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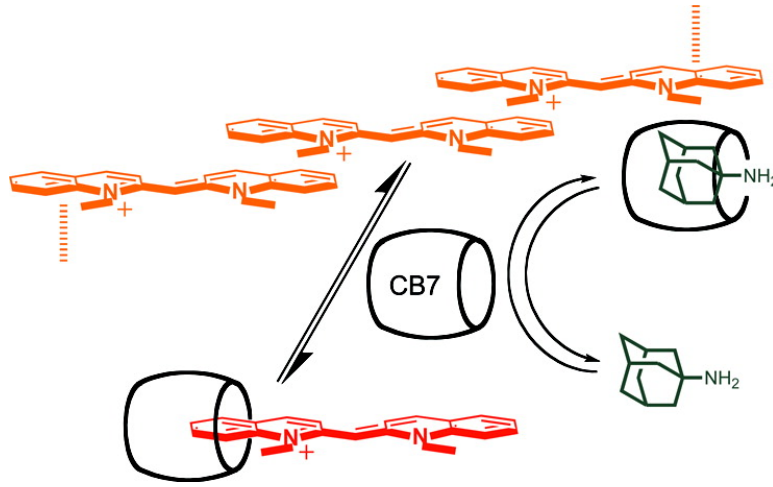

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Control of H- and J-Aggregate Formation via Host−Guest Complexation using Cucurbituril Hosts

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Abstract: The binding interactions between two cyanine dyes, pseudoisocyanine (PIC) and pinacyanol (PIN), and the cucurbit[*n*]uril hosts, cucurbit[7]uril (CB7) and cucurbit[6]uril (CB6), were investigated by electronic absorption spectroscopy and DFT computational methods. The CB7 host forms more stable complexes with both dyes than CB6 and the computational studies suggest that the cavity of the smaller host CB6 is not threaded by the dyes. The equilibrium association constants (*K*) for complexation by CB7 were measured and found to be 2.05×10^4 and 3.84×10^5 M^{-1} for PIC and PIN, respectively, in aqueous media at 23 °C. CB7 complexation was found to effectively disrupt the intermolecular forces responsible for the aggregation of both dyes. Thus, CB7 completely disrupts the J-aggregates formed by PIC and the H-aggregates (as well as lower concentrations of J-aggregates) formed by PIN. In both cases a competing guest, 1-aminoadamantane (AD), could be used to adjust the extent of aggregation of the cyanine dye. AD regulates aggregate formation because it forms an extremely stable complex with CB7 ($K \approx 10^{12}$ M^{-1}) and exerts a tight control on the CB7 concentration available to interact and bind with the dye.

Introduction

The aggregation of organic dyes is often observed in aqueous solution due to the development of short-range noncovalent forces, such as van der Waals or $\pi-\pi$ stacking interactions, among the dye molecules.[1] Aggregate formation may have a strong effect on the electronic absorption and emission spectra of dye solutions. One of the most extensively investigated classes of dye aggregates, the so-called J-aggregates,[2] exhibit red-shifted and very sharp absorption bands (as compared to monomer and dimer absorptions), which result from exciton delocalization over a large number of molecular building blocks in the noncovalent aggregate. While our knowledge of the structure of J-aggregates in the solution phase is limited, they are of considerable technological interest because of their applications in photography, and potential uses in photodynamic therapy, optoelectronics, and photoelectric cells.[3]

In contrast to J-aggregates, H-aggregates[4] give rise to blue-shifted absorption bands. A second important difference between these two classes of aggregates is that H-aggregates are usually poor emitters, whereas J-aggregates typically show efficient luminescence. It is widely accepted that both types of aggregates result from the parallel stacking of dye molecules. While in H-aggregates the dye molecules align face-to-face giving rise to a sandwich-like arrangement, J-aggregates are composed of dye molecules staggered in an edge-to-edge configuration (Figure 1).[5] At this time, our understanding of aggregate size or average number of dye molecules associated in J- or H-aggregates is very limited. In the solution phase, the extent of aggregation depends on the temperature, medium composition and the structural features of the dye molecule,[6] but only scattered attempts to control dye aggregation have been reported. Recently Kim, Whitten and co-workers[7] have shown that the presence of excess carboxymethyl amylose leads to enhanced J-aggregation of a cyanine dye and formation of superhelical assemblies between amylose and the cyanine J-aggregates. Other

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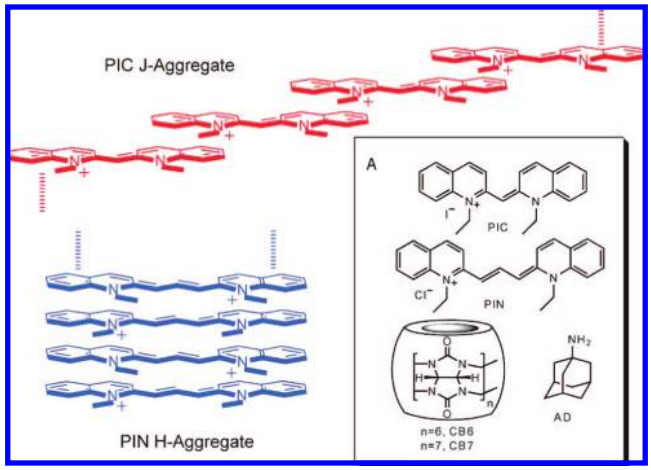

Figure 1. (A) Structures of the CBn hosts and guests used in this work. Postulated dye assemblies for a PIC J-aggregate (red) and a PIN H-aggregate (blue) are also shown outside panel A.

examples of enhanced J-aggregation driven by various additives in solution have been reported.[8]

Interest in the family of the cucurbit[*n*]uril hosts (CBn, see Figure 1A for structures) has been increasing rapidly in the past few years.[9] There is growing interest in the stabilization of organic dyes in solution by CB complexation.[10] Halterman and co-workers have recently prepared rhodamine B dimers and shown that H-dimer aggregation could be decreased by complexation with CB7.[11] In this work, we show that two cyanine dyes, pseudoisocyanine (PIC) and pinacyanol (PIN), form stable inclusion complexes with the CB7 host and that these binding interactions disrupt the formation of PIC J-aggregates and PIN H-aggregates. Furthermore, the extent of formation of the aggregates can be controlled using the host−guest association equilibrium between CB7 and a competing guest (1-aminoadamantane, AD).

Results and Discussion

In aqueous solution, the monomer form of the cyanine dye PIC exhibits absorption maxima at 485 and 525 nm.[12] The formation of J-aggregates is generally favored by increasing the dye concentration or by lowering the solution temperature. The ionic strength of the solution also has an effect on the aggregation, and increasing salt concentrations tend to foster the formation of J-aggregates.[13] The presence of PIC J-aggregates is highlighted by a sharp absorption band at 575 nm. In order to investigate the binding interactions between PIC and the hosts CB7 and CB6, it is important to ensure that the experimental conditions are such that no dye aggregation takes place. In solutions containing 0.2 M NaCl and 8.0 μM PIC, we observe absorption spectra corresponding to the monomeric form, with no indication of a narrow absorption band at 575 nm. As observed with other included guests,[14] addition of increasing concentrations of CB7 gradually depresses the intensity of the monomer absorption bands (Figure 2A). We can thus follow the absorbance of either band as a function of added CB7 concentration and fit the observed variation to a 1:1 binding isotherm. From the optimization of the fit (Figure 2B), we can obtain the corresponding equilibrium association constant (K), which in this case was determined to be 2.1×10^4 M^{-1}.

The monomeric form of PIN shows absorption maxima[15] at 548 and 600 nm and CB7 additions depress the molar absorptivity coefficients (ε) of both absorption bands (Figure 2C), which allows the use of the same method for the determination of the corresponding K value (3.8×10^5 M^{-1}) for the formation of the PIN•CB7 complex. Similar experiments were carried out with the smaller cavity host CB6 and Job plots were obtained in all cases to confirm the 1:1 stoichiometry of the complexes (see Supporting Information). Table 1 gives the parameters describing the complexation between these two dyes and the hosts CB7 and CB6. Notice that for both dyes, the K value with CB7 is higher than the corresponding value with CB6. This is probably a reflection of the cross section of both dyes, which facilitates interactions with the larger cavity host, CB7, while restricting CB6 to shallower binding modes. However, the differences in the K values from the CB7 to the CB6 complex are relatively small for both dyes, a finding which is not well understood at this time (see discussion of the computational results below). Furthermore, the dye PIN was found to give rise to more stable complexes than PIC, which should be related to the presence of the longer unsaturated bridge between the aromatic groups in PIN.

The limited aqueous solubility of both dyes, as well as their tendency to aggregate even at submillimolar concentrations, has hampered our attempts to investigate binding interactions with CB hosts using NMR spectroscopy. In order to determine the best binding sites on the dye structures for each of the CB hosts, we have used computational methods. We used an ONIOM-type[16] approach in which the supramolecular complex was divided into two components: (1) the CB host, described by a simple molecular mechanics field (UFF), and (2) the guest (dye), treated with more sophisticated DFT methodology (B3LYP/3−21G*). The host and the dye were manually positioned relative to each other in at least five starting positions, typically

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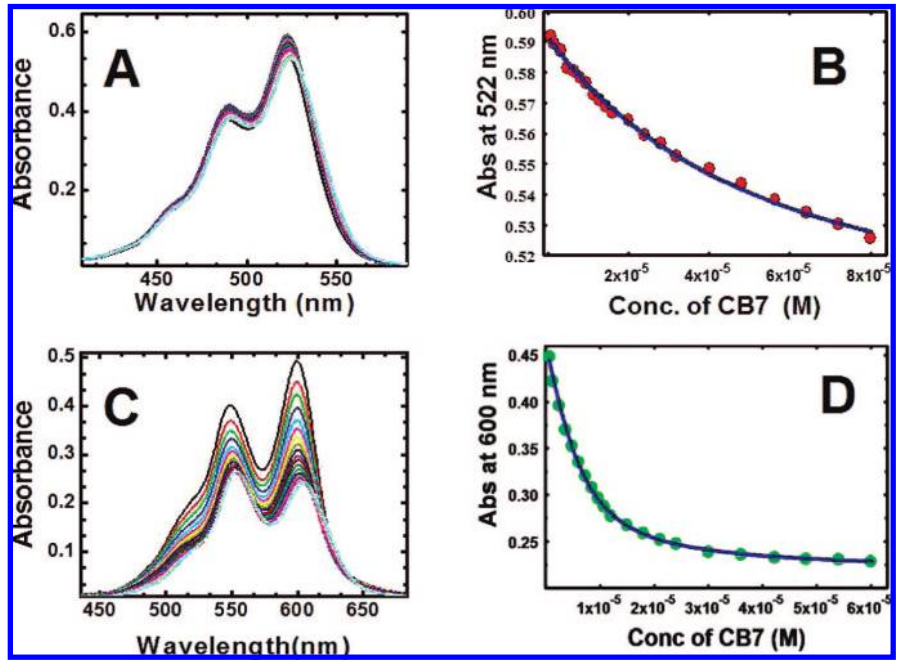

Figure 2. Effect of CB7 additions on the visible spectra of (A) PIC (8.0 μM) and (C) PIN (6.0 μM). Variation of the absorbance of (B) PIC and (D) PIN, at the specified wavelengths as a function of the CB7 concentration. The line through the experimental data points (filled circles) corresponds to the optimum fit using a 1:1 binding isotherm (see Table 1 for fitting parameters).

Table 1. Equilibrium Constants (K) and Molar Absorptivity Coefficients (ε_{comp}) of the Complexes Formed by the Association of the Dyes PIC and PIN with the Hosts CB6 and CB7 at 23 °C in Aqueous Solution

	CB6		CB7	
	K (M^{-1})	ε_{comp} (M^{-1} cm^{-1})	K (M^{-1})	ε_{comp} (M^{-1} cm^{-1})
PIC	9.8×10^3	2.7×10^4	2.1×10^4	6.1×10^4
PIN	2.1×10^5	3.0×10^4	3.8×10^5	3.6×10^4

with the guest partially or fully piercing through the host cavity and the host-dye system was allowed to evolve and find the local energy minimum. Once the energy minimum was reached, a single-point energy calculation in which the entire complex was described by B3LYP/6−31G* methods was carried out.[17] In the case of PIN and CB7 we found small energy differences as the host slides along the dye molecule, but the overall energy of interaction was negative, suggesting that a true inclusion complex is formed in which the dye threads through the host cavity. The complex structure corresponding to the absolute energy minimum obtained by this procedure is shown in Figure 3C and D. The distortion of the CB7 cavity, which is clearly seen in this complex, has been previously observed by us in an X-ray crystal structures of a stable CB8 inclusion complex,[14d] as well as in the energy-minimized structure of a CB7 inclusion complex,[14c] which was found to be stable by experimental means. Similar procedures led to the structure of the PIC•CB7 complex shown in Figure 3A and B, in which the distortion of the CB7 cavity is minimal, since the penetration of the guest in the cavity is less pronounced. The binding energies obtained (−38.3 kcal/mol for PIC and −89.4 kcal/mol for PIN) correspond well with the respective K values obtained in the solution phase (Table 1), in spite of the fact that solvent molecules were not considered in the computational studies.

Similar computational procedures with CB6 yield large positive binding energies for any complex configuration in which

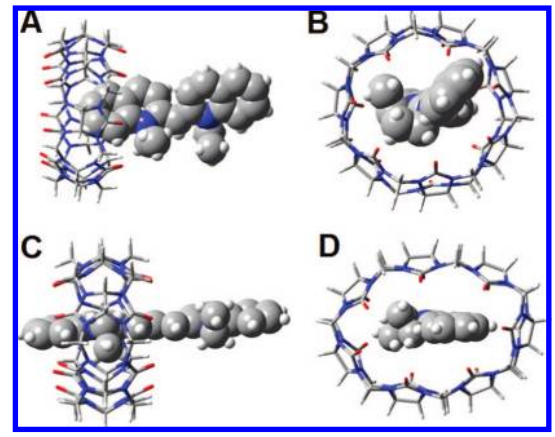

Figure 3. Minimized structures of the CB7 complexes with PIC (A and B) and PIN (C and D). The binding energies obtained using B3LYP/6−31G* methods are −38.3 and −89.4 kcal/mol, respectively.

the main axis of the guest penetrates inside the host cavity. Clearly, the smaller cavity of CB6 does not support guest threading. For both dyes, energy minimization leads to complex structures in which the CB6 host exhibits a shallow interaction with one of the two *N*-ethyl groups adjacent to points of substantial positive charge density on the guest (see Supporting Information).

In order to prepare solutions of PIC with significant content of J-aggregates,[18] we dissolved enough PIC (as its iodide salt) to make 0.3 mM solutions in hot (80 °C) 0.2 M NaCl and cool down the solutions to a final temperature of 10 °C. The spectra of the resulting solutions exhibit an intense, sharp band centered at 575 nm, which corresponds to the absorption of the J-aggregates (Figure 4A). Upon addition of two equiv of CB7 (0.6 mM) to this solution, we observed the complete disappear-

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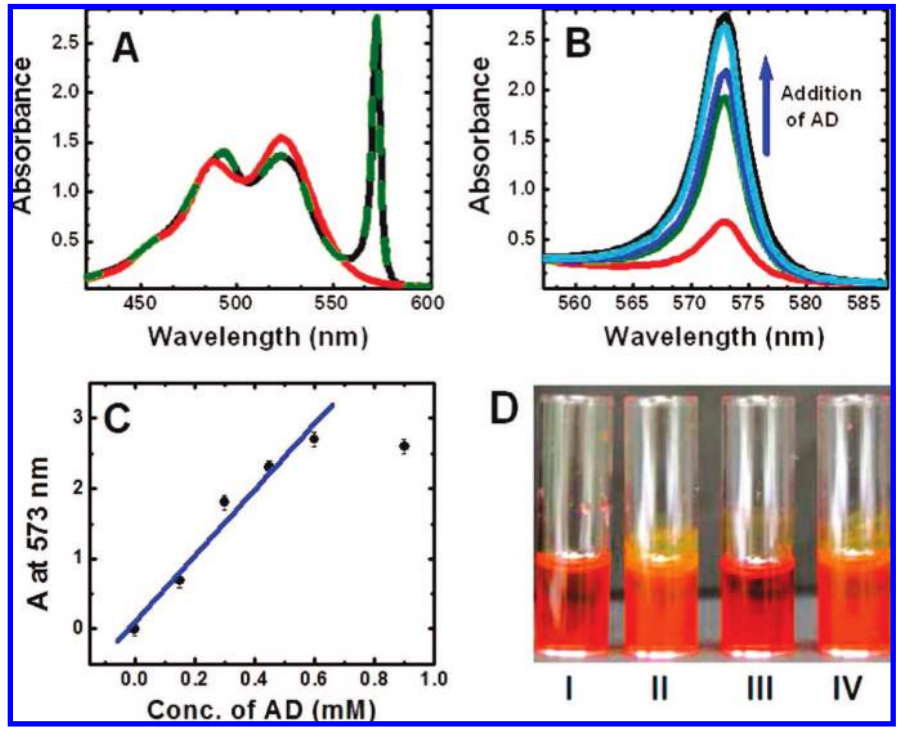

Figure 4. (A) Visible spectra (1.0 mm cell, 10 °C) of 0.3 mM PIC (green), 0.3 mM PIC + 0.6 mM CB7 (red), and 0.3 mM PIC + 0.6 mM AD (discontinuous blue). (B) Regeneration of the J-band at 573 nm as AD is added to a solution containing 0.3 mM PIC and 0.6 mM CB7. (C) Absorbance at 573 nm as a function of the added AD concentration to a solution initially containing 0.3 mM PIC + 0.6 mM CB7. The blue line was calculated by linear regression of all the points in the range [AD] < 0.7 mM (correlation coefficient: 0.983). (D) Color comparison: (I) 0.3 mM PIC at ca. 80 °C (II) 0.3 mM PIC at 23 °C, (III) 0.3 mM PIC + 0.6 mM CB7 at 23 °C (IV) 0.3 mM PIC + 0.6 mM CB7 + 0.6 mM AD at 23 °C. All solutions were prepared in 0.2 M NaCl.

ance of the J-band with a slight increase in monomer absorbance. Clearly, this finding reveals that the formation of the PIC•CB7 complexes in the solution disrupts the noncovalent interactions between the dye molecules and prevents the formation of J-aggregates under these conditions. The presence or absence of J-aggregates in these solutions can easily be detected by the naked eye, as evidenced by the pictures shown in Figure 4D.

Having established that CB7 complexation of PIC effectively disrupts the formation of J-aggregates by the dye molecules, we set out to re-establish J-aggregation in a controlled fashion by gradually removing the CB7 host from its complex with PIC. In order to accomplish this, we used AD as a competing guest. This compound was selected because it forms a highly stable complex with CB7, which favors host removal from the complex with PIC. The reported K value for the AD•CB7 complex[19] [$(4.23 \pm 1.00) \times 10^{12}$ M^{-1} in 50 mM sodium acetate buffer] is about 8 orders of magnitude higher than that measured in this work between PIC and CB7. Even taking into account that we use a medium of higher ionic strength (0.2 M NaCl), where the K value between AD and CB7 is probably about 1 order of magnitude lower,[20] the difference in the binding constants is so large in favor of AD that the removal of CB7 from its PIC•CB7 complex is essentially quantitative at the submillimolar concentrations used in this work and should follow, equivalent by equivalent, the amount of AD added to the solution. This is strongly supported by the data in Figure 4. In the absence of CB7, a solution containing 0.3 mM PIC shows extensive J-aggregation (Figure 4A). As mentioned before, upon addition of 0.6 mM CB7, the J-aggregates are dissolved and the absorption band at 575 nm is completely lost. Further addition of 0.6 mM AD (1.0 equiv in relation to the CB7 present in the solution) fully regenerates the J-band, with a maximum absorbance very similar to that exhibited before the addition of the CB7 host (Figure 4A). Furthermore, gradual addition of AD to a solution containing 0.3 mM PIC and 0.6 mM CB7 leads to the progressive growth of the J-aggregate band (Figure 4B). In fact, the maximum absorbance of the J-band seems to linearly increase with the added concentration of the competing guest AD, until 1.0 equiv is reached, at which point further additions of AD have no effect on the absorbance recorded at 575 nm (Figure 4C). Control experiments, in which AD was added to solutions containing PIC J-aggregates and no CB7, showed that the intensity of the J-band was unaffected by AD (in the absence of CB7). Therefore, our data unequivocally show that the formation of PIC J-aggregates can be controlled by the relative amounts of CB7 and AD present in the solution. We also conducted experiments with CB6, but this host was much less effective than CB7 at preventing the formation of PIC J-aggregates, that is, higher concentrations of CB6 were needed to achieve similar reductions in aggregate formation. Therefore, we only carried out minimal experimentation with the smaller cavity host.

Similar results were obtained using fluorescence measurements. The PIC J-aggregates exhibit a sharp, intense fluorescence emission band at 581 nm upon excitation at 532 nm, whereas the PIC monomer does not show any fluorescence emission.[21] Addition of 2.0 equiv. of CB7 to a solution containing PIC J-aggregates quenches the fluorescence of the

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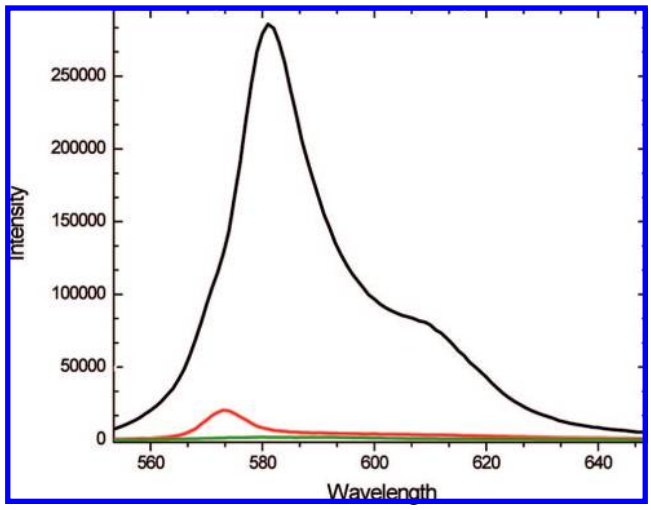
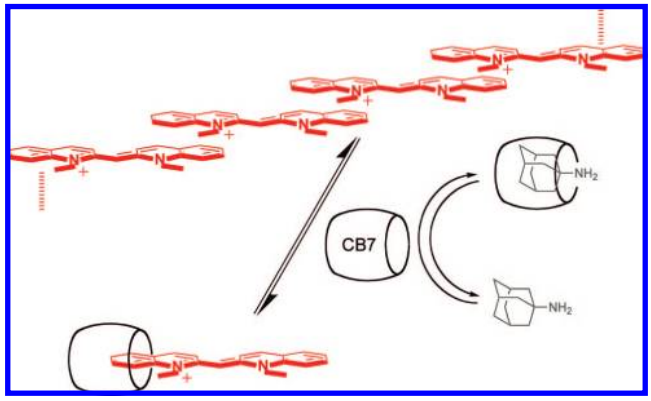


Figure 5. Fluorescence emission spectra (excitation wavelength: 532 nm) of 0.3 mM PIC (black, recorded at 10 °C), 0.3 mM PIC + 0.6 mM of CB7 (red, at 10 °C), 0.3 mM of PIC monomer (green, at 80 °C). All solutions were prepared in 0.2 M NaCl.

Scheme 1. Pictorial Representation of the Competition for the CB7 Host between the Two Competing Guests PIC and AD, Which Allows the Fine Control of PIC J-Aggregate Formation



J-aggregates (Figure 5), providing additional confirmation that CB7 forms a complex with PIC and disrupts the noncovalent interactions leading to J-aggregation. However, we must point out that the fluorescence emission of the PIC•CB7 complex, although still weak, shows a ca. 10-fold enhancement compared to that of free, monomeric PIC as seen in Figure 5. Addition of increasing AD concentrations to a solution containing PIC and CB7 results in increased fluorescence intensity as the competing guest complexes the host, releasing PIC for J-aggregation. The relevant equilibria involved in these phenomena are given below:

$$n\text{PIC} \rightleftarrows \text{J-aggregates} \quad (1)$$

$$\text{PIC} + \text{CB7} \rightleftarrows \text{PIC}\cdot\text{CB7} \quad (2)$$

$$\text{AD} + \text{CB7} \rightleftarrows \text{AD}\cdot\text{CB7} \quad (3)$$

The PIN aggregation experiments were all conducted in aqueous solutions -also containing 1.0% (v/v) of methanol and 0.05 M NaCl- that were prepared as described in the Experimental Section. The small volume of methanol present in these solutions was necessary to solubilize the PIN dye and the salt at the required concentration levels to drive aggregate formation as described below. The electronic absorption spectrum of a 0.2 mM solution of PIN exhibits several visible absorption peaks (Figure 6A). The highest energy absorption (λ_{max} = 473 nm) corresponds to H-aggregates,[22] since it is not detected at lower concentrations and it is blue-shifted from the monomer absorptions. At this concentration level, the main monomer band has its maximum at 600 nm and a smaller, red-shifted absorption at 640 nm, which is ascribed to the formation of J-aggregates.[22b] Addition of excess CB7 (0.8 mM) results in pronounced changes on the absorption spectrum, which is now dominated by absorption bands corresponding to monomer absorptions (550 and 607 nm). The absorption bands corresponding to H- and J-aggregates are not detected under these conditions (Figure 6A−B). Again, we must conclude that the formation of PIN•CB7 complexes disrupts the noncovalent interactions that give rise to both types of dye aggregates. In spite of its higher binding affinity for PIN (Table 1), CB7 seems to be less effective at breaking up PIN H-aggregates than PIC J-aggregates, as we must add a larger stoichiometric excess of the host to completely disrupt aggregation in the PIN solution than in the PIC solution (4 equiv with PIN vs 2 equiv CB7 for PIC). In this regard, we must point out that the aggregation of PIN is more complex than that observed with PIC. While the latter only forms J-aggregates, the former gives rise to H-aggregates, J-aggregates and even well-defined dimers, depending on the experimental conditions. In addition to this complexity in its aggregation, the extent of intermolecular contacts in H-aggregates is certainly larger than in J-aggregates, thus making their dissociation thermodynamically more costly. All these factors play a role in the case of PIN aggregation and are useful to rationalize the lower efficiency of CB7 to break down PIN aggregates, in spite of the fact that the PIN•CB7 complex is thermodynamically more stable than the PIC•CB7 complex. As with PIC, CB6 was found to be considerably less effective at preventing PIN aggregation.

In the absence of CB7 addition of AD has no effect on the absorption spectrum of PIN solutions (Figure 6A). However, when AD is added to solutions containing PIN and excess CB7, AD is expected to compete effectively for the host molecules in the solution, reducing the concentration of CB7 available to disrupt PIN aggregation. This is indeed the case, as evidenced by the data shown in Figure 6B−C. Increasing AD concentrations result in a clear regeneration of the H- and J-aggregate bands at 473 and 640 nm, respectively. Specifically, the plot in Figure 6C shows that the absorbance at 473 nm grows linearly with the added concentration of AD, in analogy to our previous observations with the PIC J-aggregate band (Figure 4C). However, it is surprising that more than 1.0 equiv of AD (in relation to the CB7 present) has to be added in this case to fully regenerate the original level of aggregation. The contrast with the results obtained with PIC (Figure 4) is interesting. The reasons for this behavior are not fully understood, but we must note that the stability of the PIN•CB7 complex is higher than that of the PIC•CB7 complex, so the former may compete more effectively with the AD•CB7 complex. However, the H-aggregate absorbance still grows linearly with the added concentration of AD in the range $0 < [\text{AD}] < 1.6$ mM (Figure 6C), and effective competition between AD and PIN for the CB7 host would give rise to substantial curvature in this plot. Perhaps a more important factor at play here is the complexity in the aggregation of PIN, which includes the possible formation of dimers, J-aggregates and H-aggregates. Regardless of this

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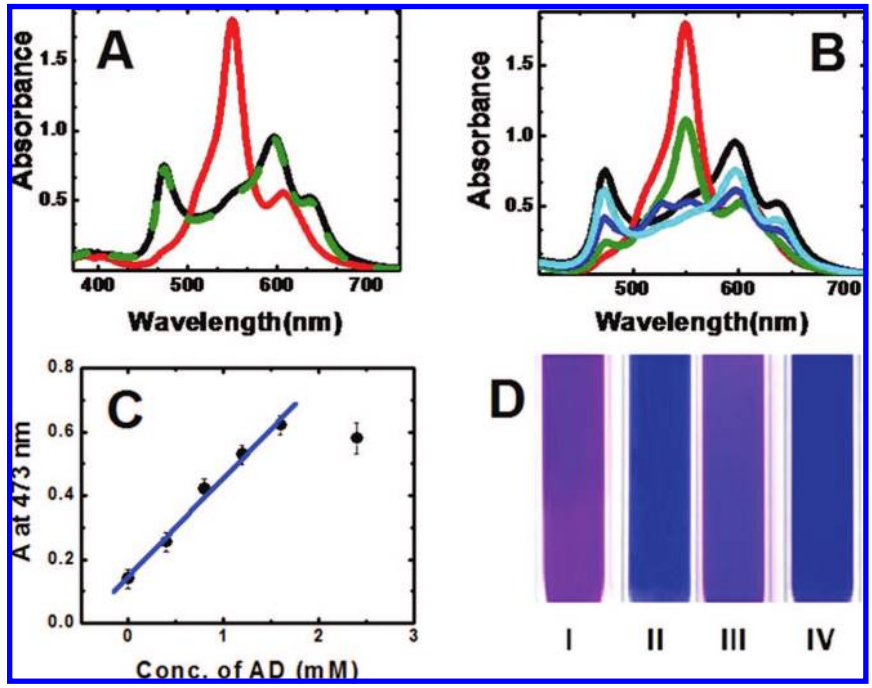

Figure 6. (A) Visible spectra (1.0-mm cell, 1 °C) of 0.2 mM PIN (black), 0.2 mM PIN + 0.8 mM CB7 (red) and 0.2 mM PIN + 2.4 mM AD (discontinuous green). (B) Visible spectra of 0.2 mM PIN in the absence (black) and in the presence of 0.8 mM CB7 (red) and after addition of 0.4 mM (green), 0.8 mM (blue) and 1.6 mM (light blue) AD. (C) Absorbance at 473 nm as a function of added AD concentration in a solution initially containing 0.2 mM PIN and 0.8 mM CB7. The blue line was obtained by linear regression of all the points in the range [AD] < 2 mM (correlation coefficient: 0.995). (D) Color comparison: (I) 0.2 mM PIN at 80 °C, (II) 0.2 mM PIN at 1 °C, (III) 0.2 mM PIN + 0.8 mM CB7 at 1 °C, (IV) 0.2 mM PIN + 0.8 mM CB7 + 2.4 mM AD at 1 °C.

complex aggregation landscape for PIN, its aggregation at these concentrations can be detected by the naked eye (Figure 6D), as was the case with PIC. All the spectroscopic changes observed with PIN solutions can be explained with a series of chemical equilibria similar to those given in eqs 1–3. The more complicated nature of PIN association may require additional equilibria, but the overall scheme would be similar to that presented with PIC.

In conclusion, this work has demonstrated that it is possible to shift the equilibrium between monomeric cyanine dyes and their aggregated forms (J aggregates for PIC and mostly H-aggregates for PIN) in a controlled fashion, taking advantage of the binding properties of the CB7 host. The PIC•CB7 complex has moderate stability, but it does interfere effectively with the formation of J-aggregates (Scheme 1). Connecting this equilibrium with the association equilibrium between CB7 and AD (an excellent guest for CB7 which gives rise to a highly stable inclusion complex) allows us to fine-tune the extent of J-aggregate formation in the solution. Similar arguments apply to the CB7-controlled, H-aggregate formation by PIN, but this system is more complex due to the possible formation of PIN dimers and J-aggregates, in addition to the predominant H-aggregates. As a result of this additional complexity, control of PIN aggregation requires relatively larger amounts of CB7 and competitive guest (AD). These phenomena may find applications, for instance, in the development of new sensors based on the intense absorption and/or fluorescence properties of J-aggregates. Further investigation of these phenomena may also contribute to increasing our still poor understanding of J-aggregate and H-aggregate structures in the solution phase.

Experimental Section

All solutions were made fresh daily. PIN solutions (2.00×10^{-4} M with 0.05 M NaCl and 1% MeOH (v/v)) were prepared by dissolving 7.76 mg PIN in 1 mL methanol and diluting with deionized water. 3.31 g NaCl was dissolved in a small amount of water and both solutions were heated to 80 °C. The NaCl solution was added dropwise to the PIN solution, sonicated and diluted to near 100 mL. The solution was protected from light and allowed to cool down to room temperature, at which point the volume was taken to exactly 100 mL by adding pure water. A second solution containing 8.00×10^{-4} M CB7 was prepared by dissolving 6.37 mg CB7 in 5 mL of the 0.2 mM solution of PIN. A third solution containing 2.4×10^{-3} M AD was prepared by dissolving 18.20 mg of AD in 50 mL of the 0.2 mM solution of PIN. All solutions were heated to 80 °C and cooled to 1 °C in an ice bath before analysis. PIC solutions (3×10^{-4} M) were made by adding 13.14 mg of PIC to 1.17 g NaCl (0.2 M) and heated at 80 °C with stirring. After complete dissolution of the dye, the solution was cooled in a water bath held at 10 °C. CB7 and AD solutions of PIC made by dissolving appropriate amounts of CB7 and AD in 0.3 mM solution of PIC.

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Supporting Information Available: Job plots for all complexes and structures of the CB6-dye complexes obtained from the computational work. This material is available free of charge via the Internet at http://pubs.acs.org.

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