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Energy transfer in multichromophoric self-assembled molecular squares†

Frank Würthner *‡ and Armin Sautter
Abteilung Organische Chemie II, Universität Ulm, Albert-Einstein-Allee 11, D-89081 Ulm, Germany

Received 3rd September 2002, Accepted 5th November 2002
First published as an Advance Article on the web 9th December 2002

Metal-ion directed self-assembly afforded well-defined molecular squares with a mass of 12 kDa incorporating four perylene bisimide and sixteen pyrene chromophores organized in a circular way. Energy transfer from the pyrene to the perylene dye manifold is investigated by emission and excitation spectroscopy.

One of the most fascinating scientific topics is the conversion of sunlight into chemical energy in natural photosynthesis.[1] Chemistry can contribute to this field of research in two ways, one is by synthesis and spectroscopic characterization of model systems for the natural counterparts,[2] another is by application of the acquired knowledge to derive 'biomimetic' photovoltaic devices.[3] In nature, two subsystems are required to achieve efficient photosynthesis which consist of the well-characterized reaction centers and the much larger light harvesting systems (LHS) that incorporate up to hundreds of dyes. Depending on the respective species and their natural inhabitation different kinds of chromophores and principles of organization (*e.g.* rods, tubes, rings) are found in the LHS but a precise positioning of the dyes in space is always provided by non-covalent interactions to proteins or between the dyes. In the last years chemists could realize extended dye aggregates[4] that are considered to be reasonable models for the rod-like LHS of green bacteria as well as multichromophoric dendrimers[5] which exhibit a spatial distribution of the dyes that resembles the LHS of green plants. On the other hand, synthetic analogues to the structurally and functionally most intriguing cyclic LHS of purple bacteria are still lacking.[6] These LHS consist of two types of cyclic arrays of bacteriochlorophyll (BChl) dyes which are organized in space through non-covalent interactions with proteins. The larger LHS I contain a single ring of ~30 strongly coupled BChls and accommodate the reaction center of photosynthesis in its interior. The smaller peripheral LHS II contain a total of 24 BChls that are distributed in two rings, a strongly coupled one of aggregated dyes and a weakly coupled one of isolated dyes around an eightfold symmetry axis.[7]

In our recent work we applied the concept of metal-directed self-assembly[8–11] to obtain highly fluorescent and electroactive perylene bisimide dye squares.[12,13] In the given work we will equip this nanosize scaffold with sixteen additional antenna dyes and demonstrate efficient energy transfer from the outer to the inner chromophores. Notably, as shown in Fig. 1, not only the structural features of these multichromophoric assemblies are reminiscent of those of the natural LHS II (circular dye arrays) but also their formation is likewise directed by non-covalent forces.

For an efficient energy transfer from the outer to the inner dye arrays (like in the natural LHS) a pair of chromophores is required which exhibit high fluorescence quantum yields, a good spectral overlap of the absorption spectrum of the energy acceptor dye with the fluorescence band of the energy donor dye and specific absorption bands in the two dyes that can be excited individually. The first two properties are a prerequisite for an efficient through-space resonance energy transfer (Förster mechanism)[14] and the latter condition is important for an easy evaluation of the energy transfer efficiency. Taking these facts into consideration our first multichromophoric molecular square was synthesized according to Scheme 1 from tetra-*p*-butoxyphenoxyperylene bisanhydride **1**[15] by imidization with 4-aminopyridine,[12] subsequent BBr_3-promoted cleavage of the butyl ether groups, and esterification of the phenolic groups with pyrene butyric acid through activation of the carboxylic acid group by dicyclohexylcarbodiimide (DCC) in the presence of dimethylaminopyridinium toluenesulfonate (DPTS).[16] All reactions proceeded smoothly yielding analytically pure **4** in an overall yield of 21% based on **1**.§ Finally, equimolar mixing of **4** and [Pt(dppp)][$(OTf)_2$] in CH_2Cl_2 at room temperature led to a quantitative conversion to molecular square **5** which could be isolated in 67% yield as a fine powder after precipitation by addition of diethylether.

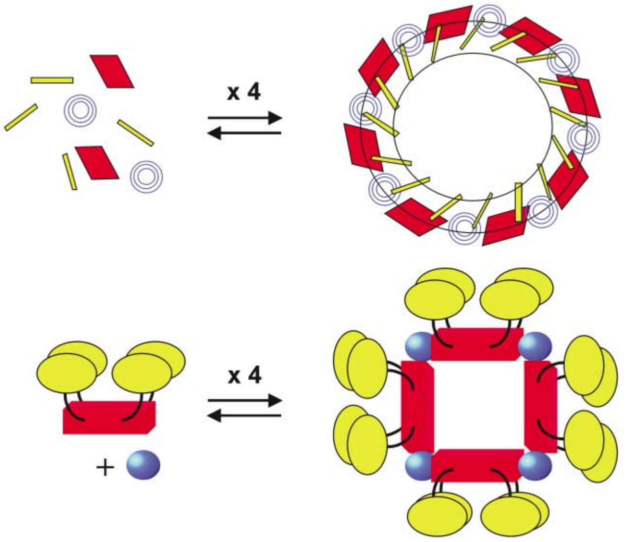

Fig. 1 Formation of the natural circular dye arrays in LHS II of purple bacteria (top)[1] and of artificial square-type dye arrays by self-assembly (bottom). The yellow and red colors indicate dye molecules. The blue color indicates proteins (top) or metal ions (bottom) that direct the self-assembly process and define the spatial arrangement of the dye molecules.

The structure of **5** was confirmed by 500 MHz ^1H and 202 MHz $^{31}P\{^1H\}$ NMR spectroscopy and Electrospray Fourier Transform Ion Cyclotron Mass Spectrometry (ESI-FTICR-MS). The $^{31}P\{^1H\}$ NMR spectrum displays only one singlet at $\delta = -14.4$ ppm (*vs.* 85% aq. H_3PO_4), shifted by about $\Delta\delta = -10$ ppm with respect to the precursor complex [Pt(dppp)]-[$(OTf)_2$], which is in accordance with coordination of two

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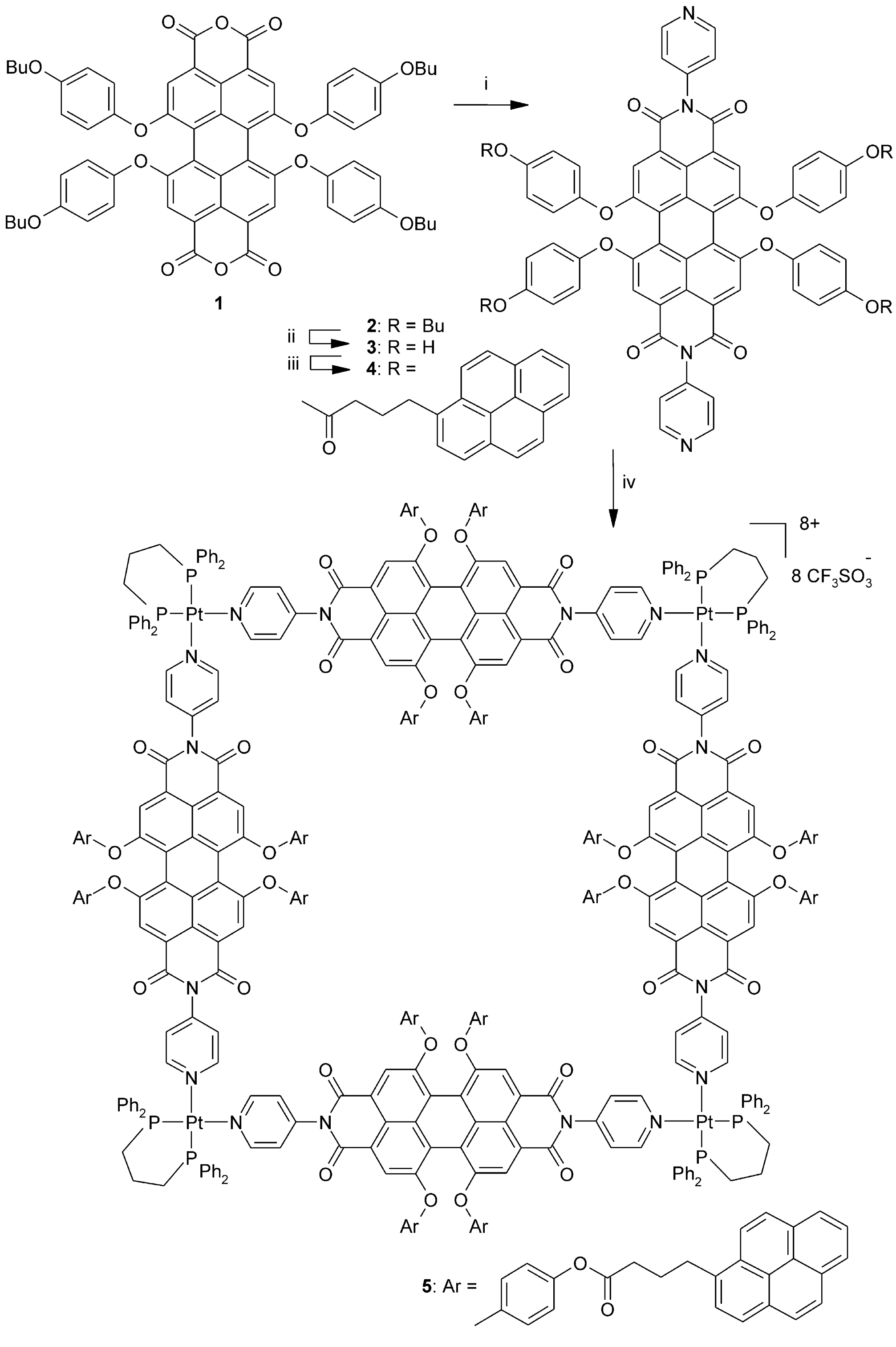
† Dedicated to Professor Waldemar Adam on the occasion of his 65th birthday

‡ New address: F. Würthner, Institut für Organische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany. E-mail: wuerthner@chemie.uni-wuerzburg.de

DOI: 10.1039/b208582h



Scheme 1 Synthesis of pyrene-substituted perylene bisimide **4** and metal-ion directed self-assembly to multichromophoric square **5**: i) 4-amino-pyridine, Zn(OAc)$_2$, quinoline, 180 °C, 16 h, Ar, 58% yield; ii) BBr$_3$, CH$_2$Cl$_2$, 25 °C, 2 h, 92% yield; iii) 4-pyrene-1-yl butyric acid, DCC, DPTS, CH$_2$Cl$_2$, 25 °C, 3 d, 40% yield; iv) [Pt(dppp)][(OTf)$_2$], CH$_2$Cl$_2$, 25 °C, 24 h, Ar, 67% yield.

pyridine ligands at the Pt(II) metal ion and the high symmetry of the square structure.[12,17] In the ^{1}H NMR spectrum typical changes of the pyridine Hα protons ($\Delta\delta = 0.4$ ppm) are observed and only one set of signals for the perylene bisimide ligand and one set for the dppp moiety are present. Several signals are significantly broadened which indicates restricted conformational flexibility as already found and discussed for more simple dpppPt(II) squares.[12,17]

ESI-FTICR-MS unambiguously proved the existence of the square structure of **5** and its considerable stability. The spectrum of **5** displays the intact square species [**5** − 4OTf]$^{4+}$ at *m*/*z* 2814.54, and [**5** − 5OTf]$^{5+}$ at *m*/*z* 2221.87 after the loss of four and five triflate anions, respectively (Fig. 2). The calculated average masses of the two species, (2814.85 and 2222.07, resp.) are in excellent agreement with the experimental results, and deconvolution of the two signals amounts to a molecular mass of 11854.65 Da (calculated average mass: 11855.65 Da) for the neutral molecular square. Several fragments could also be identified, *e.g.* loss of one corner (C) and one diaza ligand (L) [**5** − 1C − 1L]$^{4+}$, *m*/*z* 2073.77; loss of two corners and two diaza ligands [**5** − 2C − 2L]$^{3+}$, *m*/*z* 1826.80, and loss of three corners and two diaza ligands [**5** − 3C − 2L]$^{2+}$, *m*/*z* 2361.63.

The optical properties of molecular square **5** have been studied by UV/Vis absorption, excitation and emission spectro-

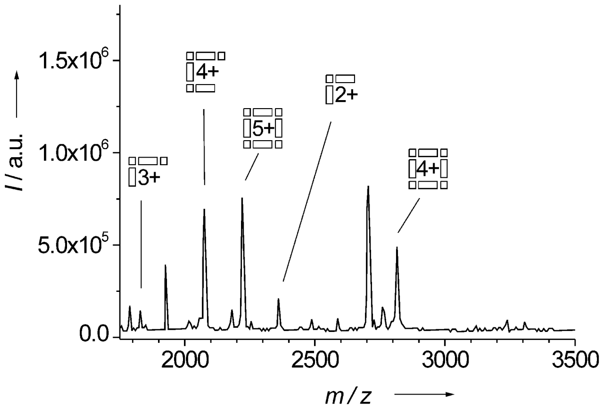
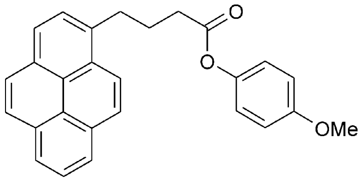


Fig. 2 ESI-FTICR-MS of light-harvesting molecular square **5** (from a solution in acetone–CH_2Cl_2 1 : 1).



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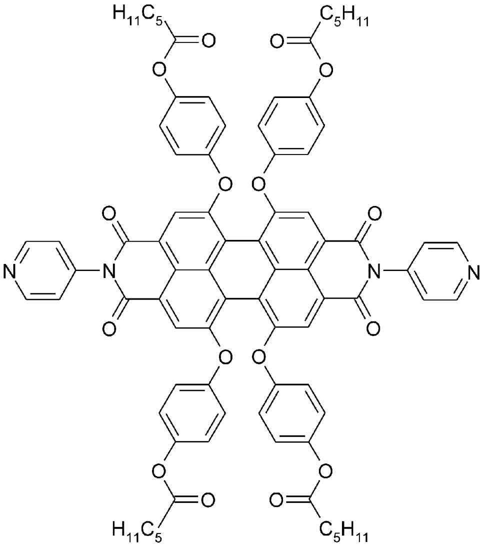

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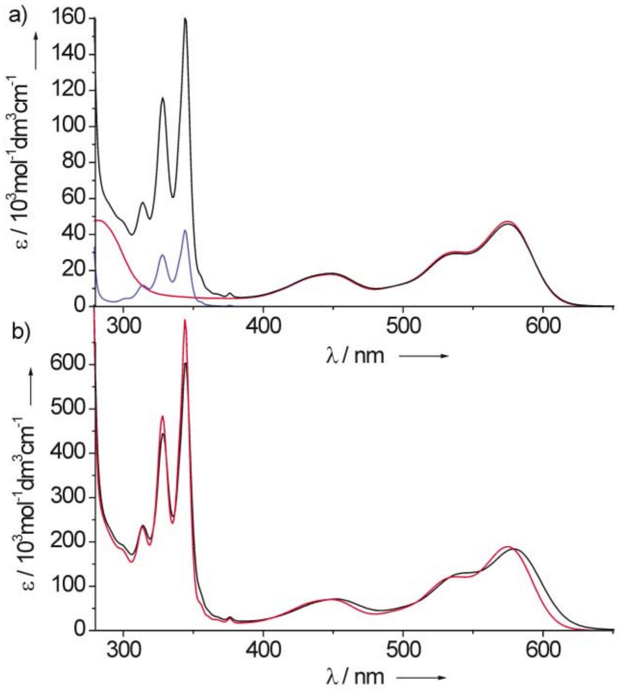

Fig. 3 UV/Vis absorption spectra in CH_2Cl_2 for a) the tetrapyrene–perylene ligand **4** (black line), pyrene **6** (blue line) and perylene **7** (red line) and b) the self-assembled molecular square **5** (black line). In addition in b) the calculated spectrum $\varepsilon = 4 \times \varepsilon(\mathbf{7}) + 16 \times \varepsilon(\mathbf{6})$ is shown (red line).

scopy. For a proper assignment of the absorption and emission bands the two dyes **6** and **7** have been synthesized and included in our study.§ In the top graph of Fig. 3 the absorption spectra of these two dyes are shown together with the spectrum of the ligand **4**. From this comparison we see that the individual bands of the pyrene and the perylene chromophores can be clearly assigned. Three sharp and intense transitions are observed for the pyrene chromophore at 314, 328 and 344 nm and two broad absorption bands are given at ~450 nm and ~575 nm for the perylene bisimide. The superposition of the perylene-related bands of dyes **4** and **7** is perfect and the intensity of the pyrene-related peaks is four times higher in **4** than in **6** as suggested by the molecular structures. Accordingly we can conclude that the pyrene and perylene chromophores of **4** exhibit no interaction in the ground state and can be excited with high selectivity at 344 nm for pyrene and at 400–600 nm for perylene. Remarkably this situation remains unchanged for the fully assembled square **5** which now incorporates sixteen pyrene and four perylene dyes. The absorption spectrum of this compound is shown in Fig. 3b with distinct bands for the pyrene and the perylene subunits. Compared to the calculated spectrum for a supermolecule containing sixteen pyrene dyes **6** and four perylene bisimide dyes **7** we note two small changes in the absorption features. For the perylene bisimide transitions slight bathochromic shifts are observed upon self-assembly. This effect is well-known from our earlier studies[12] and is attributed to the coordination of the pyridine receptor unit to the Pt(II) metal ion. The second effect is a slight broadening of the pyrene bands that lead to reduced peak intensities in the absorption maxima. However, integration shows that the oscillator strength remains unchanged. Therefore also for the self-assembled square two distinct chromophoric systems are given which exhibit no interaction in the ground state. Taking structural aspects into account we can conclude that square **5** exhibits a cyclic tetrameric scaffold of weakly coupled perylene dyes absorbing in the visible which is surrounded by another chromophoric system containing sixteen independent pyrene dyes which absorb in the UV range.¶

Upon photoexcitation of square **5** an intense red fluorescence is observed whose spectral position and shape is independent of the excitation wavelength (Fig. 4). Thus, even for selective excitation of the pyrenes at 344 nm the observed emission arises mainly from the S_0–S_1 transition of the perylene bisimides and only a very weak emission of the pyrenes is seen upon magnification (Inset Fig. 4) suggesting an almost quantitative energy transfer process from the pyrene to the perylene chromophores. This observation was surprising to us because the overlap of the fluorescence band of the pyrene chromophores at 360–440 nm with the absorption band of the perylene bisimide is not at all ideal|| for a Förster-type resonance energy transfer, that is, however, the only feasible mechanism in the case of weakly coupled chromophores.[14] Therefore we carried out another experiment in which the fluorescence intensity of the perylene emission is recorded upon excitation over the wavelength range from 320 to 620 nm.[18] As seen from Fig. 4, the thus obtained fluorescence excitation spectrum of **5** exhibits a good match to

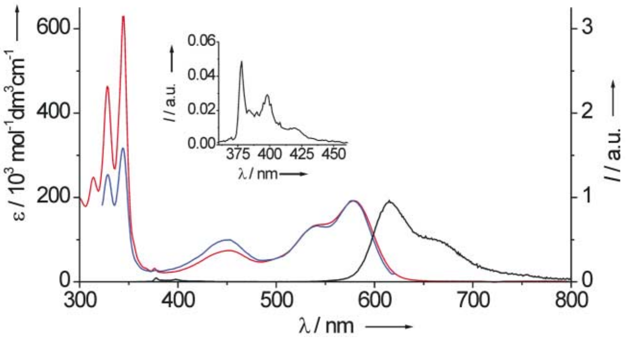

Fig. 4 UV/Vis absorption (red line), fluorescence excitation (blue line, λ_{em} = 630 nm) and emission (black line, λ_{ex} = 344 nm) spectra for square **5** in CH_2Cl_2. The inset shows a magnification of the residual pyrene emission. The absorption spectra were recorded at a square concentration of 1.7×10^{-6} M . For the fluorescence spectra this solution was diluted until an absorbance < 0.05 was reached.

the corresponding UV/Vis absorption spectrum in the area of the perylene absorption bands between 400 and 600 nm but has a significantly reduced intensity for the pyrene bands. Based on the integrated intensities from 320 to 360 nm only about 50% of the excited pyrene dyes transfer their excitation energy to the perylene manifold.

Taken together these results pinpoint a more complicated photophysical behavior of such multichromophoric assemblies which cannot be revealed by simple steady-state spectroscopy. Time-resolved and single molecule spectroscopic studies are already in progress whose suitability for a deeper understanding of the electronic interactions between dyes in dendrimers has recently been demonstrated by De Schryver and Müllen.[19] In addition a larger variety of well-defined multichromophoric superstructures is desirable to reveal structure–functionality relationships for light-harvesting systems and to understand why nature has chosen special types of chromophores and principles of organization.

We are grateful to Professor Günther Jung and Dietmar G. Schmid (University of Tübingen, Germany) for the ESI-FTICR mass spectrometric characterization of square **5** and to the Volkswagen Foundation for supporting our research within the framework "Physics, Chemistry and Biology with Single Molecules".

Notes and References

§ All new compounds are characterized by ^{1}H NMR, MS, UV/Vis spectroscopy and elemental analysis.

¶ Molecular modeling indicates that eight pyrenes are located above and eight pyrenes are located below the rigid perylene bisimide scaffold as suggested in Fig. 1b.

|| The fluorescence spectrum of pyrene **6** has a mirror-symmetry to the absorption spectrum and maxima at 378 and 397 nm. As the weak emission observed for square **5** (Fig. 4, inset) exhibits the same position and vibronic structure it unambiguously originates from the pyrene manifold.

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