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Host–guest control on the formation of pinacyanol chloride H-aggregates in anionic polyelectrolyte solutions

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The interactions of pinacyanol chloride (PIN), a cationic cyanine dye, with the anionic polyelectrolyte poly(acrylic acid, sodium salt) (PAA) towards enhancing H-aggregation were investigated by electronic absorption spectroscopy. We employed the cucurbit[7]uril (CB7) host to control the formation of these aggregates via host–guest binding interactions with the dye molecules. Absorption spectroscopic studies clearly demonstrate that PAA enhances the formation of PIN H-aggregates. Electrostatic interactions between the cyanine dye molecules and the polyelectrolyte chains assist the formation of H-aggregates at very low dye concentrations (*ca.* 10 μM). Furthermore, the presence of CB7 was found to effectively disrupt the interactions responsible for dye aggregation. Thus, CB7 completely disrupts the H-aggregates (as well as lower concentrations of J-aggregates) by forming inclusion complexes with PIN. A competing guest, 1-aminoadamantane (AD), was utilised to adjust the extent of aggregation of the cyanine dye. AD regulates aggregate formation by forming an extremely stable complex with CB7 and exerting a tight control on the CB7 concentration available to interact and bind with the dye. Our spectroscopic data clearly indicate that by varying the relative molar ratios of CB7 host, AD and polyelectrolyte acid groups, we can quantitatively control the extent of formation of PIN H-aggregates in these solutions.

Keywords: aggregation; H-aggregates; cyanine dyes; cucurbiturils; molecular recognition

Introduction

Host–guest binding interactions constitute one of the central themes in supramolecular chemistry. Among the various types of host molecules, the cucurbituril family has attracted considerable attention in recent years (*1*). A combination of ion–dipole and hydrophobic interactions plays a crucial role in their outstanding binding properties towards usually cationic guest molecules. In the last few years, the binding interactions of various photoactive guest molecules with cucurbit[*n*]urils (CBn's) have been explored, and these interactions were utilised to control the photophysical properties of the guests (*2*). Several research groups have taken advantage of the binding properties of CBn hosts to stabilise organic dyes in solution (*3*).

Cyanine dyes aggregate readily in aqueous media (*4*). These aggregates have a strong effect on the electronic absorption and emission spectra of dye solutions, due to exciton delocalisation over the structure of the non-covalent molecular assembly (dye aggregate). When compared to the absorption peaks of dye monomers, H-aggregates generally exhibit blue-shifted, broad absorbance bands, whereas J-aggregates show red-shifted, narrow absorbance bands (*5*). While both types of aggregate involve parallel stacking of the dye molecules, in H-aggregates, the molecular alignment is face-to-face while in J-aggregates the dye molecules are staggered in an edge-to-edge configuration. Recently, H-aggregates have attracted substantial attention due to their potential to perform as donors in energy transfer processes to their respective monomers. This phenomenon may find useful applications to develop novel light harvesting antennas towards mimicking natural photosynthesis and also in photography, photodynamic therapy, optoelectronics and photoelectric cells (*6*).

Several factors such as temperature, medium composition and the structural features of the dye molecule affect the extent of aggregation in the solution phase (*7*). Currently, there are only a few reports on controlling dye aggregation in the literature (*8*). Enhancement of the aggregation of cyanine dye molecules in the presence of polyelectrolytes and surfactants has received attention due to its potential applications in nonlinear optical materials (*9*). Liu and co-workers (*10*) recently reported two-dimensional aggregation of a long-chain thiacarbocyanine dye in the monolayers of synthetic polyanions such as polyelectrolyte poly(acrylic acid, sodium salt) (PAA) and poly(styrenesulphonate) (PSS). Daehne and co-workers reported extensive aggregation of a cyanine dye both

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outside and inside of a PSS/PAH polyelectrolyte capsule (*11*) with good potential in biological applications.

One of the primary research interests of our group is to develop mechanisms to switch and control the binding abilities of host molecules. This research work may be of interest to the development of novel analytical methodology. Recently, we reported the idea of utilising the binding properties of cucurbit[7]uril (CB7) to reversibly control the formation/disruption of cyanine dye H- and J-aggregates (*12*). We have further investigated this behaviour of dye aggregates by enhancing the aggregation at lower concentration (*ca.* 10 μM) with anionic PSS chains and controlling the extent of aggregation with CB7 (*13*). Intrigued by these initial results, we have continued our research on the idea of dye aggregation control through host–guest interactions. In this work, we report the effects of poly(acrylic acid) chains on the development of H-aggregates of pinacyanol chloride (PIN) and demonstrate that the extent of formation of the aggregates can be controlled using the host–guest association equilibrium between CB7 and the dye molecules. Furthermore, a second handle to control aggregation is afforded by the introduction of a competing guest (1-aminoadamantane, AD; Chart 1).

Results and discussion

Formation of dye H-aggregates triggered by PAA

Dye molecules in aqueous solution are known to form aggregates in the presence of cationic and/or anionic polyelectrolytes. The hydrophobic nature of dye molecules plays a prominent role in the process of aggregation. We have investigated in detail the interactions between the anionic polyelectrolyte PAA and the cationic PIN dye. At low concentrations in aqueous solutions, PIN exists essentially as a monomer with absorption maxima at 546 and 601 nm (*14*). Addition of increasing concentrations of PAA to a 10 μM PIN solution results in the development of a new absorption band at 495 nm, which indicates the formation of H-aggregates. At 1 equiv. of acrylate groups, the molar absorptivities of the monomer bands decrease by *ca.* 50% and a new broad peak appears at 482 nm. There is also a small, but distinguishable absorption band evolving at longer wavelengths (631 nm), indicating a small presence of J-aggregates. At 2.5 equiv. of acrylate, the 482 nm band red shifts to 495 nm and evolves as a clear H-band (Figure 1), while the monomer and J-aggregate molar absorptivities further decrease. Addition of more PAA results in an increase in the absorbance of the H-band, which reaches a maximum at an acrylate:PIN ratio of 20:1. Further additions of PAA have little effect and may cause

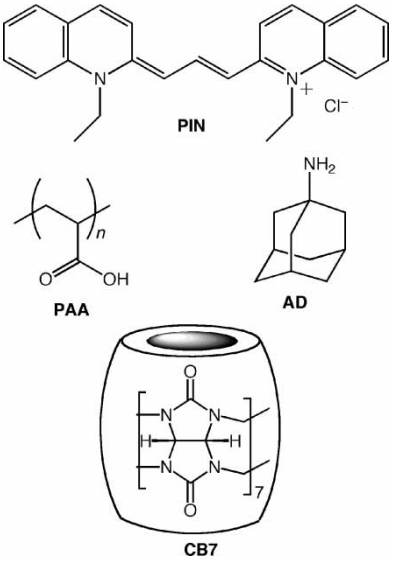


Chart 1. Structures of CB7, polyelectrolyte (PAA), 1-aminoadamantane and cyanine dye (PIN) studied in this work.

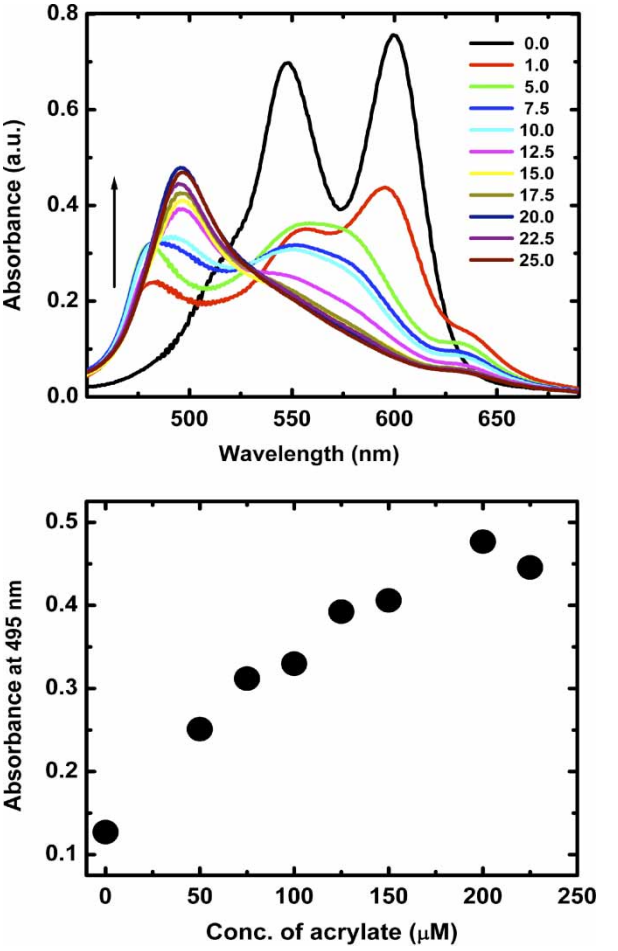


Figure 1. (Top) Visible absorption spectra of 10 μM PIN in the absence (0.0) and presence of increasing concentrations of PAA (1.0–25.0 equiv. acrylate). (Bottom) Evolution of H-aggregate absorbance as a function of added concentration of acrylate (from PAA).

a very slight decrease in the H-band absorbance, probably because the larger concentration of acrylate groups favours the dispersal and separation of the fixed concentration of PIN molecules.

The self-aggregation of amphiphilic dye molecules is usually fostered by entropic (and/or enthalpic) changes, as water molecules are removed from the vicinity of the dye aromatic surfaces to the bulk aqueous phase. In order to achieve stable aggregates in simple aqueous solution, higher concentrations of cyanine dye are normally required. The presence of anionic polyelectrolyte chains such as PAA, however, provides an electrostatic scaffold that assists dye aggregation by helping to neutralise the coulombic repulsions among the cyanine dyes and bringing the dye molecules together. This allows the hydrophobic forces to dominate and leads to aggregate formation at substantially lower dye concentrations. As a result of these factors, it is demonstrated here that aggregation of the common cyanine dye PIN can be achieved at concentrations as low as 10 μM at optimum concentrations of polyelectrolyte.

CB7 control on the formation of H-aggregates by the cyanine dye PIN

In order to control the formation of dye H-aggregates, we next explored the effects of inclusion complexation between the dye molecules and the CB7 host. Our recent work has established that PIN forms a stable complex with the CB7 host with an equilibrium association constant (K) of $3.8 \times 10^5\,M^{-1}$ in aqueous solution at 25°C. The binding energy obtained using DFT calculations (at the B3LYP/6-31G* level) is −89.4 kcal/mol for PIN·CB7. These values are in good qualitative agreement with the corresponding K values obtained from spectrophotometric studies in the solution phase (*12*).

Solutions containing PAA and PIN were prepared at the optimum acrylate:dye molar ratio to maximise H-aggregate formation (acrylate:PIN ratio of 20:1). The addition of CB7 to the above solution has significant effects on its visible absorption spectral properties. Increasing the concentration of CB7 causes a gradual decrease in the absorbance of the H-band, indicating the progressive disruption of the H-aggregates. Even though PIN forms a stable complex with the CB7 host, a large excess of CB7 is necessary to completely disrupt H-aggregation. Upon addition of CB7 (10:1 molar ratio of CB7:PIN), the H-band completely disappears and an increase in the monomer absorbance bands is observed. Only 70% (548 nm) and 40% (600 nm) of the monomer absorbance were recovered, however, with a 10 nm red shift in absorbance peak maxima (Figure 2).

The disappearance of the H-band, upon addition of CB7 (10 equiv.) to the PAA–PIN solution, indicates that CB7 fully complexes with the PIN dye molecules. A large stoichiometric excess of the host is probably needed because of the stability of H-aggregates, whose disruption is thermodynamically unfavourable. Despite the addition of excess CB7 host, the PIN monomer band absorptions remain relatively low and full recovery of absorbance levels similar to those observed before the addition of any PAA or CB7 is not achieved. This is probably due to the low molar absorptivity coefficient ($\varepsilon = 3.6 \times 10^4\,M^{-1}\,cm^{-1}$) of the PIN·CB7 complex (*12*). These results are very similar to those obtained in our previously reported work on controlling PIN H-aggregation at higher concentrations with CB7 hosts (in the absence of polyelectrolyte chains).

Recovery of the H-aggregates by using a competing guest

In previous work (*12*), we established that PIN·CB7 complexation is effectively disrupted by addition of the competing guest AD. This guest forms a highly stable inclusion complex ($K = 4.23 \times 10^{12}\,M^{-1}$) with CB7 (*15*). Addition of AD helps to re-establish H-aggregation in a controlled fashion by gradually replacing PIN in the CB7 complexes and releasing free PIN back into the solution where it can again interact with PAA.

In the absence of CB7, a solution containing a mixture of PAA and PIN (acrylate:PIN molar ratio 20:1) shows extensive H-aggregation (line b in Figure 3). As mentioned before, upon addition of 10 equiv. of CB7 (100 μM), the H-aggregates are disbanded and the absorption band at 495 nm is completely lost (0.0 in Figure 3). Further addition of AD (up to 1 mM) regenerates the H-band (Figure 3).

Gradual addition of AD to a solution containing PAA–PIN (acrylate:PIN molar ratio 20:1) and 100 μM CB7 leads to the progressive growth of the H-aggregate band (Figure 3). Upon addition of AD, we observe an increase in H-band absorbance accompanied by a decrease in the

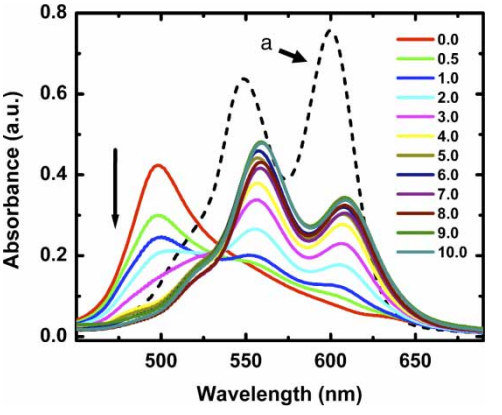


Figure 2. Visible spectra of a solution initially containing 10 μM PIN and 200 μM acrylate (0.0) after increasing additions of CB7 (up to 10 equiv. in relation to PIN). For comparison, the dashed line (a) spectrum corresponds to 10 μM PIN in the absence of any other additives.

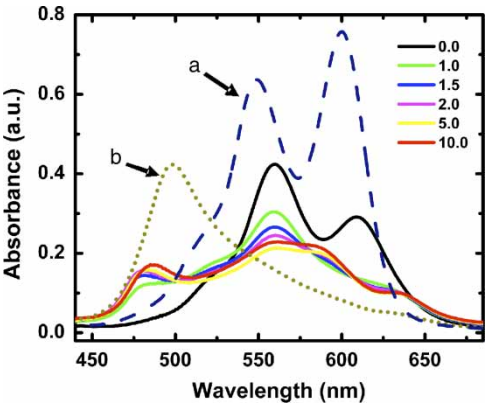


Figure 3. Visible spectra of a solution initially containing 10 μM PIN, 200 μM acrylate and 100 μM CB7 (0.0) after increasing additions of AD (up to 10 equiv. in relation to CB7). For comparison, the line (a) spectrum corresponds to 10 μM PIN and the line (b) corresponds to 10 μM PIN and 200 μM acrylate (from PAA).

monomer absorbances at 559 and 609 nm. We also notice the resurgence of the J-aggregate band at 640 nm, but it must be noted that we could not fully recover the H-band. Still, our initial results clearly indicate that AD complexes strongly with CB7 and releases PIN into solution to interact with PAA (Figure 4).

All the spectroscopic changes observed with PIN solutions can be explained with a series of chemical equilibria, depicted in Equations (1)–(3):

$$n\text{PIN} \rightleftharpoons \text{H-aggregates} \quad (1)$$

$$\text{PIN} + \text{CB7} \rightleftharpoons \text{PIN}\cdot\text{CB7} \quad (2)$$

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

Unlike our previously reported PIN H-aggregates formed in the presence of PSS (*13*), formation of PIN H-aggregates with PAA as the anionic trigger additive is much more complicated. In the case of PSS–PIN, H-aggregate formation reaches a maximum at a PSS:PIN ratio of 3:1, and any departure from the optimal sulphonate:dye molar ratio results in a diminution of H-aggregation. In the present case, the optimum acrylate:PIN molar ratio is reached at a ratio of 20:1, and addition of excess PAA has very little effect, if any, on H-aggregation. It is straightforward to understand why a larger molar ratio is required to drive aggregation for PAA than for PSS, as sulphonate groups are much more acidic than carboxylic acid groups. Due to the weak acidity of these carboxylic acid groups, an excess of PAA is required to overcome the repulsive coulombic forces among approaching PIN dye molecules and, thus, promote aggregation. Addition of the competing guest AD also works better in the case of PAA than with PSS, as AD seems to interact with the more acidic sulphonate groups and not with the carboxylic acid groups (Scheme 1).

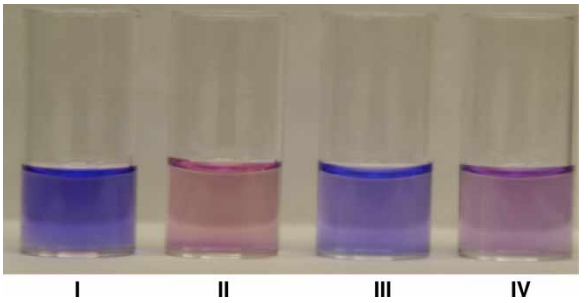


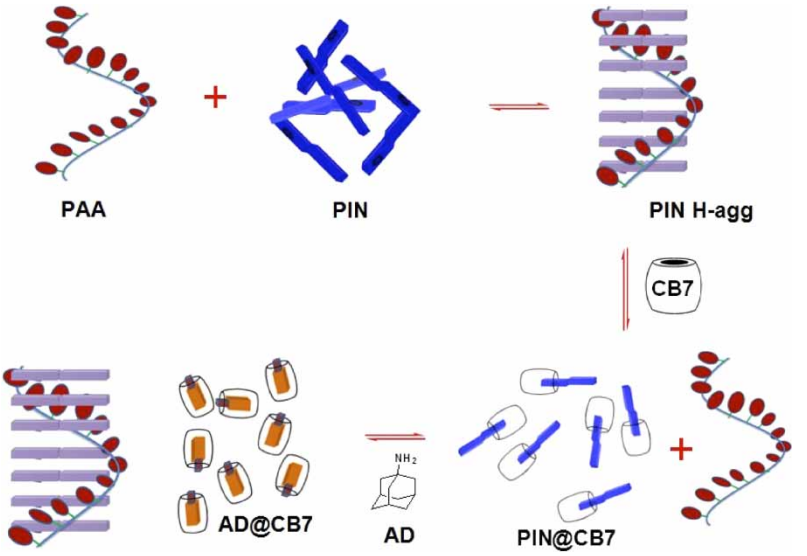
Figure 4. Colour comparison: (I) 10 μM PIN, (II) 10 μM PIN + 200 μM acrylate (from PAA), (III) 10 μM PIN + 200 μM acrylate + 10 μM CB7, (IV) 10 μM PIN + 200 μM acrylate + 10 μM CB7 + 1 μM AD.

Conclusions

The experimental results presented in this work clearly demonstrate that it is possible to drive H-aggregation of PIN even at low concentrations using poly(acrylic acid) as an anionic aggregation promoter. We have also demonstrated that it is possible to control the extent of aggregation in a systematic fashion by taking advantage of the binding properties of the CB7 host towards the PIN dye molecules. The CB7 host is used to shift the equilibrium between monomeric PIN dye molecules and its aggregated form by forming PIN·CB7 inclusion complexes and pulling the dye molecules away from the aggregates. Although the PIN H-aggregates are quite stable, CB7 does effectively disrupt the formation of H-aggregates by forming PIN·CB7 complexes. We have also demonstrated that the association equilibrium between AD and CB7, coupled with previous equilibria (Equations (1) and (2)), allows us to tune the extent of H-aggregate formation at micromolar concentrations of the PIN dye in solution. Given the proposed significance of H-aggregates towards building artificial photosynthetic antennas, it is equally important to control the relative monomer/aggregate concentrations, as this control may help regulate the energy transfer processes between monomers and molecular assemblies. These phenomena not only give us the opportunity to do that, but also may have applications to the development of new sensors based on the absorption properties of H-aggregates. Mainly due to the fact that our studies are confined to solution chemistry, it is still too preliminary to comment on the exact structure of PAA–PIN H-aggregates. Further investigation on these systems is needed to fully understand H-aggregate interactions with the various additives.

Experimental

The cyanine dye PIN, polyelectrolyte PAA and AD were purchased from Aldrich and used without further purification. The molar absorptivity coefficients (ε) for



Scheme 1. A pictorial representation of PIN H-aggregate formation in the presence of PAA, disruption of these aggregates by the CB7 host and re-establishment of the H-aggregates by the removal of PIN from the CB7 complexes using AD. The representation of the aggregate on the upper right corner is not intended as a rigorous structural proposal.

PIN were measured as 94,500 and 50,200 $M^{-1}cm^{-1}$ at 546 and 601 nm. All solutions were protected from light when not in use and stored at room temperature. A solution of PIN (10 μM) was prepared by dissolving 1.92 mg PIN (as its chloride salt) in deionised water to a total volume of 500 ml. In order to keep the concentration of PIN constant, a 250 μM solution of acrylate was then prepared by dissolving 2.33 mg PAA (average MW 2100) in the 10 μM PIN solution to a volume of 100 ml. Similarly, for the titrations with CB7 and/or AD, a 10 μM solution of PIN was prepared and, from it, a solution of 200 μM PAA was prepared in the same manner. A CB7 solution (100 μM) was prepared by dissolving 3.96 mg CB7 (MW = 1584 g/mol) in this PIN/PAA solution to a total volume of 25 ml. Lastly, this CB7 solution was used to dissolve 3.04 mg AD to a total volume of 10 ml in order to maintain the PIN concentration constant in all solutions.

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