Dye Assemblies

DOI: 10.1002/anie.200705385

# Transformation from H- to J-Aggregated Perylene Bisimide Dyes by Complexation with Cyanurates**

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Perylene bisimide (PBI) dyes have received a great deal of attention owing to their outstanding optical and electronic properties that are favorable for application as functional materials.[1] As for other π-conjugated chromophores,[1c,d,2] a long-term challenge in the supramolecular chemistry of PBI dyes is the control of the local π-stacking arrangements of the chromophores, which greatly affect the dye's optical and electronic properties.[1a] While H-aggregated PBIs exhibit the high n-type carrier mobilities desired in electronic devices,[3] the extended exciton mobility of J-aggregated[4] PBIs could be exploited in organic solar cells.[5] However, to date, J-aggregation of perylene bisimides could only be achieved by introducing bulky substituents into the so-called "bay area" (1,6,7,12-positions) of the perylene core.[1a,6] A novel example has recently been published by one of our groups, where highly fluorescent J-aggregates, with a remarkably red-shifted absorption band (570→642 nm), are formed from a core-substituted PBI through hydrogen-bond-directed supramolecular polymerization.[5f] However, soluble J-aggregates of core-unsubstituted PBIs with a dramatic red shift of the absorption spectra are not known to date,[7,8] despite the fact that such aggregates would certainly expand the scope of PBIs as functional materials. Herein, we report for the first time the transformation of H-aggregates of a core-unsubstituted PBI **1** to the J-aggregates, which exhibit a pronounced red-shifted absorption band. This H- to J-aggregate transformation is achieved by hydrogen-bond-directed complexation of the melamine unit in PBI **1** with cyanuric acid derivatives.[9–11]

During our exploration of PBI assemblies using melamine-cyanurate supramolecular complexation,[10d] we unexpectedly discovered that unsymmetrically substituted PBI **1** undergoes a transformation from H- to J-aggregate upon mixing with monosubstituted cyanurate dCA (d denotes single dodecyl group) at different stoichiometric ratios, exhibiting a pronounced absorption spectral change for the perylene chromophores (Figure 1). PBI **1** has a single monotopic melamine site that complementarily binds to cyanuric acid derivatives through triple hydrogen bonding. Interestingly, without addition of cyanurate guests, **1** self-aggregates in nonpolar methylcyclohexane (MCH)[12] predominantly through π-stacking interactions as indicated by UV/Vis spectra that are characteristic of H-aggregated core-unsubstituted PBIs.[13] The fraction of π-stacked aggregates (α) in $1.4\times10^{-5}$ M solution of **1** is 0.68 at 25 °C (yellow spectrum in Figure 2 a). When aliquots of monotopic triple hydrogen-bonding module ddCA were titrated into the solution of **1**, small spectral changes, indicating the disruption of π-stacked aggregates, were observed (see the Supporting Information), implying that the two bulky dodecyl chains of ddCA interrupt π-stacking interaction of **1** (**1**-ddCA in Figure 1). The α value decreases to 0.52 upon addition of 5 equivalents of ddCA, and an apparent binding constant of 23 000 $\text{M}^{-1}$ was calculated.[14]

In sharp contrast to monotopic ddCA, a drastic spectral change indicating an increase in α value, takes place upon addition of ditopic dCA (from yellow to red spectra in Figure 2 a). This observation strongly suggests the formation of an H-dimer locked by dCA through two triple hydrogen-bonding interactions (**1**-dCA-**1** in Figure 1).[15] The absorption of free perylene chromophores disappeared completely at **1**/dCA = 1:0.5, revealing quantitative formation of such an H-dimer by cooperative π-stacking and hydrogen-bonding interactions.[16] A "melting" temperature ($T_m$) of 68 °C was determined for a $[\mathbf{1}]=2[\text{dCA}]=1.4\times10^{-5}$ M solution from variable temperature UV/Vis measurements, a value which is significantly higher than that of self-aggregated **1** ($T_m$ = 31 °C).[14]

Surprisingly, further addition of dCA to the solution of **1**/dCA = 1:0.5 mixture resulted in a green color (Figure 1) and the growth of a new absorption band at $\lambda_{max}=620$ with concomitant decrease of the H-dimer band (red to green spectrum in Figure 2 a; also see the inset). A red shift of > 100 nm is observed for the new band compared to the absorption of monomeric PBI (515 nm). Such a striking red shift is indicative of the formation of a J-type aggregate in solution, which is, to our knowledge, unprecedented for core-unsubstituted PBIs.[7,8] The spectral change is complete at around **1**/dCA = 1:1.2 for a $c=1.4\times10^{-5}$ M solution, but the stoichiometry required for the J-aggregation was more accurately determined to be 1:1 by the additional experiments described in the Supporting Information.

The observed emission behavior of PBI **1** upon addition of dCA agrees with the transformation of self-aggregated **1** to

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[**] This work was financially supported by The Association for the Progress of New Chemistry.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

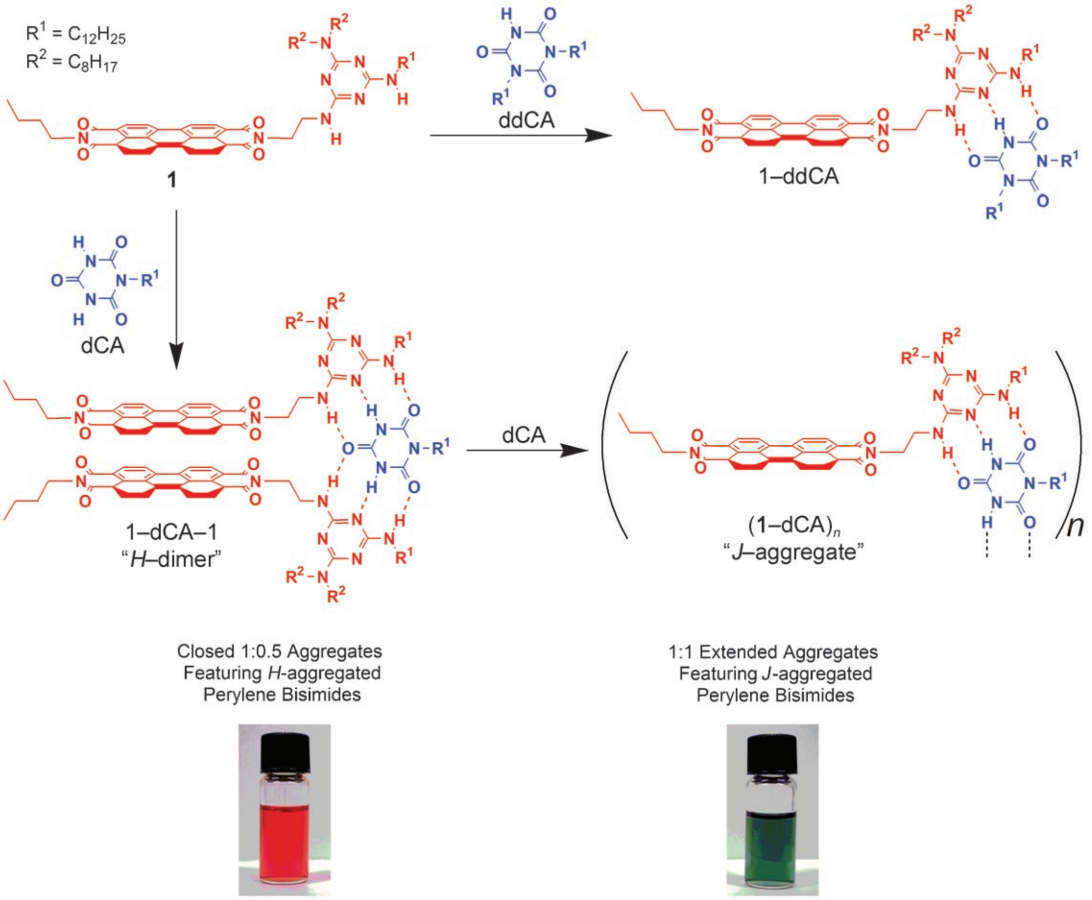

***Figure 1.*** Complexation of **1** with the monotopic cyanurate ddCA and the ditopic cyanurate dCA. For 1:0.5 and 1:1 aggregates of **1** and dCA, photographs of their methylcyclohexane solutions are shown.

the H-dimer, followed by J-aggregation. In the first stage, a gradual decrease of the structured fluorescence of non-stacked **1** was observed up to **1**/dCA = 1:0.5 along with the growth of typical excimer fluorescence[5e,17] from the H-dimer at $\lambda_{max} = 636$ nm (yellow to red spectra in Figure 2b). The second stage endure up to **1**/dCA = 1:1.5 (red to green spectrum in Figure 2b; also see the inset), showing a red shift of the emission maximum to $\lambda = 673$ nm (Stokes shift: 53 nm). This fluorescence spectral displacement clearly indicates the transformation of the H-dimer into a different type of π-stacked aggregate upon further addition of dCA.

An unusual feature of the J-aggregate is the presence of a considerably blue-shifted absorption band at around 400–500 nm, in addition to the aforementioned red-shifted band at 620 nm (Figure2a). Concentration-dependent UV/Vis measurements showed that the reversible growth and depletion of these two absorption bands are synchronized with the increase and decrease of concentration,[14] demonstrating that these two bands are arising from the same aggregated species. The results of temperature-dependent UV/Vis measurements described below also support this view. Therefore, it is reasonable to assume that the chromophore packing in the J-aggregate features not only a significant longitudinal offset with respect to the long axis of PBI but also a rotational displacement, allowing electronic transitions into both lower and higher excited-state energy levels.[18] Remarkably, the fluorescence excitation spectrum detected at 700 nm showed a notable depletion of the blue-shifted band,[14] revealing a marginal energetic interaction between these energy levels.

Temperature-dependent UV/Vis measurements further revealed that the J-aggregate could be thermally transformed into the H-dimer and then into monomers (M) in a fully reversible manner. As shown in Figure 3a, the spectral transition upon increasing temperature progresses in two nearly independent stages with clear isosbestic points at 554 (purple arrow, 20–55 °C) and 523 nm (blue arrow, 60–90 °C). The inflection point is located at 55 °C. Below this temperature, mainly the J-to-H transition occurs as revealed by the decrease of ε values at 400 and 620 nm (Figure 3b), and above 55 °C, the H-to-M transition exclusively takes place as manifested by up-down behavior of the ε value at 544 nm where the J-aggregate and H-dimer dominantly absorb. The melting temperature of the J-aggregate is determined to be about 40 °C at $[\mathbf{1}] = [\mathrm{dCA}] = 1.4 \times 10^{-5}$ M, implying that the J-aggregate is constructed by relatively weak noncovalent interactions. The fully reversible thermal transformation between H- and J-aggregates is indeed a unique property which might be utilized for a supramolecular thermometer.[19]

Another intriguing feature of the present system is the self-organization into extended structures. When 1:1 mixtures

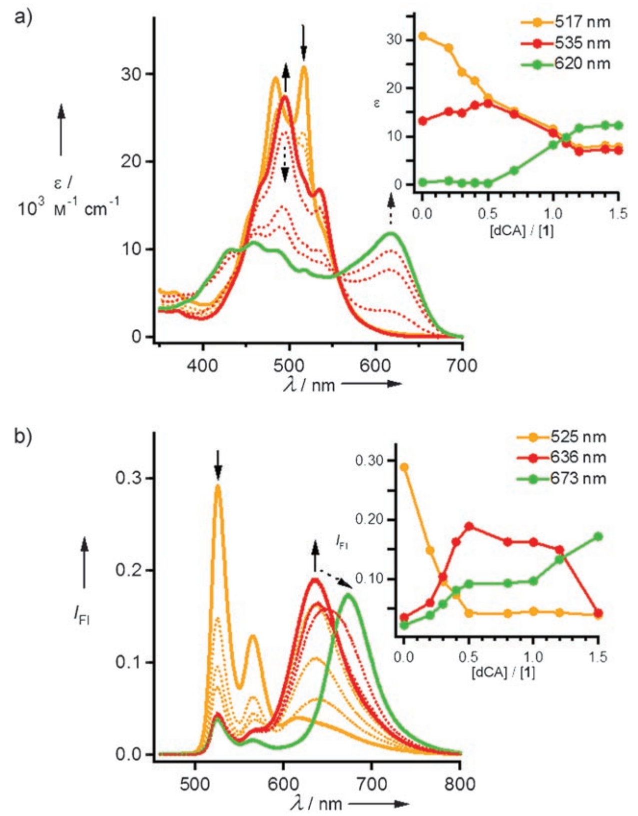

***Figure 2.*** a) UV/Vis and b) fluorescence ($\lambda_{ex} = 450$ nm) titration experiments of **1** ($c = 1.4 \times 10^{-5}$ M) with dCA. Yellow, red, and green solid curves are the spectra at **1**/dCA = 1:0, 1:0.5, and 1:1.2 (UV/Vis) or 1:1.5 (fluorescence), respectively. Solid and dashed arrows indicate the transitions from yellow to red and red to green spectra, respectively. Insets show changes of ε and fluorescence intensities at several wavelengths.

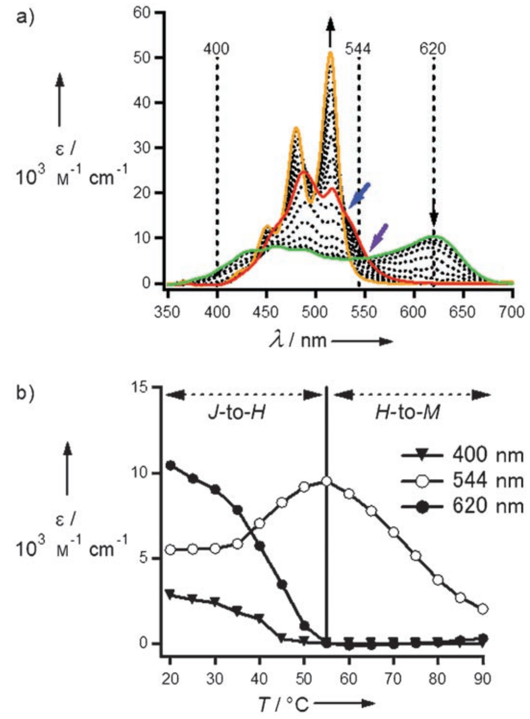

***Figure 3.*** a) Temperature-dependent UV/Vis spectra of **1**/dCA = 1:1 mixture in MCH ($c = 1.4 \times 10^{-5}$ M). The spectra at 20, 55, and 90 °C are shown as green, red, and yellow lines, respectively. Black arrows indicate spectral changes upon increasing temperature. Purple and blue arrows point the isosbestic points in the first (20–55 °C, 554 nm) and the second transitions (60–90 °C, 523 nm), respectively. b) Plot of ε at 400 (▼), 544 (○) and 620 nm (●) versus temperature.

in MCH were kept at room temperature, green precipitates formed within several hours in almost quantitative yield based on **1** and dCA.[20] This provides a clear indication for the formation of a extended supramolecular network.[21,22] Cyanuric acid and its alkylated derivatives form supramolecular lattices supported by single and/or double hydrogen-bonding interactions between neighboring molecules.[23] Thus, it can be suggested that one acceptor–donor–acceptor triple hydrogen-bonding array of dCA is occupied by the melamine site of **1**, whereas the another array is used for extended aggregation (Figure 1). Several supramolecular structures can indeed be drawn for the polymeric association of dCA with pendant **1** (see Figure S13 in the Supporting Information). These structures involve 1) cyanurate–cyanurate hydrogen bonding and 2) melamine–cyanurate hydrogen bonding. It should be noted that in these models, J-type chromophore packing can be achieved in either an intra- or inter-supramolecular manner.

We have investigated the J⇄H interconversion in the solid state. Remarkably, thin films prepared from the J-aggregated solution showed a reversible green⇄red thermochromism between 20 and 140 °C (Figure 4a), indicating the reversible transition between J- and H-type chromophore packing. The observed thermally induced color transition is completely opposite to that of the PBI pigment *N*,*N*′-bis(2-phenylethyl)-perylene bisimide reported by Mizuguchi, as in the latter case the red color was observed at low temperature and the green color at high temperature.[7] In addition, for this pigment the transition was irreversible and attributed to a change from an amorphous red to a crystalline green state.[7] Furthermore, we found that our J-aggregated film has piezochromic properties, that is, it shows a color change from green to red upon mechanical stimuli, such as scratching by spatula (Figure 4b, from left to center). The UV/Vis spectrum recorded for a scratched part showed a complete conversion into the H-type chromophore packing (Figure 4c). X-ray diffraction analysis shows the disappearance of sharp peaks at $d = 34.5$, 20.8, and 10.3 Å upon scratching, this might be due to the loss of supramolecular ordering of the J-aggregate (Figure 4d). More surprisingly, on thermal treatment of the scratched film at 130 °C for a few seconds, the green color is recovered (Figure 4b, from center to right), indicating a thermal reorganization of the supramolecular polymer network featuring the J-type chromophore packing. The mechanism of this thermo- and mechano-responsive chromophore packing is apparently different from that of the thermally inducible H-dimer⇄J-aggregate interconversion in solution (Figure 3), because such a large structural transition (Figure 1) may not be feasible in the condensed state. It is likely that the mechanically or thermally inducible disordering and reorganization of the supramolecular polymer network affects the

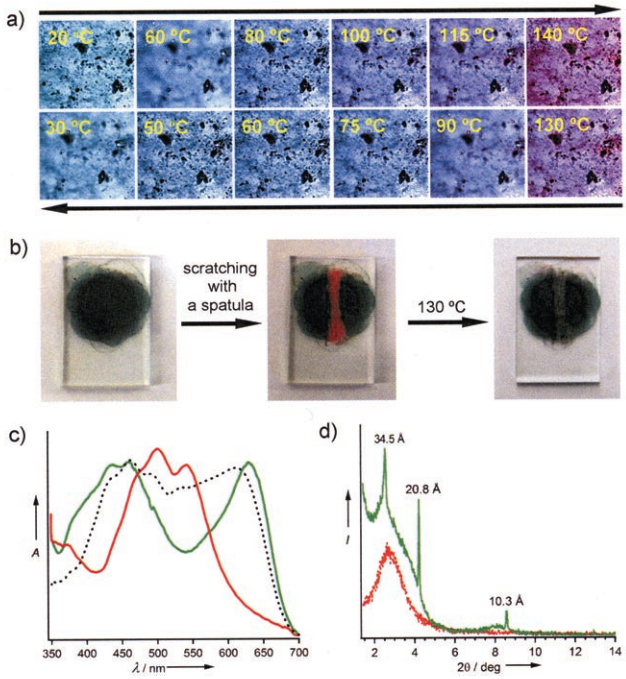

***Figure 4.*** a) Thermochromism of a thin film of J-aggregate (**1**/dCA = 1:1) observed by optical microscopy. b) Color change of the thin film by scratching, see text for details. c) UV/Vis spectra and d) X-ray diffractograms of the film before (green curve) and after scratching (red curve). The dotted curve in (c) is a spectrum of thermally recovered green film after scratching.

local chromophore packing arrangement. Nevertheless, this multi-stimuli-responsive chromophore packing with a pronounced change in optical properties is promising for a new type of information storage material.

Thus, we have serendipitously discovered a hitherto unknown phenomenon, the transformation from H- to J-aggregated perylene bisimides by using hydrogen-bond-directed complexation between melamine and cyanurate. The J-aggregation is achieved by the formation of a new supramolecular architecture consisting of ditopic cyanurate and monotopic melamine in 1:1 stoichiometry. The resulting J-aggregates shows a pronounced red-shifted absorption band (> 100 nm), which is unprecedented for soluble core-unsubstituted perylene bisimides. Such a dramatic change in absorption wavelength leads to the generation of a "green pigment" from perylene bisimide without introduction of substituents in the bay position.[24] It has also been demonstrated that the mutual transformation between H- and J-type chromophore packing can be achieved in the solid state as well as in solution by controlling the temperature. Based on these novel findings, the construction of further functional supramolecular systems can be approached from core-unsubstituted perylene bisimides, which show optical and electronic properties that can be changed by external inputs.

Received: November 23, 2007

**Keywords:** hydrogen bonding · perylene dyes · self-assembly · supramolecular chemistry

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