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Self-assembly of organic dyes in supramolecular aggregates.

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Many scientists probably consider dye aggregation in solution a curse. Here, the adjective “many” should be stressed, as some other researchers thrive on forcing dyes to aggregate in solution. This perspective paper is certainly not meant to be a comprehensive review on the topic. However, for people intrigued by this pervasive phenomenon, I will try to offer a general picture on the self-assembly of dyes into supramolecular aggregates by presenting and discussing key information on their thermodynamics, kinetics, and optical changes. More recent topics will be introduced, such as the impact of external stimuli on dye aggregation, with a particular focus on ion specific effects. Finally, aggregation-induced emission will also be examined.

The Elephant in the Room

Self-assembly of individual elements held together by weak intermolecular forces into clusters, or aggregates, considered as single units, is a crucial process in life.[1, 2] Think about the 100,000 or so different proteins in the human body and the functional role played by their tertiary and/or quaternary structures or, alternatively, the collection of lipids assembling into the cellular membrane.[1]

In chemistry, the first report of dye aggregation in solution dates from more than a century ago. In 1909, S. E. Sheppard postulated molecular aggregation to be responsible for the substantial deviation from Beer’s law by isocyanine in water.[3] However, the major turn of events came in the late 30’s when two independent researchers, Scheibe and Jelley, made the serendipitous discovery that pseudoisocyanine (PIC) exhibits atypical spectroscopic characteristics in water.[4-8] As shown in Figure 1, aggregation of PIC in aqueous solution leads to a new sharp absorption band, which is highly fluorescent with a very small Stokes shift, as explained later. Nowadays, this type of aggregate is named J-aggregate after Jelley, one of its discoverers.[4, 5]

Since then, self-assembly of individual molecules into supramolecular aggregates has been the focus of many investigations and its significance has been highlighted throughout the years. Aggregation was certainly a major research topic in photographic science in the 70’s.[9-12] But, it resurfaced recently with the advances in optoelectronics, photovoltaics and nanotechnology, where self-assembly is key to “bottom-up” approaches.[8, 13-20] The principal characteristic of aggregation is certainly its influence on the photophysical properties of a dye, and by consequence, theoretical models have been developed to describe the spectroscopic signature of molecular aggregates, as discussed later.[21-24]

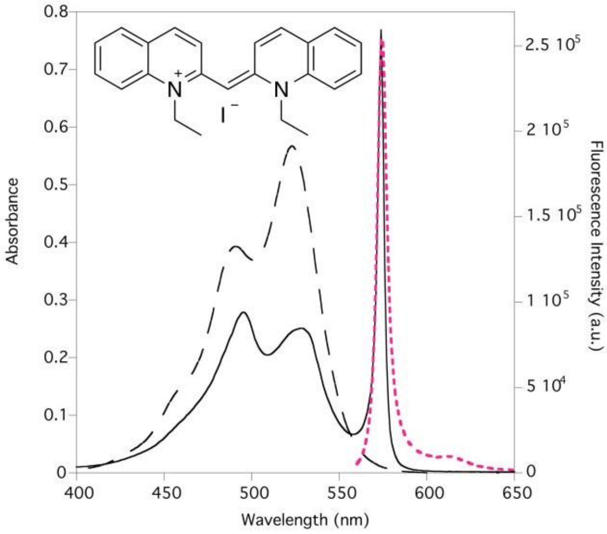

Figure 1: Absorption spectrum of a 10 μM pseudoisocyanine iodide (PIC) in ultrapure water in the absence (long dash lines) and the presence (plain line) of 5M NaCl. The small dashed (red) line represents the fluorescence spectrum of the PIC solution in presence of 5M NaCl with the excitation wavelength set at 550 nm. The inset of the figure shows the chemical structure of PIC.

More importantly, aggregation allows for the most efficient way of transferring electronic excitation energy coherently across many sites, as exemplified by light-harvesting complexes found in the membranes of higher plants, photosynthetic bacteria and algae.[25-27] Despite these important features, in practice, the word aggregation has a negative connotation attached with it. It is viewed as an undesired behaviour.

So, why has aggregation been stamped with a bad reputation? Maybe because, in many cases, aggregation of

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dyes in solution is associated with a loss of fluorescence emission, as reviewed in the section below on H-aggregates.[22, 23] Additionally, it is a complex process, which is often unpredictable. For instance, it is difficult to correlate the structure of a dye and its propensity to aggregate in solution.[28] Acridine orange and pyronin Y are prime examples, as these ionic dyes bear similar structures, but exhibit distinct dimerization constants.[29-32] Furthermore, unlike micelle formation, dye aggregation cannot be labeled as an "entropy driven" process. Aggregation of certain dyes is associated to an entropy gain, while entropy loss is observed for others.[33] Finally, interpretation of experimental data is complicated by sample polydispersity and the fact that aggregation numbers are challenging to obtain. Indeed, no correlation exists between the extent of optical changes and the degree of aggregation.[33]

Although dye self-assembly in solution is well documented, aggregation remains frequently overlooked. For instance, the absence of dimerization is often inferred from the observation of a linear relationship between the dye concentration and its absorption at a single wavelength (Beer's law). However, depending on the dimerization constant of the dye, the molar extinction coefficients (ε) of its monomeric and dimeric species at the wavelength under consideration and the range of concentrations being investigated, deviation from Beers' law might not be significant enough to be detected.[34] This is exactly what we noticed for the cyanine dye, 3,3'-diethylthiacyanine iodide (THIA), which was claimed to be present only in the monomeric form in aqueous solution.[35-37] While the absorption spectrum of THIA appears to vary linearly with respect to its concentration, further spectroscopic investigations in which the ratio of absorbance at two different wavelengths was taken into consideration, clearly reveals that the molecule exists as a mixture of monomeric and dimeric species.[35]

In this perspective article, the reader will be introduced to an overview of some of the fundamental aspects pertaining to dye aggregation in solution, including equilibria, kinetics, and influence on photophysical properties. Ion specific effects with respect to aggregation will be examined, and finally, some recent aspects will be mentioned, such as aggregation-enhanced emission. This perspective article is certainly not meant to be an exhaustive review on dye aggregation in solution, and I apologize in advance for necessarily omitting related works and topics. The focus of this article is generate critical awareness of this pervasive phenomenon.

Birth of an aggregate

The self-assembly of individual molecules into aggregates in solution is a process that originates from a complex balance between intermolecular forces.[38] Since aggregation in solution is principally observed in aqueous environments, the dyes featured in this article are ionic molecules. Therefore, the intermolecular forces consist of a set of repulsive and attractive forces. The former originate from mutual electrostatic repulsion between similarly charged ions, whereas the latter involve electrostatic attraction between oppositely charged ions, van der Waals forces, π-interaction and H-bonding.[38] The collection of forces grouped under the label of van der Waals forces are caused by correlations between the fluctuating polarizations of neighboring molecules.[39] They are divided into three categories with similar short ranges of action ($\propto r^{-6}$): orientation, induction and dispersion.[38, 39] Dipole-Dipole interactions are considered to be orientation forces, while dipole-induced dipole are the induction types.[38, 39] Dispersion forces, also known as London dispersion forces, originate from the presence of instantaneous dipoles generated by electron cloud perturbations within molecules.[39] To be complete, ion-dipole and ion-induced dipole interactions can also be regrouped under the general umbrella of van der Waals forces, while they exhibit a larger range of action ($\propto r^{-5}$) than the ones mentioned above.[38]

Since orientation forces are inversely proportional to temperature, aggregation is a temperature dependent phenomenon, which is promoted at low temperature and inhibited at high temperature.[38] In general, dyes aggregate more strongly in water when their concentration is increased or the ionic strength is elevated.[38] On the other hand, aggregation will lessen upon addition of organic solvent.[38] While this type of solvent effect could be associated hastily with dielectric constant, water having the second highest, experimental studies have disproved this hypothesis.[40] In fact, the chemical nature of the solvent proved to be more important than its dielectric constant, particularly in the presence of hydroxyl groups on the solvent molecules.[40]

Aggregation, the thermodynamics point of view

In solution, the self-assembly of molecules into supramolecular aggregates can be described as chemical equilibria between the monomer and the aggregates, as aggregation is a reversible process.[41, 42] This inherent equilibrium certainly explains why self-assembly is highly dependent on environmental conditions such as ion interactions, as will be discussed in a section below.

Different mathematical formalisms have been developed to model aggregation in solution, the simplest one being the monomer-dimer system.[30, 41, 43] In this model, two monomeric molecules (M) come together to form a single dimer ($(M)_2$), which are then at equilibrium:

$$M + M \underset{k_r}{\overset{k_f}{\rightleftarrows}} (M)_2 \text{ (Eq. 1)}$$

$$K_D = \frac{\left[(M)_2\right]}{[M]^2} = \frac{k_f}{k_r} \text{ (Eq. 2)}$$

$$C_T = [M] + 2\,[(M)_2], \text{ (Eq. 3)}$$

where K_D represents the equilibrium or dimerization constant and C_T is the total dye concentration.

Because monomer and dimer species are often characterized by different optical properties (*vide infra*), absorption spectroscopy has been repeatedly used to quantify dimerization constants in solution.[30, 43, 44] However, an issue to be considered is the possibility of overlap between the monomer and dimer absorption spectra. This problem has been addressed with the development of chemometric (multivariate) approaches, allowing for the simultaneous analysis of whole absorption spectra.[35, 45-48] However, one has to remain cautious when using these computational methods, as they can still fail to provide coherent solutions.[35]

It is important to consider that the monomer-dimer model is often a simplification, as large aggregates are commonly formed upon increasing dye concentration in solution.[33] More elaborate formalisms are thus required to describe effectively polydisperse aggregate samples. Isodesmic models, where the equilibrium constants associated to individual equilibrium are equivalent have been used with a certain degree of success. An extensive review on the different available models can be found elsewhere.[41]

Aggregation, the kinetics point of view

While thermodynamics of dimerization, in particular determination of dimerization constants, is often a primary research focus, investigations of dimerization kinetics are sparse, which might be linked to the need of more sophisticated instrumentations. However, these studies are still important as they provide indispensable information on the rate of dimer formation and dissociation (Equations 1 & 2). Temperature jump systems have played a critical role in gaining information on dimerization kinetics.[49-54] This method monitors the exponential relaxation back to an equilibrium state after an instantaneous change in temperature occurs. The method is particularly appropriate for studying the fast kinetics associated with dimerization in solution, as aggregation is a temperature dependent phenomenon. The relaxation time (τ) measured via this technique is dependent on the rate of the formation and dissociation of the dimer for a specific concentration of the monomer (Equations 1, 2 & 4).[49, 50] Consequently, by varying the monomer concentrations and monitoring the system using spectroscopy as it returns to equilibrium, one can extract values for the rate of formation (k_f) and dissociation (k_r) of the dimer.[49]

$$\frac{1}{t} = k_r + 4k_f\left[M\right]. \text{ (Eq. 4)}$$

It is important to note that both rate constants have different units and by consequence cannot be directly compared. The forward reaction is associated to a bimolecular process resulting in k_f being expressed in $M^{-1}\ s^{-1}$ (Equation 1). On the other hand, dimer dissociation is a unimolecular process and thus, k_r's unit is s^{-1} (Equation 1). Based on literature data, Kiyofumi Murakami classified aggregation of organic dyes into two categories.[55] In one group, the forward rate of dimerization is near the diffusion-controlled limit, and a linear relationship exists between $\log k_r$ and the inverse of $\log K_D$. This group includes dyes such as proflavine, acridine orange, and methylene blue.[55] The other group presents rate constants of dimerization and deaggregation a few orders of magnitude slower than in the first group, without an apparent link between rate and dimerization constants.[55] Congo Red and Rhodamine B are two examples of dyes belonging to this second category. The fact that two distinct groups of dyes emerge from kinetics studies suggests that dimerization in solution is governed by at least two types of activation process.[55] However, kinetics obtained via temperature jump have to be interpreted with some degree of caution, as these experiments require high ionic strength conditions in order to ensure rapid change in temperature. Thus, one can foresee the issue associated with these experimental conditions, as an increase in ionic strength results in an increase in aggregation, and the kinetics data might reflect polydisperse samples rather than the expected monomer-dimer equilibrium. To overcome this problem, Alexander Chibisov and his collaborators designed a novel approach based on a photochemically induced jump in the monomer concentration, as a result of the one-electron oxidation of dimers.[56, 57] This methodology, depicted in figure 2, is tailored to certain types of cyanine dyes, which present a significantly greater quantum yield of the intersystem crossing than the monomer. Their investigation shows that this particular class of dyes follows a more complex dimerization mechanism (Equation 5), where an encounter pair is established prior to dimer formation, which is the rate-limiting step ($k_{21} >> k_{23}$).[56, 57]

$$M + M \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} \left(M \cdots M\right) \underset{k_{32}}{\overset{k_{23}}{\rightleftarrows}} \left(M\right)_2 . \text{ (Eq. 5)}$$

Extensive literature search suggests this photochemical approach has been applied so far to *meso*-thiacarbocyanine derivatives only (Figure 2). However, it could be extended to other dyes if appropriate electron donors and acceptors can be found. According to early work by McRae and Kasha, the splitting of the singlet energy levels (*vide infra*) can be expected to enhance the rate of intersystem crossing for the aggregate.[58]

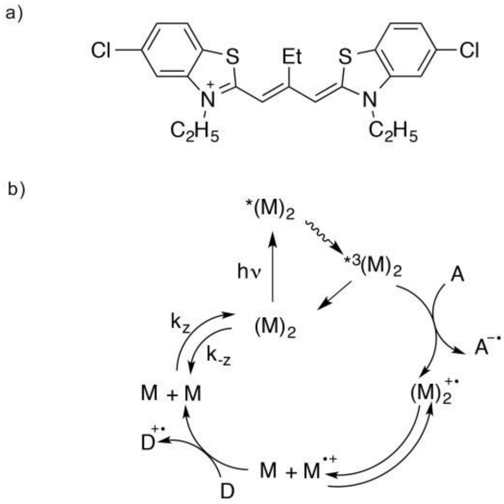

Figure 2: a) Chemical structure of a *meso*-thiacarbocyanine derivative. b) Illustration of the photochemical approach taken by Chibisov to assess the rate constants for dye association (k_z) and deaggregation (k_{-z}) in solution. Adapted from reference [56].

Photophysical properties

Conventional spectroscopic techniques, such as absorption and fluorescence, are particularly appropriate for exploring aggregation in solution, since molecular aggregates have distinct optical properties compared to individual molecules. Strong spectral shifts or splitting of the absorption band are typical aggregation characteristics (Figures 1 and 3).[35, 44, 59] As described in more detail hereafter, these spectroscopic changes are a consequence of exciton interactions between the individual molecules forming the aggregate.

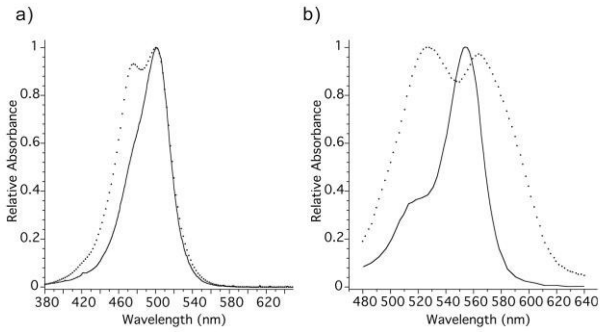

Figure 3: a) Normalized absorption of a 20 μM solution of thiazole orange in methanol (plain line) and in water (dotted line). b) Absorption spectrum of Rose Bengal ethyl ester in aqueous solution in the absence (plain line) and the presence (dotted line) of 1M potassium nitrate. Adapted with permission from Oscar Valdes-Aguilera, D. C. Neckers, Accounts of Chemical Research, 1989, 22(5), 171-177. Copyright 1989 American Chemical Society.[59]

The general concept of exciton pairs, with respect to molecular interaction, is related to electronic excitation delocalization mechanisms.[21, 22, 24] In other words, the occurrence of excitons allows one to model the transport of electronic excitation of an individual molecule across the many sites of a molecular assembly faster than any relaxation processes. The existence of excitons can be divided into two subcategories, depending on the strength holding the excited electron and its positive hole (vacancy) together.[21, 24]

In the case of weak or negligible interaction, the pair can dissociate into free carriers, resulting in significant charge separation between the electron and its positive hole. This particular model, known as the Wannier-Mott exciton, applies to inorganic semi-conductor and ionic crystals.[21, 22, 24]

On the other hand, when strong coulombic interactions exist within the pair, the electron and its positive hole remain localized on an individual molecule, and it is the electronic excitation, which is transferred.[21, 22, 24] The migration mechanism depends on the specific strength of the molecular coupling in the excited state.[22, 24] This particular type of exciton is said to be “strongly bound”. It is identified as the Davydov molecular exciton and serves to elucidate the spectral properties of aggregates. However, before jumping head first into the molecular exciton formalism, lets review some important aspects of light interaction with individual molecules.

Monomer

Absorption of a photon of appropriate energy by an individual molecule in the ground state (S_0) leads to the promotion of an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), leaving a vacancy or positive hole within the HOMO (Figure 4).[60-62] The molecule is said to be in its first excited state, denoted as $^*S_1$, and, from a physics point of view, the pair formed by the excited electron and its positive hole corresponds to the exciton.[24] Because absorption is an extremely fast process in the order of 10^{-15} s, electronic transition is assumed to occur without changes in the molecule geometry or surrounding solvation sphere.[24] This statement underlines the Franck-Condon principle for which absorption is a vertical process (Figure 4).[61] As a consequence, electronic transition is accompanied by vibrational excitation, as exemplified in the energy diagram of figure 4. These transitions are called vibronic and can readily be observed as shoulders or peaks within the principal absorption band of numerous organic molecules (Figure 1, PIC absorption without NaCl).[61, 62]

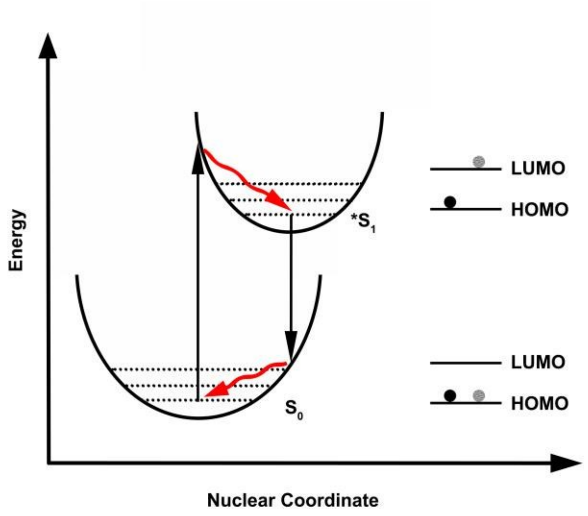

Figure 4: Two levels of a molecular energy diagram related to the excitation/de-excitation processes in an individual (monomeric) molecule. The horizontal axis corresponds to the displacement of the nuclei from their equilibrium positions. The associated molecular orbitals are depicted on the right side, where electrons are represented by dots.

Once excited, the molecule will relax rapidly to its lowest vibrational state, at the excited state equilibrium position (Figure 4). This vibrational relaxation process (10^{-12} – 10^{-10} s) often coexists with solvent reorganization around the excited state, reaching a configuration with lower total energy.[61, 62] The electronically excited molecule will remain at this equilibrium position for a certain period of time ranging from tens of picoseconds to hundreds of nanoseconds. It will then relax to the ground state, losing its excess energy via emission of a photon, known as fluorescence, or other non-radiative de-excitation processes (Figure 4).[61, 62] Because emission of a photon itself is a process as fast as absorption (10^{-15} s), it involves a vertical transition according to the Franck-Condon principle.[61, 62] Therefore, when the molecule arrives in its electronic ground state (S_0), it still possesses some excess vibrational energy. Finally, the molecule will reach thermal equilibrium with the surrounding solvent molecules and relaxes to its lowest vibrational state.[61, 62] From Figure 4, it is inferred the fluorescence emission spectrum is close to being a mirror image of the absorption spectrum. The difference in energy between the two maxima, absorption and fluorescence, is called the Stokes shift.

In this section, a third type of deactivation process from the $*S_1$ state has been omitted: intersystem crossing to the triplet excited state, $*T_1$.[61, 62] Whereas this type of excited state plays an important role in many photochemical applications, it is of no use in the interpretation of spectral properties of aggregates in solution.

H- vs. J- Aggregates

In order to interpret the optical characteristics of molecular aggregates, several presumptions have to be made. First, the rate of excitation energy transfer within the aggregate far exceeds any relaxation time mentioned in the previous section.[22, 23] Furthermore, conditions of strong exciton coupling exist where all of the vibronic transitions, referred to as the Franck-Condon envelope, are shifted across the molecular aggregate.[22-24] Another important aspect is the forces responsible for holding the molecules together within the aggregate are weak, thus limiting intermolecular electron overlap and by consequence, electron tunneling.[22-24] In other words, the molecules within the aggregate preserve their individuality in terms of electronic and nuclear structure. Therefore, any spectral change observed for molecular aggregate results from coulomb interaction between vibronic transitions in monomers. Under these assumptions, the molecular exciton can be modeled using perturbation theory.[21-24]

In this discussion, the rigorous quantum mechanical formalism will be skipped, as optical characteristics of molecular aggregates can be grasped with a semi-classical vector approach, developed by M. Kasha.[22, 23] In this approach, the excited state resonance interaction within the aggregate is approximate to electrostatic interactions between transition dipole moments of monomer units.[22, 23] The interested reader is referred to the following works on quantum mechanical formalism.[21, 23, 24]

The simplest aggregate to model is the dimer. Dimers are made of two molecules and therefore, two interacting transition dipole moments. Therefore, in this case, only two possibilities exist; the transition dipole moments are oscillating either in phase or out of phase (Figure 5a).[22, 23] In the first instance, the dipole-dipole interaction is repulsive, resulting electrostatically in an increase of energy. Whereas in the opposite situation, the dipole-dipole interaction is attractive, corresponding to a decrease in overall energy. By consequence, the exciton model describes the resonance splitting of the excited state energy levels (Figure 5b).[22, 23] While displacement of the ground state energy of a dimer is expected, exciton interactions are conveniently examined in terms of energies normalized to a common ground state (S_0) as illustrated in Figure 5b.

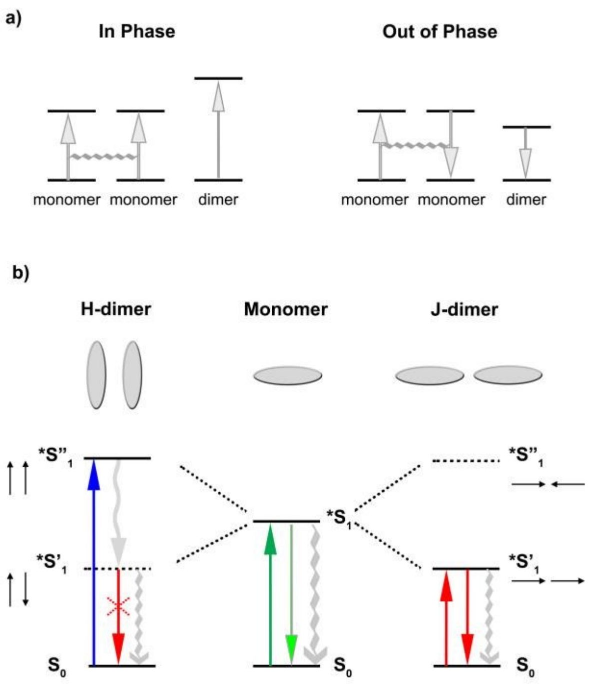

Figure 5: a) Schematic representation of the in phase and out of phase interaction of transition dipole moments, giving rise to a splitting of the dimer excited state. b) The top of the panel illustrates the molecular arrangement within the dimer. The bottom of the panel corresponds to the excitation/de-excitation processes within H (left side) and J (right side) dimer. See main text for more details.

By combining dipole-dipole interactions with molecular geometry, two utmost scenarios arise: one where the molecules are parallel with each other, and the other where the monomeric units are arranged in an “in-line” fashion (Figure 5b).[23] The transition dipole moment of the dimer as an “entity” is given by the sum of the individual transition dipole moments. It is evident from figure 5b, the highest energy level is optically allowed in the case of a parallel configuration, as the dimer transition dipole moment is different from zero, while the lowest energy level is forbidden.[23, 63] Therefore, dimers bearing this type of geometrical arrangement are characterized by an absorption spectrum blue shifted compared to the individual monomer. This situation is referred to as an H-type of dimer, H standing for hypsochromic. It is the most prevalent type of dimer amongst organic molecules. Furthermore, an important feature of the H-type of dimer is that their fluorescence is quenched, as their lowest excited energy level is forbidden (Figure 5b).[23, 63]

In the other scenario, where the molecules are organized in an “in-line” fashion, the situation is reversed, as the lowest excited energy level is the allowed one, while the highest is forbidden.[23, 63] These type of dimers, called “J-dimers”, the J standing for Jelley (*vide supra*), are characterized by an absorption and an emission spectrum red shifted compared to the monomeric unit.[23, 63] Because absorption and emission have the same exact origin (Figure 5b), and the excitation energy is transferred within the aggregate before nuclear relaxation can occur, J-aggregates are characterized by sharp and featureless spectra with very small Stokes shifts, as defined earlier.

Intermediate dimeric configurations where the two molecules are oblique with respect to each other also exist. In this case, both energy levels are allowed resulting in a splitting of the absorption band, with peaks both blue and red-shifted compared to the monomer absorption peak (Figure 3b).[23, 59, 63]

The exciton model introduced for dimers can easily be extended for larger aggregates.[22-24, 63] Indeed, a molecular aggregate formed by the self-assembly of N individual molecules will result in a splitting of the electronic excited state into N different energy levels.[63] As discussed above, the state with the highest energy level originates from the in-phase pairing of all the individual transition dipole moments.[63] On the contrary, the lowest energy level is associated to the combination of pairwise out of phase transition dipole moments.[63] By consequence, the highest energy level is the only optically allowed excited state for H-aggregates, where the monomeric units are stacked on top of each other in a parallel fashion. Perfectly aligned H-aggregates are non-fluorescent, as their lowest energy level is forbidden.[22, 23, 63] However in practice, small disorder within the aggregate’s geometry can alleviate some of the forbidden character of the lower excited level, revealing the possibility of some weak emission, red-shifted compared to the fluorescence maximum of individual molecules.[64, 65] On the other hand, the lowest excited energy level is the only optically allowed excited state for J-aggregates.[63] This fluorescent type of aggregate is characterized by a very small Stokes shift between the absorption and the emission maximum for the same reasons as the ones mentioned above (Figure 1). Furthermore, since J-aggregate fluorescence emission is a collective process, known as superradiance, it results in a strong and spectrally confined emission band (Figure 1).[63]

Not so black or white – The polaronic Frenckel exciton effect

In recent years, research in aggregation modeling has resurfaced with advances in organic electronics where self-organized conjugated polymers, such as polythiophenes, are key materials. Their photophysical behavior can be described readily via the exciton model developed for small aggregates as explained in the previous section. However, as emphasized in recent works, the picture is more complex than a purely vibronic perspective.[66, 67] Indeed, vibronically excited molecules within an aggregate are surrounded by vibrationally, but not electronically, excited neighboring molecules.[66] As elegantly described by Spano, the situation is analogous to placing a bowling ball on a spring mattress.[66] Compression of the central spring due to the weight of the ball will result in deformation of the adjacent springs. So, vibronic excitation of a central molecule within the aggregate will lead to geometrical distortion of adjacent molecules, resulting in a low-frequency vibrational field referred to as phonon.[66] Therefore, migration of the vibronic excitation across the monomeric units within the aggregate is accompanied by a displacement of the vibrational field, to the same extent that movement of the bowling ball on the mattress surface results in the compression field travelling with it. In this analogy, it is understood that excited molecules are not compressed but elongated along the vibrational coordinates. As a result of this vibronic/vibrational coupling, the optical characteristics of H- and J- aggregates are not as black and white as previously described. They will depend on the strength of exciton coupling. In the case of strong exciton coupling, so weak exciton-phonon interaction, the model described in the previous section prevails, as it was one of the key assumptions (*vide supra*).[66] H-aggregates are thus characterized by blue-shifted absorption, whereas J-aggregates are red-shifted compared to monomeric units.[66] In the case of weak exciton coupling, and therefore strong exciton-phonon interactions, spectral shifts become unreliable to distinguish between the types of aggregates.[66] Indeed, under weak exciton coupling, it is not uncommon to observe red-shifted H-aggregates, as in the case of carotenoid derivative such as lutein diacetate.[68]

From an extensive literature search, molecules exhibiting strong exciton-phonon interactions upon aggregation appear to be highly symmetrical π-conjugated molecules. In addition, the absorption spectrum of individual molecules displays already strong vibronic bands originating from a vinyl stretching mode with a vibrational energy of about 1400 cm^{-1}. Typical examples are perylene diimide,[69] carotenoid derivatives as already mentioned,[68] and pyrene derivatives.[70] More recently, weak exciton coupling or strong exciton-phonon interaction has been invoked to justify the spectral evolution of the symmetrical indocyanine Cy5 H-aggregate over time.[71]

Aggregation and ion specific effects

As already mentioned, an increase in ionic strength promotes aggregation in solution. This effect can easily be understood as added electrolytes acting as a screen, reduce the electrostatic repulsion between the charged monomers. Although this concept is very general and holds true across a broad range of electrolytes, a pertinent question is to ask whether all ions are equal at screening charged monomers. According to Debye-Huckel theory, the nature of the electrolyte added in solution shouldn't make a difference as the interaction between ions is based on molecular charge and is strictly electrostatic.[72] However, this is far from being true in reality.

The first investigation into ion specific effects dates probably from 1847, when Poiseuille studied the viscosity of aqueous solutions containing different salts.[73] However, the true impact in the field originates from Hofmeister's seminal work, where he researched the effect of a series of salts on protein precipitation.[74-76] Hofmeister discovered the ability of some salts to increase protein solubility, while others generated insoluble precipitates. He then ranked these salts in term of their propensity at inducing protein precipitation.[74, 75] To date, almost 140 years after his initial discovery, a clear explanation for the salt's effect is still hotly debated.[74, 76] Some researchers argue the importance of ion-ion interactions in justifying and predicting Hofmeister's ranking, while others view ion-water interactions where ions affect the physical behavior of aqueous macromolecular systems by making or breaking water structure, as key.[74] The fact that Hofmeister's original series relates to salts and not individual ions is often forgotten and since then, multitudes of series have emerged.[74] The important aspect is that ion specific effects do exist.

One could assume with the massive records of publications in biology and colloidal science, there would be countless studies pertaining to ion specific effects on dye aggregation; particularly in the 70's, when aggregation of organic dyes was a predominant field of research in photographic science. In reality, the influence of specific ions on dye aggregation has largely been ignored. In a study on pseudoisocyanine (PIC) aggregation from 1974, Daltrozzo et al. pointed out that the amount of inorganic salt necessary to induce J-aggregation for a fixed PIC concentration was strongly dependent on the anion nature, the cation identity being nearly irrelevant.[77] However, it was not before the late 80's that the group of D.C. Neckers undertook a deeper investigation into the effect of specific cation addition on the aggregation of negatively charged xanthene dyes.[59, 78] From these studies, it clearly transpires the size of the cation is key to aggregation.[59, 78] Few other publications on the topic can be found in the literature.[79-84]

However to the best of our knowledge, we are the first group to have embarked on a systematic study of the specific ion effect for monovalent salts on the aggregation of small cationic dyes.[35, 44] In our initial study involving an asymmetric cyanine dye, thiazole orange (TO^+), we showed aggregation could be tuned depending on the size of the monovalent anion added to the solution, the nature of its counter-cation being irrelevant (Figure 6).[44] Small anions, such as CH_3COO^-, Br^- and Cl^-, favour dimer formation, the extent of dimerization increasing with an increase in the anion bare radius (Figure 6).[44] On the other hand, larger anions, including I^-, BF_4^- and ClO_4^-, lead to the formation of larger H-aggregates with a maximum of absorption blue-shifted compared to both the monomer and dimer species.[44] In the case of large anions, ClO_4^- led to the largest increase in H-aggregates in aqueous solution. We interpreted these results in terms of water matching affinity and formation of an inner sphere contact ion pair between TO^+ and the inorganic anions.[44] Indeed, our results indicate a sharp change in aggregation behaviour when going from Cl^- to I^- (Figure 6). While the small anions, Br^- and Cl^- bear similar free hydration energies, a drastic difference of about 36 $KJmol^{-1}$ exists between Cl^- and I^-; the free hydration energy reflecting the degree of ion solvation.[44] Since smaller ions have a higher surface charge density than larger ions, they typically have a smaller hydrated radius due to a stronger interaction between water molecules in the hydration sphere of the ion. As a result, these ions are classified as being strongly hydrated and generally have higher free hydration energies.[44] For larger ions, the charge density for a similar valency ion will be lower.[44] Therefore, the ion will have a lower free hydration energy as water molecules are not as strongly associated to the apparent lower charge density. If individual ions are assumed to be initially hydrated in solution, water molecules must be removed from the separated hydration spheres and released into the bulk media for inner sphere contact ion pairs to be formed. By consequence, the number of water molecules hydrating the ion pair will be less than the number of water molecules involved in hydrating the individual ions. The release of water molecules from an ordered hydration sphere to the bulk solution is certainly entropically favoured but it requires energy, equivalent to the free hydration energy. Therefore, inner sphere contact ion pairs can only be formed when the energy associated to the ion-ion interaction is sufficient to disrupt the ordered hydration sphere of individual ions. This latter aspect is the foundation of the principle of the water matching affinity, where oppositely charged ions' interactions in water are governed by hydration-dehydration rather than purely electrostatic attraction.[85, 86] In other words, ions with dissimilar water affinity will tend to stay apart, since dehydration of the most strongly hydrated ion will require more energy than is gained by the formation of contact ion pairs.[85, 86]

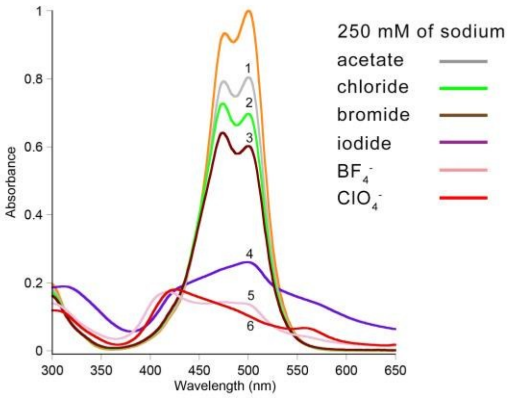

Figure 6: Change in the absorption spectrum of a 20 μM solution of thiazole orange in ultrapure water (top line) upon addition of a 250 mM concentration of monovalent sodium salt: 1, acetate; 2, chloride; 3, bromide; 4, iodide; 5, tetrafluoroborate (BF_4^-); 6, perchlorate (ClO_4^-). Adapted from reference [44].

In a later study, we showed the idea that tuning aggregation by varying the nature of the salt added could be extended to other cationic dyes.[35] In particular, we compared the effect of salt on the aggregation behavior of symmetric *vs.* asymmetric cyanine dyes, possessing different molecular geometries from planar (3,3'-diethylthiacyanine iodide, THIA) to twisted (pseudoisocyanine, PIC) molecular structures.[35] Our experimental results indicate that aggregation is readily observed when the cationic dye and the monovalent anion have matching water affinity, independently of the cyanine dye investigated.[35] Furthermore, experimental and computational data suggest the geometry of the contact ion pair, not so much the individual ions, plays an important role in the aggregate's arrangement. The more planar an inner sphere contact ion pair is, the more structured the aggregates will be.[35]

Polyelectrolytes, surfactants and some macrocycles are also important players in dye aggregation in aqueous solution.[65, 87-92] Certainly, more studies have been published over the years on the subject matter. In particular, polystyrenesulfonate has been reported on several accounts to stabilize and to act as a templating agent for aggregate formation with various cationic dyes[90, 91]. Furthermore, we, and others, have shown the ability of p-calixarenesulfonate to favor the cooperative assembly of dyes into stacked aggregates via host-guest complexation.[65, 93] This was the first example of this particular type of interaction as opposed to conventional host-guest inclusion complex.[65]

Aggregation-induced Emission

Today, it is impossible to write about aggregation without a discussion of aggregation-induced emission. This research area has literally exploded since the original work from the group of Ben Zhong Tang.[94] In 2001, they made the serendipitous discovery during the purification process of a silole derivative (Figure 7), that the molecule spotted on TLC plates was emitting light only when the solvent had evaporated.[94] This result suggested that silole's fluorescence was originating from an aggregate state. This hypothesis was challenged by forcing the silole derivative to aggregate in solution via addition of water to ethanol, where the molecule is fully soluble (figure 7). As anticipated, the silole derivative, initially non-fluorescent in ethanol, became strongly emissive once it aggregated, exhibiting a 333 fold increased fluorescence quantum yield (Figure 7).[94] While silole aggregates present a red-shifted absorption band compared to the monomer species, the 150 nm Stokes shift and broadness of the emission peak preclude these spectroscopic changes to originate from J-aggregation. Furthermore, the twisted conformation of the molecule inhibits its ability to assemble into well-organized H-aggregates (Figure 7). Certainly, this was the first reported example of a molecule developing emissive properties upon aggregation, since then a plethora of other molecules have been recognized and/or engineered to display the same behavior.[19] All these molecules show the same basic features, which are a twisted conformation and a lack of emissive properties in solution due to favorable deactivation via non-radiative pathways (rotational and/or vibrational).[19] Upon aggregation, the molecules are unable to stack into an H-aggregate configuration owing to their geometry, and their non-radiative deactivation pathways are suppressed due to congestion within the aggregates. Hence, the radiative deactivation channel is open and the molecules can relax via emission of light. These types of molecules have been labeled luminogens, as opposed to luminophores or common fluorophores, which see their fluorescence quenched by aggregation.[19] Interestingly, some luminogens have been reported to emit phosphorescence in solid state.[19]

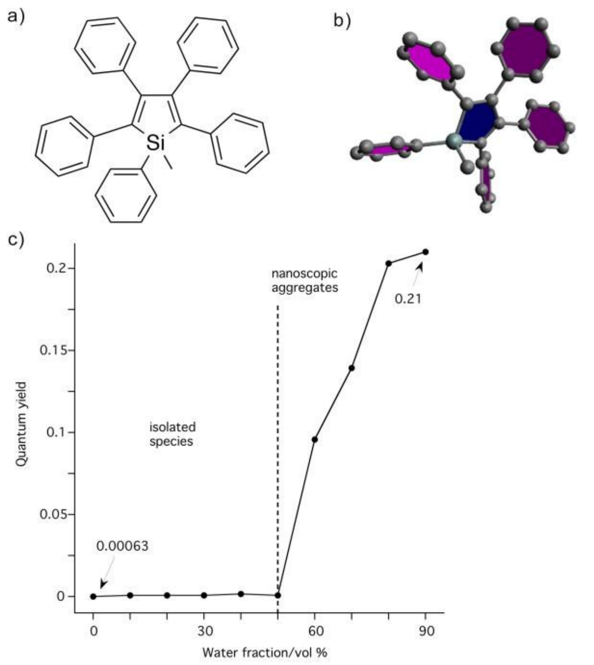

Figure 7: a) Chemical structure of the silole derivative initially investigated by the group of Ben Zhong Tang in 2001. b) Optimized geometry of the silole derivative revealing a twisted conformation (optimization performed with Avogadro).[95] c) Fluorescence quantum yield of the silole derivative in various ethanol/water mixtures. Adapted from reference [94] with permission from The Royal Society of Chemistry.

Because water is responsible for aggregation of the luminogens in solution, a major field of applications is in imaging living organisms.[20] However, aggregation induced emission is also very popular research area in materials science, since films are the ultimate aggregation state. An excellent comprehensive review on the topic can be found elsewhere.[19]

What next …

Aggregation is yet another word to describe the self-assembly of individual molecules into supramolecular units held together by weak intermolecular forces. With the current growth in nanotechnologies and the advance in engineering new smart materials, the study of aggregation is no longer limited to the behavior of dyes in aqueous solution but extends to the realm of solid/liquid interfaces, films or crystals. Today, the state of the art seems to be driven by the quest of synthesizing the most versatile molecule that will self-assembled into complex structures with functional properties. Regardless of the progress made over the last decades, it is shocking that for more than fifty years the same fundamental questions remain to be answered. They simply have changed focus with the evolution of new research applications. As pointed out already in 1977 by A.H. Herz,[10] “what we need is a large jump in our still rudimentary understanding of how variables in dye composition, substrate structure can influence dye-dye interactions and affect the self-assembly process”. Currently, many efforts are made in this direction for the benefit of modern technologies. Whether it is photovoltaic material or light emitting diode, the type of molecular aggregation makes a difference in term of device’s performance. However, a critical aspect often missing is the impact of external stimuli on dye aggregation, in particular the addition of electrolytes. In a dye-sensitized solar cell, electrolytes are a necessary component that ensures the proper flow of electrons between electrodes as well as the regeneration of the dye. As highlighted in our recent work,[35, 44] not every salt acts in a similar way when it comes to inducing dye organization. Thus, we are far from the conventional Debye and Hückel model where interaction between ions is strictly electrostatic. It is now clear that ion specific effects play a prominent part in molecular aggregation.

In light of the current state of research, it is apparent that the old topic of dye aggregation remains an important and ongoing research area, as new questions have emerged.

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