

Liquid-Crystalline J-Aggregates Formed by Aqueous Ionic Cyanine Dyes

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Abstract

Cyanine dyes are used extensively in photographic systems as silver halide spectral sensitizers in order to extend and enhance the intrinsic light sensitivity of AgX grains.¹ Due to the strong intermolecular van der Waals attractive forces operating between these planar poly-cyclic molecules, self-association or aggregation occurs frequently both on solid surfaces (*e.g.* silver halide crystals) and in bulk aqueous solution.² The so-called "J-aggregate" is the most commercially important dye assembly for spectral sensitization and is characterized by a narrow and intense red-shifted absorption band. Their discovery dates back over half a century,^{3,4} though detailed solution structures have remained the subject of some speculation and controversy.

Our recent experimental studies have revealed, however, that the onset of solution J-aggregation for many disparate ionic cyanine dyes is practically concomitant with the formation of a supramolecular lyotropic liquid-crystalline phase possessing nematic or smectic order.^{5,6} The J-aggregate entities are generally 1-D dye columns or 2-D dye monolayers composed of many hundreds or thousands of dye monomers. Conversely, the small H-aggregate precursors give rise to structurally isotropic fluid systems. It is clearly demonstrated that the J-aggregate mesophase properties (structure, order, dimensions and stability) are governed largely by the molecular structure of the dye and *vide infra* the short-range intermolecular interactions (electrostatic, steric and van der Waals).

Introduction

The generic cyanine dye structure is composed of two basic (electron donating) heterocyclic rings, usually containing nitrogen, linked by a conjugated chain commonly possessing an odd number of methine carbons (Figure 1). The positive charge on the chromophore is extensively delocalized between the two nitrogen atoms. The characteristic solution absorption spectrum of such molecules is generally modified upon aggregation.¹ Deviations from Beer's Law, accompanied by distinct changes in band-shape and large spectral shifts relative to the monomer M-band, have been attributed to the formation of dye dimers, trimers, tetramers and *n*-mers. Blue shifts to relatively shorter wavelengths are customarily referred to as H-bands

(for hypsochromic) while bathochromic shifts to longer wavelengths may give rise to excitonic J-bands (probably named after Jelley³). Similar spectral transitions occur for H- and J-aggregates adsorbed to silver halide surfaces.

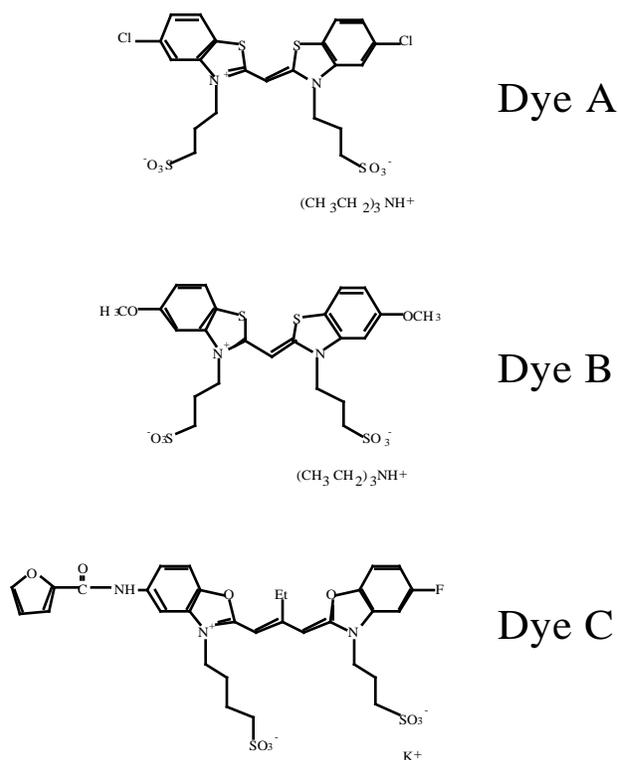


Figure 1: Anionic Cyanine Dye Structures

There appears to be a consensus that both the H- and J-aggregates formed at interfaces are composed of parallel dye molecules stacked plane-to-plane and end-to-end forming two-dimensional crystals (Figure 2a). In solution, analogous one-dimensional dye assemblies have been proposed (Figure 2b). According to theoretical point-dipole, extended-dipole and transition density calculations, whether a dye aggregate exhibits a bathochromic or hypsochromic spectral absorption shift depends on the angle of slippage, α , between successive molecular planes (where α defines the angle between the line-of-centres of a column of dye molecules and the long axis of any one of

the parallel molecules). Large molecular slippage (e.g. $\alpha < \sim 32^\circ$) results in a bathochromic shift while small slippage (e.g. $\alpha > \sim 32^\circ$) results in a hypsochromic shift.⁸

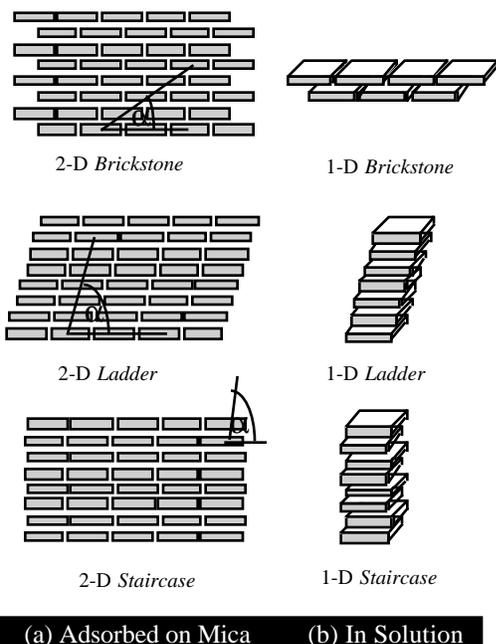


Figure 2. Schematic representations of cyanine dye aggregates (a) dye molecules adsorbed on a mica surface (the surface is in the plane of the paper), (b) dye aggregates in solution. Reproduced from reference 7.

In bulk solution, the spontaneous self-association of cyanine dyes displays a complex dependency upon factors such as dye structure, concentration, solvent polarity, pH, ionic strength and temperature. Consequently, definitive dye aggregate structures have never been determined directly at the molecular level and remain the subject of much speculation and controversy. Many different, often conflicting, solution aggregate models have been proposed largely on the basis of indirect experimental evidence.

Here, the aqueous phase behaviour and spectral absorption characteristics of three anionic cyanine dyes have been quantified in detail using synchrotron X-ray diffraction, polarized-light optical microscopy, NMR spectroscopy and visible absorption spectrophotometry. The equilibrium superstructures of the self-assembled solution J-aggregates have been determined, unequivocally, for the first time and their architectures compared with postulated aggregate models (e.g. Kuhn's 2-D brickstone model).

Table 1: Spectral Absorption Data For Cyanine Dyes In Aqueous Solution (Subscripted s) and Adsorbed To Silver Halide Grains (Subscripted a).

Dye	λ -M _s (nm)	λ -H _s (nm)	λ -J _s (nm)	λ -J _a (nm)	J _s -band onset in H ₂ O (%w/w dye)
A	428	406	463	466	0.01
B	440	401	458	474	14.0
C	502	470	542	543	0.13

Spectral Absorption Characteristics

Irrespective of molecular structure, each dye exhibited a similar concentration-dependent sequence of spectral transitions in aqueous solution at room temperature. Progressive increases in dye concentration resulted in an initial loss of monomer M-band intensity at the expense of co-existing H-band(s), followed by the sudden appearance of an additional, characteristically sharp, J-band above a critical dye concentration. Subsequent dye additions shifted the $M \leftrightarrow H \leftrightarrow J$ -band equilibria in favour of a single J-aggregate state. The data for the solution and silver halide (AgBrI octahedra) aggregated dye species are summarized in Table 1.

Polarized-Light Optical Microscopy

In polarized light, thin-film aqueous preparations of all three J-aggregated dyes revealed characteristic liquid-crystalline (mesophase) textures and morphology. Based on their mesophase structural elements (dye layers versus dye columns) two distinct types of phase behaviour have been identified. These phase assignments were confirmed by deuterium NMR and small-angle X-ray diffraction studies.

Dye A generally exhibited ill-defined grainy microscopic textures at low concentrations. These dilute fluid solutions also possessed a distinctive macroscopic turbid opalescence. More concentrated mesophase preparations generally exhibited a non-geometric "frond-like" optical texture and possessed rather unusual rheological characteristics. Unlike conventional aqueous surfactant lamellar mesophases, the dye A smectic phase tended to flow as viscous birefringent domains along well-defined boundaries when shear was applied to the cover slip. Furthermore, the homeotropic, oily-streak and mosaic textures commonly associated with surfactant lamellar phases were not readily adopted.

Dye B exhibited a vast array of distinctive microscopic textures characteristic of a (low temperature) smectic mesophase, including oily streaks and striated focal conics, and a (high temperature) fluid discotic-nematic meso-phase (N_b), displaying classical Schlieren, threaded and reticulated forms.

In marked contrast to dyes A and B, a viscoelastic tiger-skin texture characterized the dilute columnar-nema-

tic (N_C) mesophase of dye C. At relatively higher dye concentrations, a broken fan-shaped texture typified the viscous hexagonal (M) mesophase. The aqueous phase behaviour of dye C conformed to the archetypal columnar-nematic/hexagonal (N_C/M) mesophase sequence⁹ exhibited by similar drug and azo-dye molecules (*e.g.* Figure 7).

For all three dyes, the dilute H-aggregate solution state was microscopically and macroscopically isotropic (non-liquid crystalline) and fluid.

²H NMR Spectroscopy

NMR measurements of the quadrupole splitting of deuterium in labelled water (²H₂O) are unparalleled as an experimental method for mapping phase diagrams and studying the mechanism of phase transitions in aqueous mesophase systems. Here, the quadrupole splitting, Δ^2H , can provide valuable information about the aggregate geometry and ordering of different anisotropic phases as a function of both concentration and temperature.

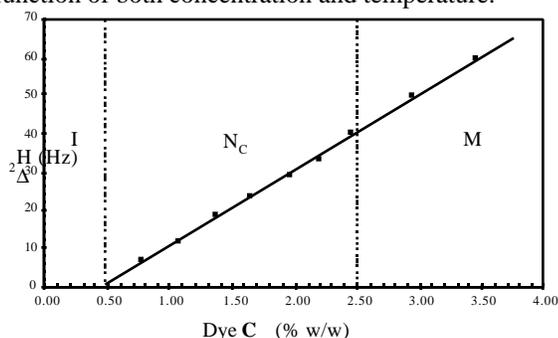


Figure 3: Deuterium quadrupole splitting, Δ^2H , versus dye C concentration at $\sim 26^\circ\text{C}$. I = isotropic solution; N_c = columnar-nematic mesophase; M = columnar hexagonal mesophase.

For all three dyes, concentration- and temperature-dependent ²H quadrupole splittings were observed from the J-aggregated dye mesophases in ²H₂O. For dyes A and C, the linear concentration dependence of Δ^2H at low dye levels and nonzero intercept (*e.g.* Figure 3) are consistent with a biphasic (liquid crystal plus isotropic solution) co-existence regime, in accordance with the Gibbs' phase rule and the lever rule. Here, decreases in Δ^2H were accompanied by decreases in J-band absorbance (meso-phase) at the expense of the co-existing M- and H-bands (isotropic dye solution). A linear extrapolation of Δ^2H to zero provides an estimation of the mesophase concentration onset for dyes A and C. Within experimental error, these values were practically concomitant with the J-aggregate onset determined spectrophotometrically. (Table 1.) Within these dilute heterogeneous biphasic regions, ²H spectra for the individual phases were not resolved due to prevailing fast-solvent-exchange conditions. For dye B, however, mesophase formation at comparatively higher dye concentrations gave rise to slow solvent-exchange

conditions for heterogeneous multiphase samples, enabling a facile and detailed mapping of the binary phase diagram.

By monitoring the magnetic-field-induced alignment of the J-aggregate mesophases, it was possible to differentiate between the layered J-aggregates of dyes A and B (smectic and N_D) and the columnar J-aggregates of dye C (N_C and M). Hence, the positive diamagnetic susceptibility anisotropy, $\Delta\chi$, of the layered J-aggregates and the negative $\Delta\chi$ of the columnar J-aggregates were wholly consistent with the aggregate structures derived from small-angle X-ray diffraction studies.

X-Ray Diffraction

In aqueous solution, dyes A and B exhibited concentration-dependent small-angle XRD patterns with sharp Bragg reflections in positions corresponding to lattice spacings of d , $d/2$, $d/3$, $d/4$, $d/5$ etc. These spacings are characteristic of $\{00l\}$ reflections from a stratified smectic mesophase possessing long-range one-dimensional periodicity. Here the stacked and alternating layers are composed of dye monolayers and water, respectively (Figure 4). The position of the $\{001\}$ reflection gives the total repeat spacing, d_0 , (the unit cell dimension) equivalent to the thickness of one dye layer, d_t , plus one water layer, d_w . For dye A, the mesophase structural elements (J-aggregates) are, by inference, 2-D dye monolayers assumed to be rigid, well-ordered and continuous (infinite). These assumptions are consistent with the molecular architecture, the observation of an unusually large number of both small- and wide-angle Bragg reflections and the relatively large ²H NMR quadrupole splittings of mesophase-bound ²H₂O molecules.^{5,6} In reality, the smectic domain (J-aggregate) size will be determined by both the free energy of defects and the sample history *e.g.*, shear and temperature effects. For dye B, however, the unusual biaxiality of the smectic phase (revealed by ²H NMR "powder" lineshapes) may result from the condensation of finite-sized disc-like (tabular) J-aggregates from the nematic N_D phase onto smectic planes, rather than the stabilization of continuous smectic sheets.

Within these layered phases, the dye molecules are close-packed with an intermolecular separation of $\sim 3.5 \text{ \AA}$ (determined by wide-angle XRD) and arranged *a priori* with their sulphonate moieties uniformly distributed above and below the layer plane. Such an arrangement would provide the net negative charge distribution necessary for the electrostatic stabilization of the long-range smectic order. In order to produce the characteristic J-aggregate spectral absorption band, the molecules are probably arranged in a brickwork-like array. Indeed, our observations of multiple, often sharp and intense XRD reflections in the approximate range 3-50 Å , with concentration-invariant

positions, (for dye A and other smectic-forming dyes not reported here) are congruent with an unusually high degree of intralayer molecular order.⁵ For these rigid, biaxial molecules, this introduces a potential for complex intralayer structural polymorphism, reminiscent of the thermotropic smectic mesophases.

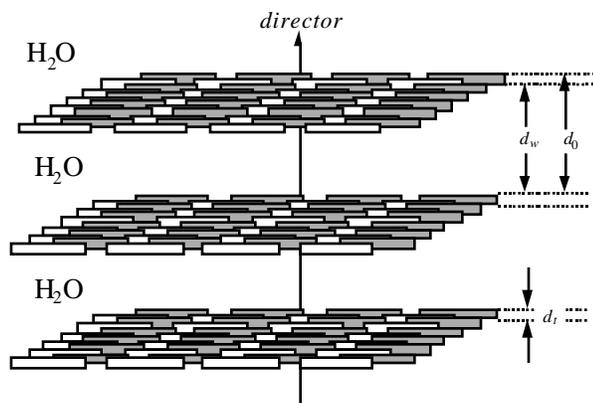


Figure 4: Schematic representation of an aqueous smectic dye mesophase. The rectangles represent individual dye molecules which are packed into "infinite" 2-D brickstone-like monolayers (J-aggregates). The biaxial monolayers may be oriented identically or randomly with respect to each other to produce a bi-axial (as shown) or uniaxial smectic mesophase.

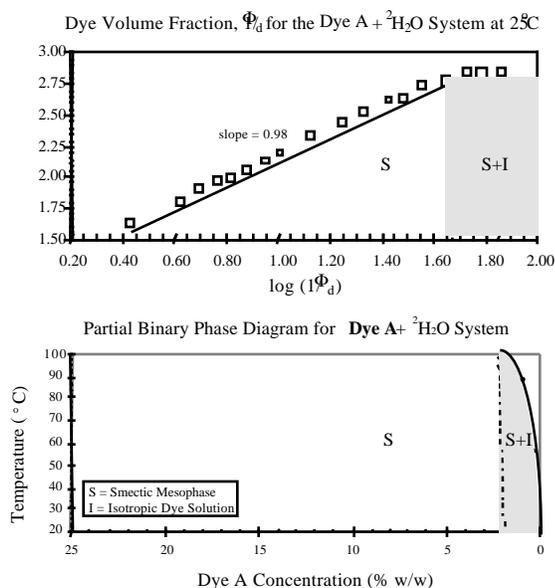


Figure 5. Variation of the X-ray diffraction first-order Bragg spacing, d_0 , with reciprocal dye volume fraction, $1/\phi_d$, for dye A in $^2\text{H}_2\text{O}$ at 25°C (top). A partial phase diagram for the dye A + $^2\text{H}_2\text{O}$ system (bottom).

In marked contrast to aqueous surfactant systems, where the lamellar (smectic) phase usually has a limited swelling range, many dye smectics, exemplified by dye A, are stable over a considerably larger dilution range. This is illustrated in the plot of the XRD spacing, $\log d_0$,

versus reciprocal volume fraction of dye, $\log(1/\phi_d)$, in Figure 5. Here, the maximum interlayer spacing of dye A ($\sim 697 \text{ \AA}$) coincides with a pronounced discontinuity in slope, from a gradient of ~ 1 to, essentially, zero at approximately 2% w/w dye. Here, the water layer thickness ($d_w \sim 688 \text{ \AA}$) is nearly 2 orders of magnitude larger than that of the dye layers ($d_l \sim 9 \text{ \AA}$). This point corresponds to a first-order transition between the homogeneous (one-phase) smectic liquid crystal and a heterogeneous (two-phase) dispersion, composed of swollen smectic mesophase (J-aggregates) in equilibrium with dilute isotropic dye solution (composed of monomer and H-aggregates). For dye B, however, the water-swelling capacity of the smectic phase is far less, and this transition occurs at $\sim 30\%$ w/w dye, corresponding to a maximum interlayer separation of only $\sim 61 \text{ \AA}$.

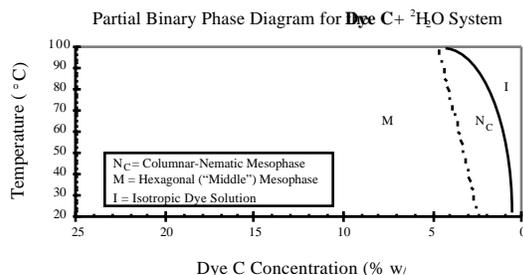
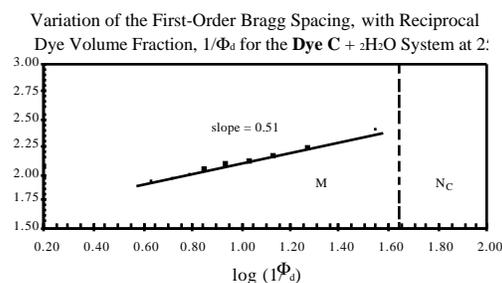


Figure 6. Variation of the X-ray diffraction first-order Bragg spacing, d_0 , with reciprocal dye volume fraction, $1/\phi_d$, for the hexagonal M mesophase of dye C in $^2\text{H}_2\text{O}$ at 25°C (top). A partial phase diagram for the dye C + $^2\text{H}_2\text{O}$ system (bottom).

In marked contrast to dyes A and B, dye C (at concentrations $\geq 3\%$ w/w dye) exhibited a series of sharp, concentration-dependent Bragg reflections with spacings of d , $d/\sqrt{3}$, $d/\sqrt{4}$, $d/\sqrt{7}$, $d/\sqrt{9}$, etc. These XRD reflections are characteristic of a hexagonal mesophase possessing long-range two-dimensional periodicity. The mesophase structural elements in this case are, by inference, 1-D columns of dye molecules stacked plane-to-plane, with the columnar long axis perpendicular to the molecular planes (consistent with ^2H NMR mesophase-alignment studies⁶). For dye B, the calculated values for the cross-sectional area of these columns ($1310 \pm 51 \text{ \AA}^2$) exceeds, by far, the dye molecular area of $\sim 151 \text{ \AA}^2$. Clearly, the individual dye stacks possess a multimolecular cross-section, and not the unimolecular structure reported previously for

similar systems. The precise molecular architecture of these highly-ordered 1-D columns is currently a matter of speculation. Postulated models include the uniaxial hollow cylinder and the biaxial rectangular stack.⁶

Upon dilution, the hexagonal mesophase of dye C swells progressively in two dimensions *i.e.*, the dye stacks simply separate in directions normal to their long axes. This is reflected in the $\log d_0$ versus $\log (1/\phi_d)$ slope of 0.5 (Figure 6). Across this composition range, the centre-to-centre separation of the columns increases monotonically from ~ 94 Å at 24.8% w/w dye, to ~ 282 Å at 3.0% w/w dye. Furthermore, the linearity of this plot indicates a concentration-invariant aggregate composition (size and anisotropy) throughout this region. Further dilution to $\sim 2.5\%$ w/w dye (defined by optical microscopy and ^2H NMR), induced a transition from a columnar-hexagonal to a columnar-nematic mesophase (not represented in Figure 6). Continued dilution, to $\sim 0.42\%$ w/w dye (as determined by ^2H NMR) brings about a second distinct (first-) order transition between the N_C mesophase (J-aggregates) and isotropic dye solution ($M \leftrightarrow H$ -aggregates) via a narrow intervening two-phase zone.

Summary & Conclusions

The J-aggregate is the most commercially important dye assembly for the spectral sensitization of photographic silver halide grains. Their discovery dates back over half a century, though their detailed solution structures have remained the subject of some speculation and controversy. Here, the equilibrium supramolecular architectures of "free-standing" J-aggregates have been elucidated and quantified for the first time using a combination of experimental techniques.

It has been established, unequivocally, that the solution J-aggregate state of several disparate anionic cyanine sensitizing dyes is largely liquid-crystalline in nature. Indeed, the pioneering J-aggregation studies of the aqueous cationic sensitizing dye 1,1'-diethyl-2,2'-cyanine chloride (PIC), conducted by Jelley³ and Scheibe⁴ some 60 years earlier, had intimated as much. The J-aggregate mesophase properties (structure, order, dimensions and stability) are governed largely by the molecular structure of the dye, and *vide infra* the short-range intermolecular interactions (electrostatic, steric and van der Waals). For example, dilute liquid crystals possessing long-range translational smectic or hexagonal periodicity and long-range orientational nematic order (Figure 7) may all exhibit characteristic spectroscopic J-bands.

The individual mesogenic J-aggregates (generally 2-D monolayers or 1-D columns) must, by inference, be composed of many hundreds or thousands of dye monomers, depending on the mesophase structure and concentration. Thus, typical association numbers of four molecules,² estimated for the "polymer-like" J-aggregates

of aqueous ionic cyanine dyes from mass action considerations of absorption spectra ($M \leftrightarrow J$ -band equilibrium), do not correspond to the number-molecular weight of the aggregate itself. Clearly, the simple mass action model used does not apply to heterogeneous biphasic dye dispersions.

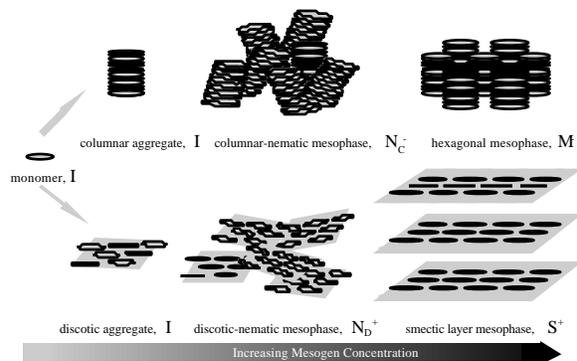


Figure 7. Schematic representation of possible aggregate and mesophase structures formed by cyanine dyes in water.

Conversely, the H-aggregate precursors of dyes A, B and C are comparatively small, probably anisometric, dye assemblies such as dimers, trimers *etc.* They constitute both structurally and optically, isotropic fluid systems. The $M \leftrightarrow H \leftrightarrow J$ -aggregate equilibria of these aqueous ionic dyes may be considered similar, though not strictly analogous, to the monomer \leftrightarrow micelle \leftrightarrow mesophase equilibria of aqueous surfactant systems. Thus, for dilute smectic dye systems in particular, where extensive heterogeneous two-phase coexistence regions may exist, the J-aggregate mesophase may be isolated from dilute solution simply by centrifugation.

In marked contrast to aqueous amphiphilic systems, such as surfactants, the driving force for dye self-association is believed to result, primarily, from short-range intermolecular attractive forces involving both σ and π electrons and not the *hydrophobic effect*. Thus, in a similar fashion to thermotropic mesogens, seemingly minor changes to the generic cyanine dye structure can have a profound effect on the number, type and stability of the mesophases observed (*c.f.* dyes A and B).

In reality, the 2-D monomolecular J-aggregate layers composing the smectic solution mesophase of dyes A and B (Figure 4) bear more than a passing resemblance to Kuhn's proposed 2-D brickwork model for mica-adsorbed cyanine dyes (Figure 2a). In both cases, the planar molecules are parallel and close-packed edge-to-edge and plane-to-plane, with the in-plane molecular short-axis perpendicular to the layer plane, and neighbouring molecular rows mutually staggered. Indeed, for many smectic-forming dyes the absorption wavelengths of the "free-standing" solution- and AgX-adsorbed J-aggregates are practically identical (*e.g.* dye A, Table 1).

For cyanine dye C, which forms aqueous columnar-nematic and hexagonal mesophases, the precise molecular architecture of the 1-D dye columns (J-aggregates) remains equivocal. In direct contrast to the uni- and bimolecular dye stacks previously proposed for 1-D solution aggregates (*e.g.* the "ladder" & "staircase" models reproduced in Figure 2b), the X-ray data presented here are consistent with columns of multimolecular cross-section. Furthermore, ^2H NMR and XRD results for dye C are also incompatible with the 1-D "brickstone" model proposed for the aqueous J-aggregates of PIC, where the columnar long axis is coincident with the molecular long axes (Figure 2b). Irrespective of the detailed topology of their solution J-aggregates, both dye C and PIC, perhaps significantly, exhibit wavelength-invariant J-bands both in solution (N_D mesophase) and adsorbed to AgBrI cubic and octahedral microcrystals, respectively.

It is necessary for many other J-aggregating dyes to be examined before the apparent correlation between "spontaneous" J-aggregation and mesophase formation can be considered a general phenomenon. Experimental studies are also continuing to elucidate the precise molecular ordering within the solution J-aggregates of both smectic and nematic/hexagonal mesophase-forming cyanine dyes. However, this significant advancement of our rudimentary perception of solution J-aggregates may now

be exploited in the long-term development of dye structure-aggregation relationships, both in aqueous solution and on silver halide surfaces.

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