

# Bay-substituted perylene bisimides: Twisted fluorophores for supramolecular chemistry\*

Frank Würthner<sup>‡</sup>

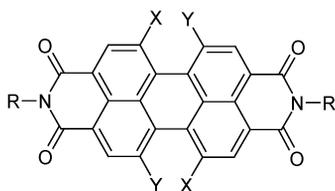
Universität Würzburg, Institut für Organische Chemie, Am Hubland,  
97074 Würzburg, Germany

**Abstract:** Perylene bisimides bearing four aryloxy substituents in the 1,6,7,12 positions (so-called bay area) and two receptor units at the imide nitrogens are most useful fluorescent building blocks for the realization of a broad variety of supramolecular architectures. As discussed in this review, this versatility is not only due to the outstanding fluorescence properties of these dyes with quantum yields close to unity, but also a consequence of pronounced twisting of the  $\pi$ -system with an inversion barrier of around 60 kJ/mol (leading to atropisomerism) and conformational flexibility of aryloxy units. The latter two properties endow these dyes with high solubility even in least polar aliphatic solvents and enable the dyes to maintain a distance of  $\geq 4$  Å in their supramolecular assemblies. This feature particularly reduces the, otherwise often observed, fluorescence quenching in dye aggregates. Thus, bright luminescent cyclic and polymeric supramolecular architectures have become available from these dyes by hydrogen-bond and metal-ion directed self-assembly. In those cases where additional  $\pi$ - $\pi$ -stacking interactions come into play, luminescent organogels and liquid crystals are obtained.

**Keywords:** dyes/pigments; dye assemblies; fluorophores; supramolecular chemistry; twisted  $\pi$ -systems.

## INTRODUCTION

Fluorophores are widely applied functional dyes that are characterized by a radiative depopulation of an excited singlet state. Owing to other competing processes, such as intersystem crossing to the triplet state and internal conversion to the ground state, only few fluorophores exhibit high fluorescence quantum yields (>95 %) in a broad range of solvents as observed for many perylene bisimide derivatives (Scheme 1).



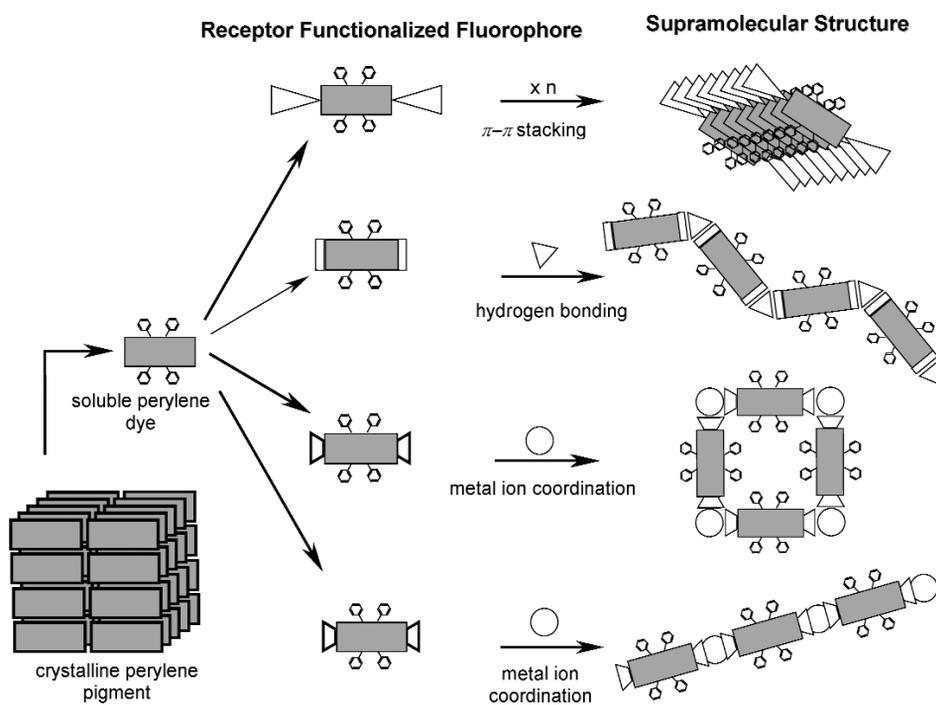
<b>1a:</b> X = Y = H:	$\lambda_{fl}$ = 531 nm, $\Phi$ = 1.00
<b>1b:</b> X = Y = F:	$\lambda_{fl}$ = 512 nm, $\Phi$ = 0.93
<b>1c:</b> X = Y = Cl:	$\lambda_{fl}$ = 548 nm, $\Phi$ = 0.93
<b>1d:</b> X = H, Y = Br:	$\lambda_{fl}$ = 547 nm, $\Phi$ = 0.76
<b>1e:</b> X = H, Y = OPh:	$\lambda_{fl}$ = 575 nm
<b>1f:</b> X = Y = OPh:	$\lambda_{fl}$ = 608 nm, $\Phi$ = 0.96

**Scheme 1** Perylene bisimide fluorophores and their fluorescence maxima and quantum yields (for R = 2,6-diisopropylphenyl) in dichloromethane or chloroform. The fluorescence data for **1a,b** and **1d-f** are taken from refs. [8–10], see below. To complete this series, compound **1c** was currently measured by us.

\*Paper based on a presentation at the XXI<sup>st</sup> IUPAC Symposium on Photochemistry, 2–7 April 2006, Kyoto, Japan. Other presentations are published in this issue, pp. 2193–2359.

<sup>‡</sup>E-mail: wuerthner@chemie.uni-wuerzburg.de

Moreover, perylene bisimides possess exceptionally high photostability, and their emission color can be tuned by proper selection of substituents from green to red [1]. Accordingly, beyond classical applications as fluorescent or laser dyes [2], perylene bisimides have been the fluorophores of choice in particularly demanding fields of materials science, such as single-molecule fluorescence spectroscopy [3], due to their negligible triplet population rate [4]. However, as expected for such an extended  $\pi$ -system with a large quadrupole moment, perylene bisimides are prone to aggregation and crystallization to afford typically nonluminescent pigment particles [1]. As a matter of fact, dye aggregates with bright fluorescence are quite rare, despite the early discovery of fluorescent J-aggregates of cyanine dyes in aqueous solution by Scheibe and Jelley [5,6]. The lack of a generally applicable dye for obtaining highly fluorescent supramolecular assemblies in solvents of diverse properties was the incentive to start with our project, in which we aimed toward well-defined self-assembled cyclic and polymeric dye architectures (Fig. 1). In the course of our investigations, it became apparent that the bright fluorescence of the building block is important not only for many interesting applications, but it is also very beneficial for the elucidation of the structural integrity of the assemblies.



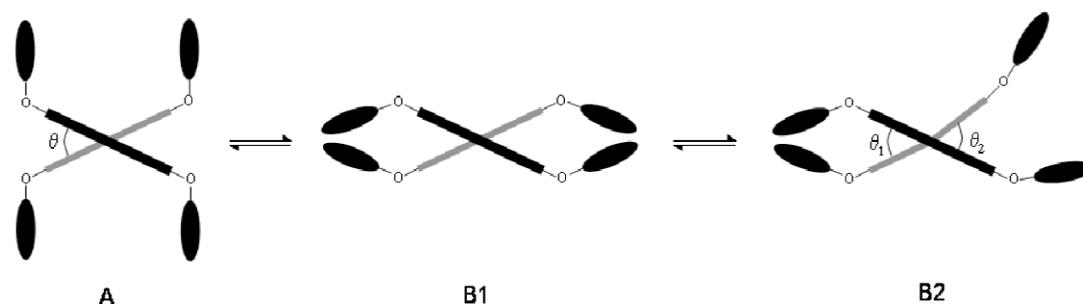
**Fig. 1** Concept for perylene bisimide-based supramolecular chemistry: Attachment of substituents in the four bay positions of perylene bisimides distorts the  $\pi$ -system out of planarity. By this means, the energy of  $\pi$ - $\pi$ -stacking is strongly reduced. Thus, an originally insoluble pigment chromophore (with high lattice energy) is liberated as a soluble dye that can be equipped with receptor groups to realize desired luminescent supramolecular architectures.

As a most promising starting point, we have chosen Seybold's dye **1f**, a perylene bisimide derivative with a highly twisted  $\pi$ -system of unprecedented solubility within the class of perylene bisimide dyes [7]. Despite this twisting of the  $\pi$ -system and the high conformational flexibility (for details, see later), these dyes are outstanding fluorophores [7]. Many derivatives exhibit fluorescence quantum yields between 90 and 100 % in a whole range of organic solvents [8] and, recently, even bright fluorescent water-soluble derivatives could be realized by Müllen and coworkers [9]. Another beneficial feature of these dyes is that their absorption and emission properties are fairly unchanged by the imide

substituents owing to nodes in the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) at the nitrogens [1,2].

### PROPERTIES OF BAY-SUBSTITUTED PERYLENE BISIMIDES

X-ray crystallography [10b,11–16], molecular modeling [17,18], and NMR studies have provided insight into the deformation of the perylene bisimide core upon attachment of substituents at the bay positions. According to molecular modeling, a significant number of conformations have to be considered for aryloxy-substituted compounds (Scheme 2), whilst twisting angles  $\theta_1$  and  $\theta_2$  are sufficient to describe the structure of halogenated perylene bisimides. Table 1 summarizes the twist angles  $\theta$  calculated with AM1 methods and those observed in single crystals by X-ray diffraction analysis.



**Scheme 2** Schematic representation of twisted perylene bisimides and conformational isomerism arising from different orientations of the tetraaryloxy substituents.

**Table 1** Observed (XRD) and calculated (AM1) twisting angles  $\theta$  ( $^\circ$ ) for perylene bisimides **1a–f** and coalescence temperatures  $T_c$  and barriers of inversion  $\Delta G^\ddagger$  in  $\text{CDCl}_3$ .

Compound	$\theta$ ( $^\circ$ ) <sup>a</sup>	$\theta$ ( $^\circ$ ) <sup>b</sup>	$T_c$ (K)	$\Delta G^\ddagger$ (kJ/mol)
<b>1a</b>	0	0 [1]	–	–
<b>1b</b>	21	28/18 [10b]	n.d.	n.d.
<b>1c</b>	36	37 [14]; 35/37 [15]	>376 <sup>c</sup>	>85 <sup>c</sup>
<b>1d</b>	24	24 [13]	n.d.	n.d.
<b>1e</b>	15	n.d.	n.d.	n.d.
<b>1f</b>	27	25 [11,12], 33 [12]	271	60

<sup>a</sup>From AM1 calculations for R = Me.

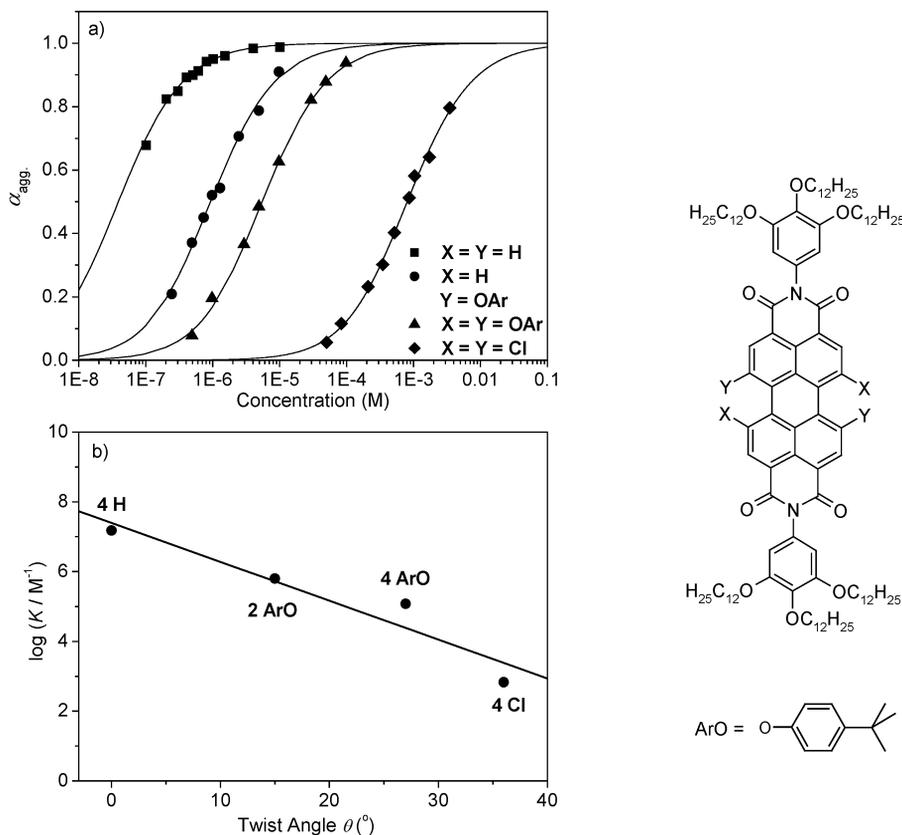
<sup>b</sup>Found in crystal structures (dihedral angles involving four carbon atoms at one of the two bay regions).

<sup>c</sup>Measured in  $\text{Cl}_2\text{DC-CDCl}_2$ .

As the data in Table 1 reveal, only in the unsubstituted derivative proper planarity of the  $\pi$ -system is maintained. The same holds true for the compound with two cyano substituents (X = H, Y = CN in Scheme 1) as shown recently by Wasielewski and coworkers [19]. Otherwise, already for two substituents, steric crowding enforces the distortion of the  $\pi$ -system into two twisted naphthalene imide subunits. Depending on the number and steric demand of the substituents, angles from  $18^\circ$  to  $37^\circ$  are found in the solid state by single-crystal X-ray analysis which are in good agreement with those estimated by semiempirical calculations.

The distortion of the  $\pi$ -system has a significant impact on the intermolecular  $\pi$ – $\pi$ -stacking energy of these compounds in the solid state and for aggregates in solution as well. For perylene bisimides with

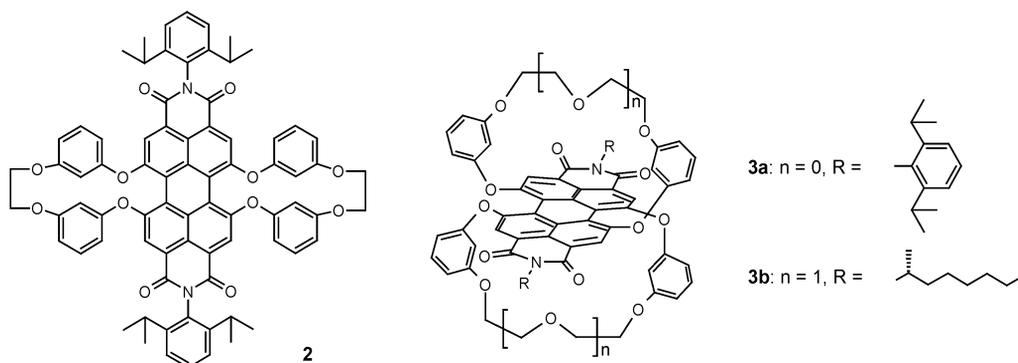
solubilizing imide substituents, spectral changes upon aggregation can be monitored by concentration-dependent UV/vis and fluorescence spectroscopy. Figure 2a shows the concentration dependency of the amount of aggregated dyes in an aliphatic solvent (most related situation to the gas phase) for perylene bisimide dyes bearing different bay substituents. In Fig. 2b, the relationship between the logarithm of the aggregation constant  $K$  (proportional to the Gibbs interaction energy  $\Delta G^0$ ) and the twisting angle  $\theta$  is depicted. The highest driving force for  $\pi$ - $\pi$ -stacking is found for the flat parent chromophore and the lowest one for the most twisted tetrachlorinated compound. Empirically, we can derive an almost linear relationship between  $\log K$  and  $\theta$ .



**Fig. 2** (a) Molar fraction of aggregated molecules as a function of the total concentration in methylcyclohexane and calculated lines according to the isodesmic aggregation model from concentration-dependent UV/vis absorption spectra [24]. (b) Correlation of the logarithm of the aggregation constant  $K$  and the twist angle  $\theta$  of the perylene core estimated by semiempirical calculations.

Besides its impact on solubility and applicability of these dyes for various purposes [7], such twisting of the  $\pi$ -system imparts to bay-substituted perylene bisimides conformational chirality, thus, these twisted  $\pi$ -systems are of interest of their own. In this article, we will denote these stereoisomers as atropisomers, despite the fact that in a strict sense we deal here with planar chirality, and not with axial chirality [20]. The possibility of obtaining helically twisted fluorophores from this class of dyes has already been recognized some years ago [21], but it was only recently that the barriers of inversion have been determined by temperature-dependent  $^1\text{H}$  NMR spectroscopy [22]. The values given in Table 1 show that a resolution of the racemic mixtures of tetrachlorinated derivatives **1c** might be feasible by low-temperature chromatography on a chiral phase, whilst the barrier for tetraphenoxy-substituted com-

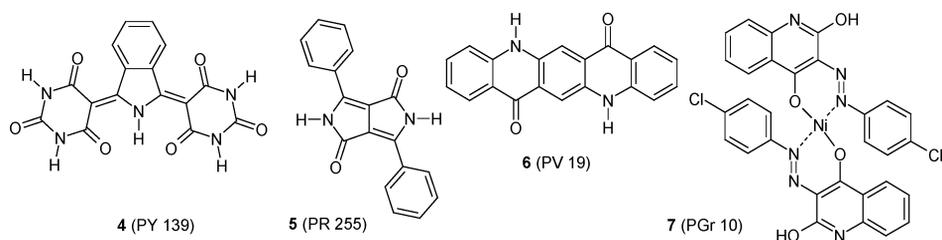
pounds is apparently too low. For a recently synthesized macrocyclic compound **2**, a significant increase of the inversion barrier is observed ( $\Delta G^\ddagger = 74$  kJ/mol), and for the isomeric species **3a** as well as for related compounds with longer oligoethyleneglycol chains ( $n = 1-4$ ) the conformation is completely fixed (Scheme 3) [12]. This has enabled the isolation of a pure diastereomer of **3b** by high-performance liquid chromatography (HPLC) and the investigation of its chiroptical properties [23].



**Scheme 3** Macrocyclic perylene bisimides with conformational chirality.

As expected from the macrocyclic isomeric structures shown in Scheme 3, different conformational possibilities arise also for unfixed aryloxy-substituted perylene bisimides. The coexistence and interconversion of such conformational isomers was indeed the reason that macrocycles with side-on linkage like **2** and top-bottom linkage like **3** could be obtained from the same tetraresorcinol-substituted precursors upon addition of ditosylated oligoethyleneglycols [12]. In different laboratories, structure A (Scheme 2) has been calculated as the lowest energy conformation for tetraphenoxy-substituted perylene bisimides **1f** in the gas phase by semiempirical and force field methods as well [17,18]. However, in the solid state, stretched conformations of type B2 are found [11,12]. Originally, this discrepancy has been attributed to the fact that stretched conformations like B1 and B2 enable stronger intermolecular  $\pi$ - $\pi$ -stacking interactions in the solid state that will increase the lattice energy. As the same packing forces also apply for aggregates of these dyes in solution and in columnar liquid crystals [24], also for these phases stretched conformations have been considered as the more likely structures. However, recent comparative investigations of the NMR, absorption and fluorescence properties of resorcinol-substituted perylene bisimides with and without macrocyclic fixation (like in **2** and **3**) strongly suggest that also unfixed tetraphenoxy-substituted perylene bisimides do preferentially populate a stretched conformation like B1 or B2 in solution [12].

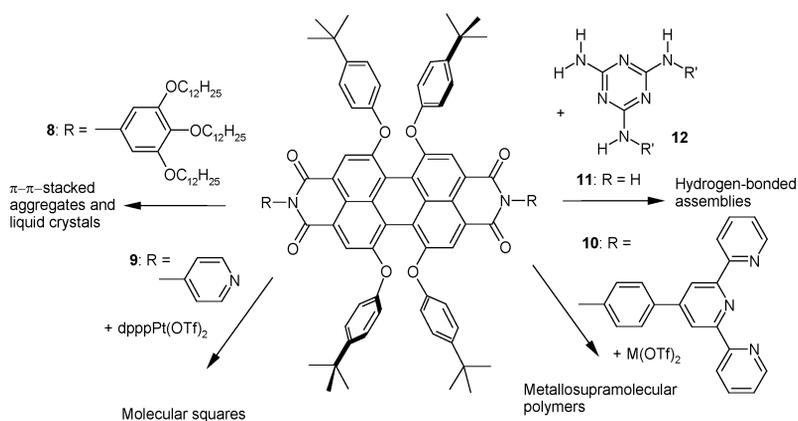
Macrocyclic perylene bisimides that were fixed in stretched conformations of type B showed higher fluorescence quantum yields compared to macrocycles that are fixed in conformation A, at least for the case of electron-rich aryloxy substituents like resorcinol. However, depending on the exact electronic and steric properties of the aryloxy substituent, the equilibrium between these energetically quite similar conformations might shift toward conformation A as suggested for dendron-derivatized compounds [17]. It is noteworthy that the population of different conformations has a very beneficial influence on solubility properties due to an increase of entropy. This feature leads to unprecedented solubility for perylene bisimides that is the prerequisite for obtaining broadly applicable supramolecular building blocks and self-assembled multichromophoric architectures. This behavior is in strict contrast to conventional chromophores, which form insoluble pigments in the presence of receptor units for hydrogen bonding or metal ion coordination. Illustrative examples are given by the yellow isoindoline pigment **4**, the red diketopyrrolo pigment **5**, violet quinacridone pigment **6**, and the greenish-yellow metal complex pigment **7** shown in Scheme 4.



**Scheme 4** Insoluble chromophores applied in commercial color pigments. Note that the combination of strong  $\pi$ - $\pi$ -stacking interactions between flat chromophores and hydrogen-bonds (for **4–6**) or metal ion coordination (for **7**) provides the high lattice energies required to afford insoluble pigments.

## SELF-ASSEMBLED PHOTOLUMINESCENT ARCHITECTURES

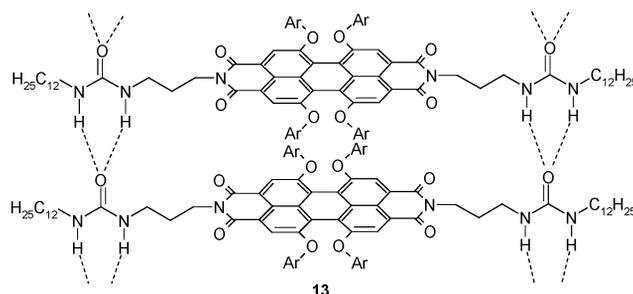
In the last years, our group has synthesized all the architectures suggested in Fig. 1 by the self-assembly approach from the receptor-functionalized perylene bisimide derivatives shown in Scheme 5 [1]. Taking advantage of the strongest noncovalent interactions, namely, metal ion coordination, extended metallocsupramolecular polymers could be obtained even in solvents of high polarity like dimethylformamide (DMF) [25]. Owing to the polyelectrolyte nature of these polymers, a further level of hierarchy could be realized by applying the electrostatic layer-by-layer deposition approach [26]. Although the coordinative forces are not as strong as for the tridentate terpyridine ligand, *cis*-Pt(II)-pyridine coordination motif has proven to be a suitable supramolecular corner unit for the synthesis of well-defined metallocsupramolecular squares [27]. Finally, also weaker hydrogen bonding and  $\pi$ - $\pi$  interactions could be applied in solvents of lower polarity like methylcyclohexane to enable the growth of columnar aggregates, nano- and mesoscopic assemblies, or liquid-crystalline mesophases with a remarkably bright fluorescence [24,28,29].



**Scheme 5** Soluble tetraphenoxy-substituted perylene bisimides equipped with receptor units to control their self-assembly.

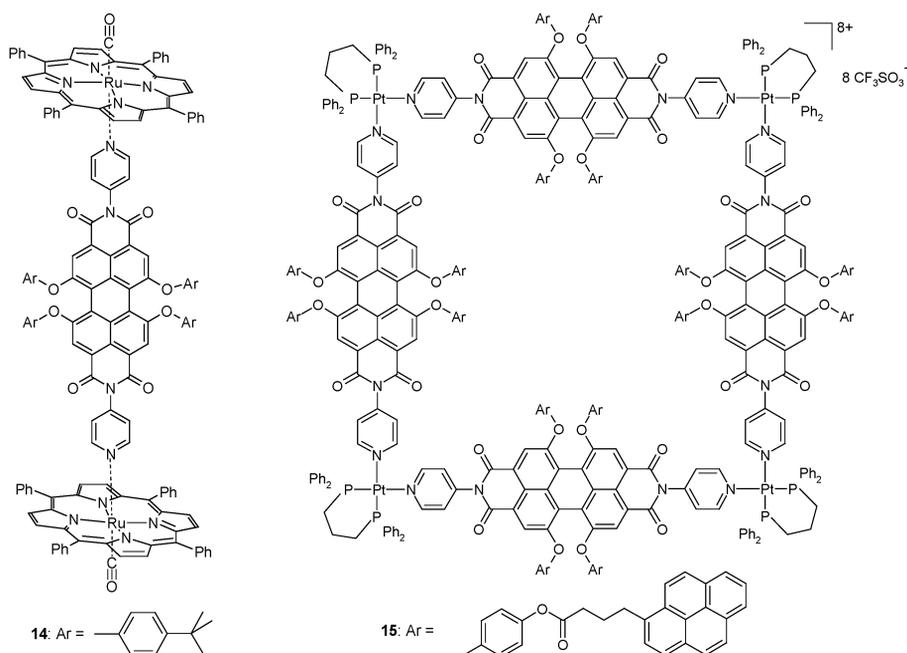
The latter examples provide a particularly convincing demonstration for the capabilities of the supramolecular approach. Thus, whilst an individual triple hydrogen-bonding interaction is too weak to overcome the entropic costs that are demanded to form polymeric chains in dilute solution, assistance by  $\pi$ - $\pi$ -stacking forces triggers self-assembly giving rise to hierarchical superstructures [30] in the nano- and mesoscopic regime [29,31]. The entropic cost associated with self-assembly can be further reduced if both kinds of interactions are combined in one molecule as it is the case in perylene bisimide

**13** that has proven to be a good gelator for aliphatic as well as aromatic solvents (Scheme 6) [32]. The same situation holds true if the self-assembly process is templated by a surface as has been shown by De Feyter et al. for hydrogen-bonded perylene bisimides **11** [33].



**Scheme 6** Organogelator **13** (Ar = *p*-*t*BuPh) and enhanced stacking by hydrogen bonding between urea units.

In addition to the above-mentioned assemblies that conserve the fluorescence properties of constituent perylene bisimide, more complex architectures have recently been assembled that incorporate further functional dyes (Scheme 7).



**Scheme 7** Metallosupramolecular multichromophoric architectures for which novel photophysical properties arise upon self-assembly from the individual components.

For porphyrin-peryene bisimide triad **14**, different cascades of photophysical processes take place upon excitation of the perylene and the porphyrin chromophores [34]. Thus, photoinduced electron transfer from the ruthenium porphyrin to the perylene bisimide is observed upon illumination of the perylene bisimide subunit, whilst ultrafast intersystem crossing followed by triplet energy transfer to the perylene bisimide is observed upon illumination of the ruthenium porphyrin. As a result, a long-

lived ( $\tau = 9.8 \mu\text{s}$ ) perylene bisimide triplet state is formed that is not easily accessible for perylene bisimide chromophores by other means. For multichromophoric square **15**, in which a perylene bisimide molecular square scaffold is surrounded by 16 additional pyrene antenna chromophores, ultrafast energy and electron-transfer processes have been observed between the two dye manifolds [35]. In a further study, electron-rich oligophenylenevinyls have been co-assembled with electron-poor perylene bisimide dyes by hydrogen bonds and  $\pi$ - $\pi$ -stacking interactions to construct supramolecular p-n-heterojunctions with ultrafast photoinduced charge separation [36,37].

To conclude, perylene bisimides bearing four aryloxy substituents in their bay area have been introduced as highly versatile fluorescent supramolecular building blocks. In this overview, we have elucidated the structural design principles of these chromophores that have been the prerequisite for broad supramolecular applications. These design principles involve the highly twisted  $\pi$ -core and the conformational flexibility of the appended aryloxy groups. When equipped with supramolecular receptor units for metal-ion or hydrogen-bond directed self-assembly processes, a broad variety of dye assemblies can be made available upon addition of a complementary binding partner. If this partner likewise contains two binding sites, cyclic oligomers or extended polymers are obtained which quite often conserve the bright fluorescence of the incorporated perylene bisimide. With binding partners containing a second functional  $\pi$ -conjugated system, novel photophysical functionalities are achievable on the nanoscale. An ultimate goal of this research is to derive self-assembled nanoelectronic and nanophotonic devices [38] and to engineer functional assemblies with the capability to interact with functional structures abundant in nature [39].

## ACKNOWLEDGMENTS

Our work on perylene bisimides has been supported by the Deutsche Forschungsgemeinschaft (DFG), the Volkswagen Foundation, the Alexander von Humboldt Foundation, the Fonds der Chemischen Industrie, and BASF AG. I am deeply indebted to the coworkers from my group and many collaborators from other laboratories (names are mentioned in references) who have diligently contributed to understand the intriguing properties of core-substituted perylene bisimide dyes and their self-assemblies.

## REFERENCES

1. F. Würthner. *Chem. Commun.* 1564 (2004).
2. H. Langhals. *Heterocycles* **40**, 477 (1995).
3. F. C. De Schryver, T. Vosch, M. Cotlet, M. van der Auweraer, K. Müllen, J. Hofkens. *Acc. Chem. Res.* **39**, 514 (2005).
4. (a) E. Lang, F. Würthner, J. Köhler. *ChemPhysChem* **6**, 935 (2005); (b) E. Lang, F. Würthner, J. Köhler. *ChemPhysChem* **7**, 283 (2006).
5. G. Scheibe. *Z. Angew. Chem.* **49**, 563 (1936).
6. E. E. Jelley. *Nature* **138**, 1009 (1936).
7. G. Seybold, G. Wagenblast. *Dyes Pigm.* **11**, 303 (1989).
8. R. Gvishi, R. Reisfeld, Z. Burshtein. *Chem. Phys. Lett.* **213**, 338 (1993).
9. (a) J. Qu, C. Kohl, M. Pottek, K. Müllen. *Angew. Chem., Int. Ed.* **43**, 1528 (2004); (b) C. Kohl, T. Weil, J. Qu, K. Müllen. *Chem. Eur. J.* **10**, 5297 (2004).
10. (a) C.-C. Chao, M.-K. Leung, Y. O. Su, K.-Y. Chiu, T.-H. Lin, S.-J. Shieh, S.-C. Lin. *J. Org. Chem.* **70**, 4323 (2005); (b) F. Würthner, P. Osswald, R. Schmidt, T. E. Kaiser, H. Mansikkamäki, M. Könemann. *Org. Lett.* **8**, 3765 (2006); (c) T. van der Boom, R. T. Hayes, Y. Zhao, P. J. Bushard, E. A. Weiss, M. R. Wasielewski. *J. Am. Chem. Soc.* **124**, 9582 (2002).
11. F. Würthner, A. Sautter, C. Thalacker. *Angew. Chem., Int. Ed.* **39**, 1243 (2000).
12. P. Osswald, D. Leusser, D. Stalke, F. Würthner. *Angew. Chem., Int. Ed.* **44**, 250 (2005).

13. F. Würthner, V. Stepanenko, Z. Chen, C. R. Saha-Möller, N. Kocher, D. Stalke. *J. Org. Chem.* **69**, 7933 (2004).
14. Z. Chen, M. G. Debijs, T. Debaerdemaeker, P. Osswald, F. Würthner. *ChemPhysChem* **5**, 137 (2004).
15. S. Leroy-Lhez, J. Baffreau, L. Perrin, E. Levillain, M. Allain, M.-J. Blesa, P. Hudhomme. *J. Org. Chem.* **70**, 6313 (2005).
16. M. Sadrai, G. R. Bird, J. A. Potenza, H. J. Schugar. *Acta Crystallogr., Sect. C* **46**, 637 (1990).
17. (a) J. Hofkens, T. Vosch, M. Maus, F. Köhn, M. Cotlet, T. Weil, A. Herrmann, K. Müllen, F. C. De Schryver. *Chem. Phys. Lett.* **333**, 255 (2001); (b) J. Qu, N. G. Pschirer, D. Liu, A. Stefan, F. C. De Schryver, K. Müllen. *Chem. Eur. J.* **10**, 528 (2004).
18. A. Sautter, D. G. Schmid, G. Jung, F. Würthner. *J. Am. Chem. Soc.* **123**, 5424 (2001).
19. B. A. Jones, M. J. Ahrens, M.-H. Yoon, A. Facchetti, T. J. Marks, M. R. Wasielewski. *Angew. Chem., Int. Ed.* **43**, 6363 (2004).
20. (a) E. L. Eliel, S. H. Wilen. *Stereochemistry of Organic Compounds*, pp. 1119–1190, Wiley-VCH, New York (1994); (b) U. Weiss, L. Merlini, G. Nasini. *Prog. Chem. Org. Nat. Prod.* **52**, 1 (1987).
21. S. Hien. PhD thesis, Universität Regensburg (1995).
22. P. Osswald. PhD thesis, Universität Würzburg, planned for 2007.
23. P. Osswald, M. Reichert, G. Bringmann, F. Würthner. Unpublished results.
24. (a) F. Würthner, C. Thalacker, S. Diele, C. Tschierske. *Chem. Eur. J.* **7**, 2245 (2001); (b) Z. Chen, U. Baumeister, C. Tschierske, F. Würthner. *Chem. Eur. J.* In press.
25. R. Dobrawa, M. Lysetska, P. Ballester, M. Grüne, F. Würthner. *Macromolecules* **38**, 1315 (2005).
26. R. Dobrawa, D. G. Kurth, F. Würthner. *Polym. Prepr.* **45**, 378 (2004).
27. (a) F. Würthner, A. Sautter. *Chem. Commun.* 445 (2000); (b) F. Würthner, A. Sautter, D. Schmid, P. J. A. Weber. *Chem. Eur. J.* **7**, 894 (2001).
28. F. Würthner, C. Thalacker, A. Sautter. *Adv. Mater.* **11**, 754 (1999).
29. F. Würthner, C. Thalacker, A. Sautter, W. Schärfl, W. Ibach, O. Hollricher. *Chem. Eur. J.* **6**, 3871 (2000).
30. J. A. A. W. Elemans, A. E. Rowan, R. J. M. Nolte. *J. Mater. Chem.* **13**, 2661 (2003).
31. Y. Liu, J. Zhuang, H. Liu, Y. Li, F. Lu, H. Gan, T. Jiu, N. Wang, X. He, D. Zhu. *ChemPhysChem* **5**, 1210 (2004).
32. F. Würthner, B. Hanke, M. Lysetska, G. Lambright, G. S. Harms. *Org. Lett.* **7**, 967 (2005).
33. S. De Feyter, A. Miura, S. Yao, Z. Chen, F. Würthner, P. Jonkheijm, A. P. H. J. Schenning, E. W. Meijer, F. C. De Schryver. *Nano Lett.* **5**, 77 (2005).
34. A. Prodi, C. Chiorboli, F. Scandola, E. Iengo, E. Alessio, R. Dobrawa, F. Würthner. *J. Am. Chem. Soc.* **127**, 1454 (2005).
35. A. Sautter, B. K. Kaletaş, D. G. Schmid, R. Dobrawa, M. Zimine, G. Jung, I. H. M. van Stokkum, L. De Cola, R. M. Williams, F. Würthner. *J. Am. Chem. Soc.* **127**, 6719 (2005).
36. F. Würthner, Z. Chen, F. J. M. Hoeben, P. Osswald, C.-C. You, P. Jonkheijm, J. van Herrikhuyzen, A. P. H. J. Schenning, P. P. A. M. van der Schoot, E. W. Meijer, E. H. A. Beckers, S. C. J. Meskers, R. A. J. Janssen. *J. Am. Chem. Soc.* **126**, 10611 (2004).
37. E. H. A. Beckers, S. C. J. Meskers, A. P. H. J. Schenning, Z. Chen, F. Würthner, P. Marsal, D. Beljonne, J. Cornil, R. A. J. Janssen. *J. Am. Chem. Soc.* **128**, 649 (2006).
38. A. P. H. J. Schenning, E. W. Meijer. *Chem. Commun.* 3245 (2005).
39. S. Krauß, M. Lysetska, F. Würthner. *Lett. Org. Chem.* **2**, 349 (2005).