. Fürstenberg, E. Vauthey, S. Matile, Angew. Chem. Int. Ed. 2008, 47, 3727-3729; Angew. Chem. 2008, 120, 3787 - 3789; b) A. D. Shaller, W. Wang, H. Gan, A. D. Q. Li, Angew. Chem. Int. Ed. 2008, 47, 7705-7709; Angew. Chem. 2008, 120, 7819-7823; c) T. Fujii, H. Kashida, H. Asanuma, Chem. Eur. J. 2009, 15, 10092-10102; d) R. Bhosale, J. MíŠek, N. Sakai, S. Matile, Chem. Soc. Rev. 2010, 39, 138-149; e) A. Das, S. Ghosh, Angew. Chem. Int. Ed. 2014, 53, 2038-2054; Angew. Chem. 2014, 126, 2068-2084; f) P. Ensslen, Y. Fritz, H.-A. Wagenknecht, Org. Biomol. Chem. 2015, 13, 487-492; g) C. B. Winiger, S. M. Langenegger, G. Calzaferri, R. Häner, Angew. Chem. Int. Ed. 2015, 54, 3643-3647; Angew. Chem. 2015, 127, 3714-3718; h) M. Weiser, H.-A. Wagenknecht, Chem. Commun. 2015, 51, 16530-16533.
- [6] D. Bialas, E. Kirchner, F. Würthner, Chem. Commun. 2016, 52, 3777-3780.
- [7] W. Herbst, K. Hunger in Industrial Organic Pigments: Production, Properties, Applications, 2nd edn., WILEY-VCH, Weinheim, 1997.
- [8] a) F. Würthner, Chem. Commun. 2004, 1564-1579; b) C. Huang, S. Barlow, S. R. Marder, J. Org. Chem. 2011, 76, 2386-2407.
- [9] a) X. Zhan, A. Facchetti, S. Barlow, T. J. Marks, M. A. Ratner, M. R. Wasielewski, S. R. Marder, Adv. Mater. 2011, 23, 268-284; b) Z. Liu, G. Zhang, Z. Cai, X. Chen, H. Luo, Y. Li, J. Wang, D. Zhang, Adv. Mater. 2014, 26, 6965-6977.
- [10] a) Y. Zhong, M. T. Trinh, R. Chen, G. E. Purdum, P. P. Khlvabich, M. Sezen, S. Oh, H. Zhu, B. Fowler, B. Zhang, W. Wang, C.-Y. Nam, M. Y. Sfeir, C. T. Black, M. L. Steigerwald, Y.-L. Loo, F. Ng, X.-Y. Zhu, C. Nuckolls, Nat. Commun. 2015, 6, 8242; b) D. Meng, D. Sun, C. Zhong, T. Liu, B. Fan, L. Huo, Y. Li, W. Jiang, H. Choi, T. Kim, J. Y. Kim, Y. Sun, Z. Wang, A. J. Heeger, J. Am. Chem. Soc. 2016, 138, 375-380.

Chem. Eur. J. 2016 , 22, 1–9	www.chemeurj.
-------------------------------------	---------------

ora

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

These are not the final page numbers! **77**





- [11] F. Würthner, C. R. Saha-Möller, B. Fimmel, S. Ogi, P. Leowanawat, D. Schmidt, Chem. Rev. 2016, 116, 962–1052.
- [12] a) S. Yagai, T. Seki, T. Karatsu, A. Kitamura, F. Würthner, Angew. Chem. Int. Ed. 2008, 47, 3367–3371; Angew. Chem. 2008, 120, 3415–3419; b) P. P. Neelakandan, T. A. Zeidan, M. McCullagh, G. C. Schatz, J. Vura-Weis, C. H. Kim, M. R. Wasielewski, F. D. Lewis, Chem. Sci. 2014, 5, 973–981.
- [13] a) J. Seibt, P. Marquetand, V. Engel, Z. Chen, V. Dehm, F. Würthner, *Chem. Phys.* 2006, 328, 354–362; b) J. Seibt, T. Winkler, K. Renziehausen, V. Dehm, F. Würthner, H.-D. Meyer, V. Engel, *J. Phys. Chem. A* 2009, 113, 13475–13482.
- [14] a) H. Yoo, J. Yang, A. Yousef, M. R. Wasielewski, D. Kim, J. Am. Chem. Soc.
 2010, 132, 3939–3944; b) K. A. Kistler, C. M. Pochas, H. Yamagata, S. Matsika, F. C. Spano, J. Phys. Chem. B 2012, 116, 77–86; c) F. Gao, Y. Zhao, W. Z. Liang, J. Phys. Chem. B 2011, 115, 2699–2708; d) R. Ide, L. Mereau, L. Ducasse, F. Castet, Y. Olivier, N. Martinelli, J. Cornil, D. Beljonne, J. Phys. Chem. B 2011, 115, 5593–5603.
- [15] a) D. Veldman, S. M. A. Chopin, S. C. J. Meskers, M. M. Groeneveld, R. M. Williams, R. A. J. Janssen, *J. Phys. Chem. A* **2008**, *112*, 5846–5857; b) J. M. Giaimo, A. V. Gusev, M. R. Wasielewski, *J. Am. Chem. Soc.* **2002**, *124*, 8530–8531.
- [16] a) J. Feng, Y. Zhang, C. Zhao, R. Li, W. Xu, X. Li, J. Jiang, *Chem. Eur. J.* 2008, *14*, 7000–7010; b) K. E. Brown, W. A. Salamant, L. E. Shoer, R. M. Young, M. R. Wasielewski, *J. Phys. Chem. Lett.* 2014, *5*, 2588–2593; c) P. Spenst, F. Würthner, *Angew. Chem. Int. Ed.* 2015, *54*, 10165–10168; *Angew. Chem.* 2015, *127*, 10303–10306.
- [17] F. Schlosser, M. Moos, C. Lambert, F. Würthner, Adv. Mater. 2013, 25, 410-414.
- [18] a) F. Würthner, C. Thalacker, S. Diele, C. Tschierske, *Chem. Eur. J.* 2001, *7*, 2245–2253; b) J. Gershberg, F. Fennel, T. H. Rehm, S. Lochbrunner, F. Würthner, *Chem. Sci.* 2016, *7*, 1729–1737.

- [19] a) P. Osswald, D. Leusser, D. Stalke, F. Würthner, Angew. Chem. Int. Ed. 2005, 44, 250–253; Angew. Chem. 2005, 117, 254–257; b) P. Osswald, F. Würthner, Chem. Eur. J. 2007, 13, 7395–7409; c) P. Osswald, F. Würthner, J. Am. Chem. Soc. 2007, 129, 14319–14326.
- [20] E. Fron, G. Schweitzer, P. Osswald, F. Würthner, P. Marsal, D. Beljonne, K. Müllen, F. C. De Schryver, M. Van der Auweraer, *Photochem. Photobiol. Sci.* 2008, 7, 1509–1521.
- [21] R. Gvishi, R. Reisfeld, Z. Burshtein, Chem. Phys. Lett. 1993, 213, 338-334.
- [22] a) M. J. Ahrens, M. J. Tauber, M. R. Wasielewski, J. Org. Chem. 2006, 71, 2107–2114; b) P. Leowanawat, A. Nowak-Król, F. Würthner, Org. Chem. Front. 2016, 3, 537–544.
- [23] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 2010, 132, 154104.
- [24] F. Weigend, R. Ahlrichs, Phys. Chem. Chem. Phys. 2005, 7, 3297-3305.
- [25] R. F. Fink, J. Seibt, V. Engel, M. Renz, M. Kaupp, S. Lochbrunner, H.-M. Zhao, J. Pfister, F. Würthner, B. Engels, J. Am. Chem. Soc. 2008, 130, 12858–12859.
- [26] F. Würthner, Pure Appl. Chem. 2006, 78, 2341-2349.
- [27] C. Hippius, I. H. M. van Stokkum, E. Zangrando, R. M. Williams, M. Wykes, D. Beljonne, F. Würthner, J. Phys. Chem. 2008, 112, 14626–14638.
- [28] S. F. Völker, A. Schmiedel, M. Holzapfel, K. Renziehausen, V. Engel, C. Lambert, J. Phys. Chem. C 2014, 118, 17467–17482.
- [29] T. Holstein, Ann. Phys. 1959, 8, 325-342.
- [30] R. L. Fulton, M. Gouterman, J. Chem. Phys. 1964, 41, 2280-2286.
- [31] N. J. Hestand, F. Spano, J. Chem. Phys. 2015, 143, 244707.
- [32] E. J. Heller, Acc. Chem. Res. 1981, 14, 368-375.
- [33] C. Brüning, K. Renziehausen, V. Engel, J. Chem. Phys. 2013, 139, 054303.

Received: July 5, 2016 Published online on ■■ ■, 0000

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

8



FULL PAPER

Dyes/pigments: The absorption properties of a series of three cyclophanes comprising either the same or different perylene bisimide (PBI) dyes have been studied. All cyclophanes exhibit different absorption features with respect to the corresponding constituent monomeric dyes (see figure).



Supramolecular Chemistry

D. Bialas, C. Brüning, F. Schlosser, B. Fimmel, J. Thein, V. Engel,* F. Würthner*

Exciton-Vibrational Couplings in Homo- and Heterodimer Stacks of Perylene Bisimide Dyes within Cyclophanes: Studies on Absorption Properties and Theoretical Analysis