Synthesis and Properties of a Covalently Linked Angular Perylene Imide Dimer
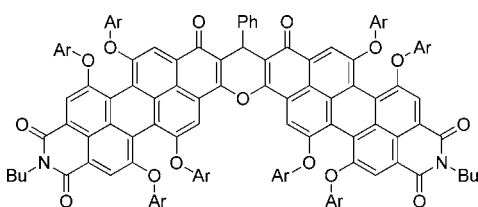
Karl J. Thorley and Frank Würthner*

Universität Würzburg, Institut für Organische Chemie, Am Hubland, 97074 Würzburg, Germany

wuerthner@chemie.uni-wuerzburg.de

ABSTRACT

Utilizing the unexplored chemistry of a monocarbon analog to perylene bisimide, a covalently linked angular perylene dimer was synthesized. On the basis of measured optical properties and molecular modeling, the spectral changes relative to a monomeric reference perylene can be explained by an angle-dependent oblique exciton coupling model. With a roughly trigonal interchromophore arrangement, the dimer building block is promising for larger, cyclic assemblies to mimic naturally occurring light harvesting complexes.

Inspired by natural systems such as photosystem I and II, there is currently a strong interest in the formation of synthetic macrocyclic systems to replicate and understand efficient light-harvesting processes. These range from supramolecular self-assembled systems,[1] as well as covalently linked persistent cycles,[2] with examples of both isolated and fully conjugated extended π-systems. Such macrocycles include cyclic oligomers of porphyrins,[2,3] thiophenes,[4] and phenylacetylenes.[5] Until recently,[6] perylene bisimides (PBIs) had not been widely investigated in this respect, despite their alluring electronic and optical properties.

Here, we report the synthesis of a covalently linked angular perylene dimer **1**, which might form the basis of

larger macrocyclic system **2** (Figure 1). Owing to the trigonal arrangement of the perylene units in dimer **1** interchromophore interactions of the closely spaced perylene chromophores can be derived. While the optical properties of perylene dyes can be drastically changed by chemical modification of the aromatic system,[7] interactions between adjacent molecules also strongly affect these properties.[8−10]

Most interchromophore interactions in perylene systems are of the H-aggregate type, where π−π stacking of molecules leads to hypsochromically shifted absorption.[8] The opposite effect has been observed in J-aggregate formation[9] as well as covalently linked perylene oligomers.[10] However, defined angle dependent perylene excitonic coupling has yet to be explored, and only a few examples of

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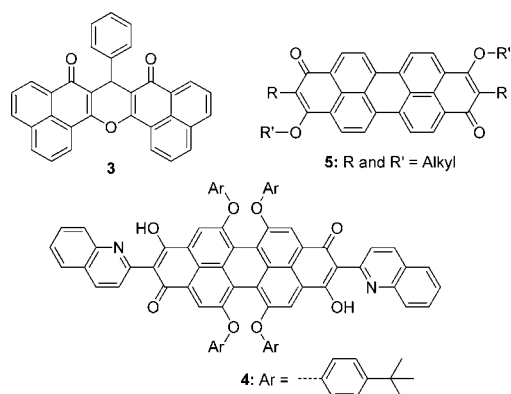
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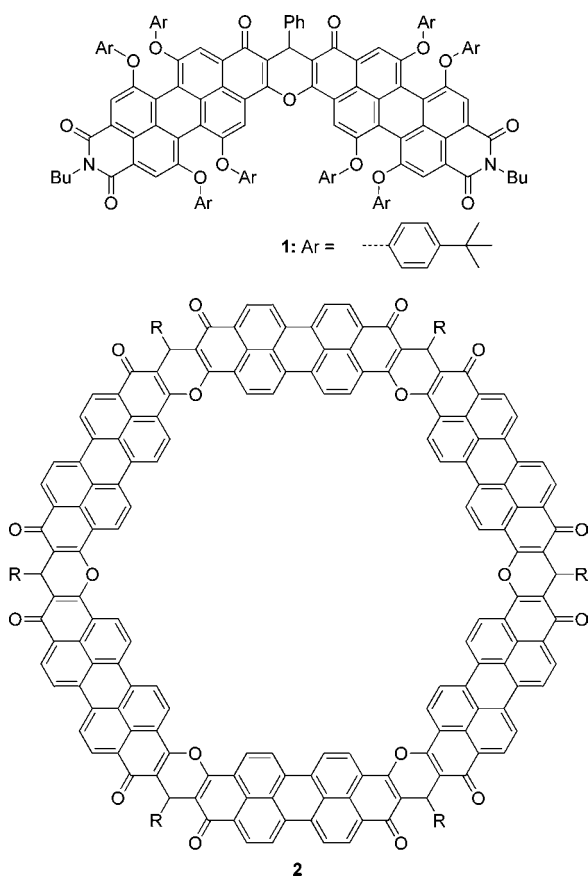
Figure 1. Structure of the target molecule **1** of this work, and general structure of possible macrocycle **2**.

Figure 2. Structures of literature known phenalenone derivative **3** and benzoperylenes **4** and **5**.

this phenomenon with PBI dyes[10] and other chromophores have been reported.[11] Longer range energy transfer between perylene dyes at defined angles has, however, been studied.[12]

The structure of target compound **1** was inspired by the previously reported phenalenone dimer **3** (Figure 2), which was synthesized over three steps from naphthalene anhydride.[13] Using a similar reaction scheme with perylene derivatives should lead to the target dimer **1**. However, only two reports of benzoperylenones, where an enol oxygen is available to undergo further reaction, exist in the literature. In 2008, Feng and co-workers reported the reaction between a bay-substituted perylene bisanhydride with 2-methylquinone, leading to π-extended perylene dyes such as **4**.[14] In 2010, Buffet et al. reported the synthesis

of similar structures such as **5**, utilizing the basic coupling of two hydroxyphenalenone molecules.[15] In contrast to these two reports, we have targeted an unsubstituted methine position to allow for further functionalization.

For the synthesis of target **1** (Scheme 1), the reaction conditions of Wurm[13] were applied to a perylene system **6** containing both imide and anhydride functionalities. Additionally, *p-tert*-butylphenoxy bay substituents were chosen to provide excellent solubility to the perylene dyes to aid their isolation and characterization. The reaction of **6** with dialkylmalonate occurs only at the anhydride position, yielding a monofunctionalized intermediate **7** along with an alkylated side product **8**. Unfortunately, the desired product **7** showed low stability, so condensation with benzaldehyde was performed without fully purifying the intermediate. The resulting covalently linked perylene dimer **9** was isolated in a 20% yield calculated over the two steps from perylene **6**. Formation of a central pyran ring between the perylenes was achieved by heating with acetic anhydride to give **1** in 72% yield.

Perylene dimers **1** and **9** were characterized by NMR spectroscopy (the spectra with assignments are shown in the Supporting Information (SI)). Despite the relatively broad ¹H NMR peaks, presumably due to the restricted rotation of the phenoxy substituents and perylene units, all of the resonances of dimer **9** could be assigned. Notably, the presence of hydrogen bonding[16] at the center of the molecule is observed. A sharp signal at 13 ppm with an integral of 1 proton is seen at room temperature, while an additional broader peak becomes observable at lower temperature. The broad resonances of protons on the phenoxy solubilizing groups also become more distinguishable at lower temperatures. The central "bridge" proton appears at 6.2 ppm indicating the location on a saturated carbon, but being affected by the ring current of the nearby perylene π-cores. Upon formation of compound **1** the

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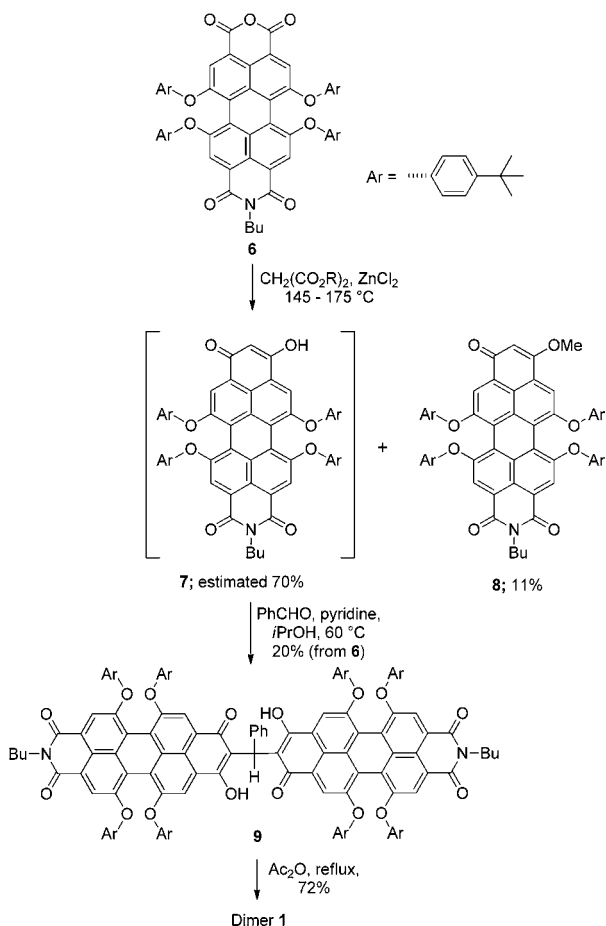
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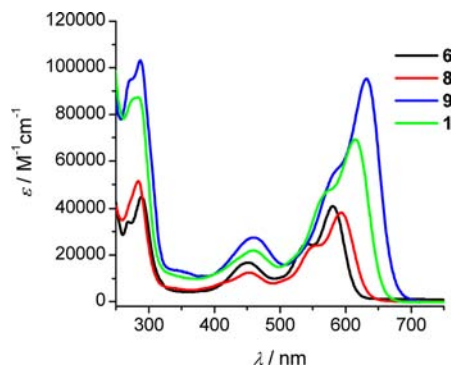
Scheme 1. Synthesis of Covalently Linked Perylene Dimers

Figure 3. UV/vis absorption spectra of perylene derived compounds measured in CH_2Cl_2 at 298 K at concentrations in the range of 10^{-5} M.

absorption band between around 500−700 nm, reveals smaller than expected values for both **9** and **1** (per perylene) when compared to the monomer. The fluorescence spectrum of methoxybenzo[*c,d*]perylenone **8** (see SI) retains the mirror image band shape (λ_{max} = 633 nm) and high quantum yield (Φ_{fl} = 0.87 in CH_2Cl_2) observed for perylene bisimides. However, for each of the dimerized compounds **9** and **1**, no fluorescence was observed. This lack of fluorescence might be due to the formation of triplet states which has previously been reported for covalently linked perylene dimers.[17]

Table 1. Properties of the First Optical (S_0−S_1) Transition of Benzoperylene Compounds in CH_2Cl_2 at 298 K

	λ_{max} (nm)	ν_{max} (cm^{-1})	ε (M^{-1} cm^{-1})	fwhm (cm^{-1})^a	μ_{ag} (D)^b
6	579	17 300	40 700	1210	6.8
	541	18 500	24 700		
8	592	16 900	38 100	1260	6.9
	550	18 200	23 700		
9	632	15 800	95 300	1110	11.0
	584	17 100	55 400		
1	615	16 300	69 200	1170	9.6
	565	17 700	45 100		

^{a} Measured for the lowest energy transition only. ^{b} Measured between approximately 500 and 700 nm. See SI for more details.

hydrogen bonding is lost, while the bridge proton shifts upfield to 5.5 ppm with minor shifts observed for the aromatic signals.

Absorption and fluorescence spectroscopy reveal more about the structural features of **1** and **9**. The alkoxy-benzoperylenone **8** was used as a reference compound due to its high stability. It exhibits a small red shift in the lowest energy absorption band relative to the anhydride parent molecule **6**, due to the slight reorganization of the π-system. Relative to the monomeric precursor **8**, dimerized molecule **9** exhibits a bathochromic shift of 40 nm. After formation of the pyran ring between the perylenes, dimer **1** shows the lowest energy absorption lying between that of monomer **8** and dimer **9** (Figure 3). The absorption maxima might be expected to double in intensity due to the presence of two chromophores. However, for dimer **9**, the extinction coefficient of the lowest energy transition is in fact 19 000 M^{-1} cm^{-1} larger than the expected value.

In addition, the full width at half-maximum (fwhm, measured from only the low energy side of the band) decreases by 150 cm^{-1} (Table 1). In contrast, the pyran annelated dimer **1** has an extinction coefficient slightly smaller than double that of monomer **8**, although the fwhm value is again decreased. The transition dipole moment μ_{ag}, measured for the whole of the S_0−S_1

The origin of the spectral changes can be explained using an excitonic coupling model.[18] For two excitonically coupled chromophores, two excitonic states originate, one located at higher and one at lower energy compared to the transition energy of the monomer. If the two dyes are parallel, only one transition is allowed leading to either a

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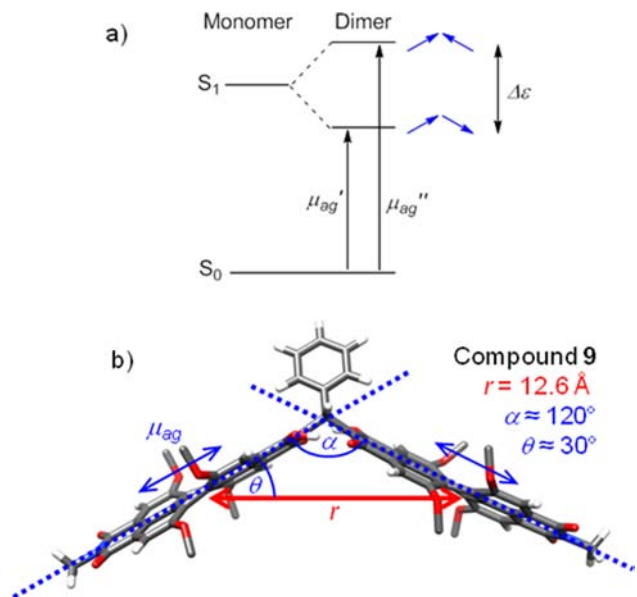
Figure 4. (a) Splitting of energy levels in an oblique excitonic coupling showing the excitonic coupling $\Delta\varepsilon$ and transition strengths μ_{ag}' and μ_{ag}''. (b) MMFF94 energy minimized structure of covalently linked perylene dimer **9**, and parameters α, θ, r, and μ_{ag} (*t*Bu-phenyl groups omitted for clarity).

blue or red shift in the absorption spectrum, depending on the orientation of the chromophores. In an oblique coupling case (Figure 4), transitions to both of the excited states are partially allowed since the transition dipoles can never fully cancel each other. Therefore, both a red- and a blue-shifted band should be observed with differing intensity. The parameters which describe the new system are the exciton splitting ($\Delta\varepsilon$) between the two new excited states, and the transition dipole moments (μ_{ag}' and μ_{ag}'') between the ground state and each new excited state. Both are dependent on μ_{ag} (the transition dipole moment of the individual perylene chromophores) and θ (the angle between this transition dipole moment and the distance vector r).

In order to visualize the interaction between the chromophores in **9**, the structure was modeled using the MMFF94 force field[19] (Figure 4b). First, the modeled structure confirmed the proximity of the protons in the center of **9** for hydrogen bonding. Importantly, this

inhibits the rotational fluctuation of the perylene groups, instead holding them at a defined angle from each other. Assuming the transition dipoles of the perylenes lie along the long axis of the perylene dyes, the angle between the transition dipoles, α, was estimated to be $\alpha \approx 120°$. The distance between the centers of the perylenes was measured to be 12.6 Å for **9**. Since α is larger than 90°, the excitation to the lower energy excited state is stronger than to the higher excited state (see the SI for more details). Therefore, the red-shifted absorption band has a large intensity, while a blue-shifted absorption band is not visible due to its weak intensity and overlapping bands from higher energy transitions. Similar effects give rise to the absorption spectrum observed for dimer **1**.

In conclusion, we reported the synthesis of spatially fixed, covalently linked perylene dimers **9** and **1**. A carbon analog of perylene bisimide allowed the construction of such systems due to the availability of an enol oxygen, which can either form stabilizing hydrogen bonding interactions or undergo further reaction thus affecting the molecular geometry. This is not possible with regular perylene bismides. Angle dependent excitonic coupling between adjacent perylene chromophores leads to bathochromically shifted absorption. The trigonal arrangement between the two perylene chromophores in dimer **1** suggests that further work might yield hexagonal cyclic assemblies showing similar interchromophore interactions.

Note Added after ASAP Publication. After ASAP publication on November 19, 2012, references 10c,d were added regarding bichromophoric perylene bisimides and excitonic coupling within them; the new version reposted November 30, 2012.

Supporting Information Available. Experimental details and characterization of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.