

# Supramolecular Assembly of Complementary Cyanine Salt J-Aggregates

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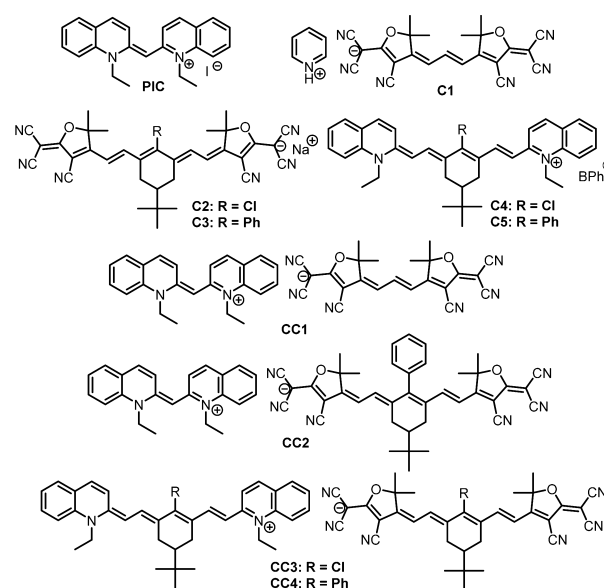
**S** Supporting Information

**ABSTRACT:** An understanding of structure–property relationships in cyanine dyes is critical for their design and application. Anionic and cationic cyanines can be organized into complementary cyanine salts, offering potential building blocks to modulate their intra/intermolecular interactions in the solid state. Here, we demonstrate how the structures of these complementary salts can be tuned to achieve highly ordered J-type supramolecular aggregate structures of heptamethine dyes in crystalline solids.

Organizing organic dyes by self-assembly is an efficient approach to create defined molecular architectures with appealing topology and properties for light-harvesting and other optoelectronic applications.<sup>1</sup> Among various supramolecular structures, J-aggregates (also called Scheibe aggregates) are particularly interesting<sup>2</sup> because they provide promising optical properties such as an intense, red-shifted absorption band (J-band) and a high fluorescence quantum yield in the solid state, due to extended delocalization of excitons over several molecular units.<sup>3</sup>

Cyanines are a class of ionic organic compounds with carbon skeletons containing an odd number of conjugated carbon atoms, which have been widely studied as photosensitizers for photography or biological probes.<sup>4</sup> Due to their ionic nature and strong intermolecular interactions, they show a major tendency to aggregate with each other. Indeed, the first example of a dye J-aggregate was discovered in a cyanine called pseudoisocyanine (PIC, Figure 1).<sup>2</sup> Nowadays, self-assembly of cyanine dyes, in particular in the J-aggregate form, is an active area of research, but most examples reported so far have focused only on cyanines with relatively short conjugation length (number of carbons in the conjugation bridge,  $L \leq 3$ ).<sup>3a,c,5</sup>

Cyanines with much longer conjugation length ( $L \geq 7$ ), such as heptamethines, are usually near-infrared (NIR) absorbing and emitting, making them attractive for various applications such as in vivo cell imaging,<sup>6</sup> photovoltaics,<sup>7</sup> and nonlinear optics.<sup>8</sup> However, the uncontrolled aggregation of these highly polarizable dyes, especially the formation of H-aggregates, often limits their applicability. For example, H-aggregates can give rise to a blue-shifted absorption band and strong fluorescence quenching, which prevents their biomedical applications.<sup>9</sup> In addition, the



**Figure 1.** Molecular structure of cyanines and complementary cyanine salts studied.

strong and random ion-pairing/aggregation between these dyes in the solid state has been shown to induce adverse changes in their nonlinear optical properties for all-optical switching (AOS) applications.<sup>10</sup> Therefore, it is important to understand the implications of the varying structural properties in order to design suitable materials.<sup>11</sup>

Understanding the role of counterions in the extended structures of cyanines will provide an effective way to manipulate the organization of chromophores toward favorable molecular assemblies.<sup>11b,12</sup> Because of their ionic nature, it is possible to organize anionic and cationic cyanines into complementary salts for functioning not only as mutually polarizable counterions but also as useful building blocks to form favorable supramolecular assemblies in the solid state.<sup>13</sup> By rationally tuning the structure of cyanine dyes as complementary salts, we have recently demonstrated a new molecular design strategy to achieve J-type self-assembly of highly polarizable heptamethine dyes in

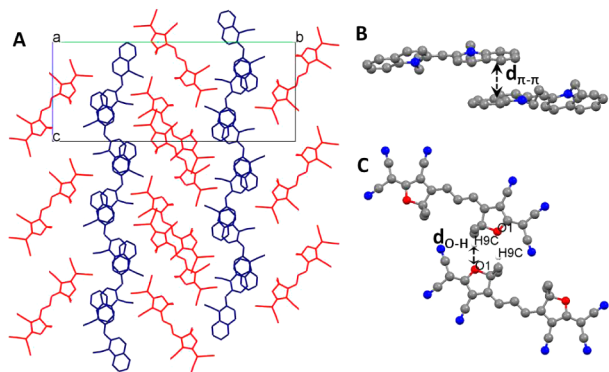
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crystalline solids. It enables us to better understand the structural properties of these aggregates at the molecular level.

In this study, we have used 2-(3-cyano-4,5,5-trimethyl-5H-furan-2-ylidene)malononitrile (TCF) and *N*-ethyl-2-methylquinolinium as end groups for anionic and cationic cyanines, respectively. The TCF end group has high electronic delocalization and was developed initially as an efficient electron acceptor for dipolar chromophores with strong intramolecular charge transfer properties.<sup>14</sup> TCF-heptamethines, such as C2 (Figure 1), absorb in the NIR ( $\sim 900$  nm) with a large extinction coefficient ( $>3 \times 10^5$  M<sup>-1</sup> cm<sup>-1</sup>),<sup>15</sup> which enables them to have many possible applications.<sup>7b,16</sup> For example, C2 with aromatic counterions has been demonstrated to have large third-order nonlinearities for AOS applications.<sup>16c</sup> However, the crystal structure of C2 has shown unfavorable supramolecular assembly with an unexpected anti-conformation in which dimethyl groups in TCF are on the different sides of polymethine backbone and break symmetry in the solid state.<sup>15</sup> This deleteriously affects its optical properties. However, quinolinium-cyanines are known to exhibit diverse aggregations dependent on their conjugated backbone, due to strong  $\pi$ - $\pi$  interactions between their end groups.<sup>3c</sup> The PIC compound with  $L = 1$  is known to form J-aggregates, while the pinacyanol compound (PIN) with  $L = 3$  is reported to form H-aggregates. In this context, the cationic PIC molecules are anticipated to maintain their J-aggregation characteristics in the solid state, which can function as a template to organize complementary anionic TCF-cyanines into an extended structure.

To validate this idea, we first mixed PIC with the TCF-cyanine C1 ( $L = 3$ ) to form a new complementary salt CC1 (Figure 1 and Scheme S1). A single crystal of CC1 was successfully obtained. Its refined structure (monoclinic,  $P2_1/n$  space group) is presented in Figure 2 (See SI for details). As shown in Figure

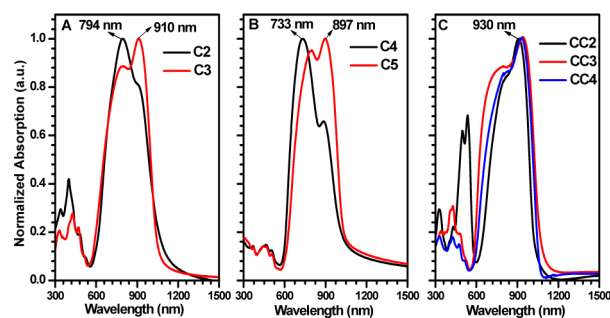


**Figure 2.** Crystal structure of CC1: (A) molecular packing of the quinolinium (marked in blue) and TCF (marked in red), cyanines viewed along the  $a$  axis; (B) packing mode of the quinolinium-cyanines with a slippage angle ( $\theta_{\text{qui}} = 23.8^\circ$ ) and a  $\pi$ - $\pi$  interaction distance ( $d_{\pi-\pi} = 3.42$  Å); (C) packing mode of the TCF-cyanines through the O1-C9H contact with a distance of 2.56 Å (the C-H...O bond angle is  $159.3^\circ$ ). For clarity, most of the hydrogen atoms are omitted. The oxygen atoms are marked in red, nitrogen atoms in blue, carbon atoms in gray, and hydrogen atoms in white.

2A, both the PIC and C1 in CC1 show a highly ordered molecular packing structure along the (110) plane; in particular, the PIC molecules form extended J-aggregates as we expected, which potentially dictates the spatial arrangement of the anionic TCF-cyanines to be J-type as well. Figure 2B depicts a typical  $\pi$ - $\pi$  stacking mode among PIC molecules with a small slippage

angle ( $\theta_{\text{qui}}$ ) of  $23.8^\circ$  and a  $\pi$ - $\pi$  interaction distance of 3.42 Å. It is also found that there occurs C-H...O bonding between two neighboring TCF-cyanines (Figure 2C), which may play a role in forming such a construct. This result suggests that it should be able to use PIC as a templating counterion to modulate the spatial arrangements of highly polarizable dyes in the solid state. To this end, PIC was mixed with TCF-heptamethine C3 to form a complementary salt, CC2 (Figure 1 and Scheme S2). However, we could not obtain a single crystal for structure analysis. This is likely due to the incompatibility in molecular size between PIC and C3, making it difficult to form an extended structure.

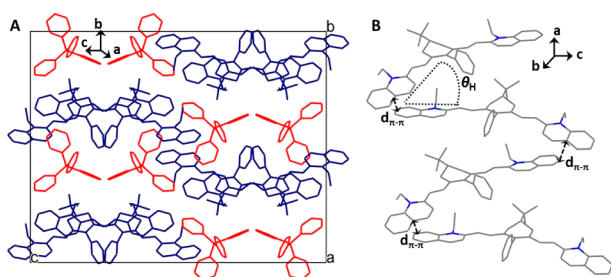
Therefore, quinolinium-heptamethines C4 and C5 (Figure 1 and Scheme S2) were further designed and synthesized as compatible counterions for C2 and C3, respectively. Here, the phenyl substitution at the center of the bridge in C3 and C5 is introduced to suppress potential H-type aggregation. Indeed, a comparison of thin-film absorption spectra between C2 and C3 (Figure 3A), or C4 and C5 (Figure 3B), clearly suggests that H-



**Figure 3.** Neat thin-film absorption spectra for cyanine dyes: (A) TCF-cyanines C2 and C3; (B) quinolinium-cyanines C4 and C5; (C) complementary cyanine salts CC2-CC4. Note: The absorption maxima in diluted solutions of dyes are listed in Table S1: 900 nm for C2; 880 nm for C3; 861 nm for C4; 858 nm for C5; 882 nm for CC1; 868 nm for CC2; and 870 nm for CC4.

type aggregation is mitigated when the chloride atom in the bridge is replaced with a phenyl ring. Moreover, it is worth to note that phenyl substitution also leads to a blue-shifted absorption band when compared to chloride substitution, due to the inductive effect of the substituents (Figure S2). However, the absorption peaks from quinolinium-cyanines ( $<0.01$  eV) showed a smaller blue shift than those of TCF-cyanines ( $\sim 0.03$  eV). Results from time-dependent density functional theory (TD-DFT) calculations suggest that this difference in blue shift is attributed to the extent of delocalization of the frontier molecular orbitals of the respective cyanines near their end groups (Table S5, see SI for details).

The single-crystal structure (orthorhombic,  $Pbca$  space group) of C5 has been refined also (see SI for details). The unit cell is shown in Figure 4a, where continuous parallel double-layers of cationic cyanines were separated by a single sheet of borate anions. The symmetric molecules exhibit a quasi-planar conjugated skeleton (Figure S5), and the phenyl substituents are significantly twisted relative to the conjugated backbone ( $\sim 70^\circ$ ) as a result of steric hindrance between the *ortho*-hydrogen atoms of the phenyl ring and the backbone. As noted previously, the quinolinium-cyanines exhibit diverse aggregation behaviors dependent on their conjugation length. Here, as shown in Figure 4B, even with the long heptamethine chains, strong  $\pi$ - $\pi$  interactions between the end groups still lead to the formation of a highly ordered herringbone-type molecular



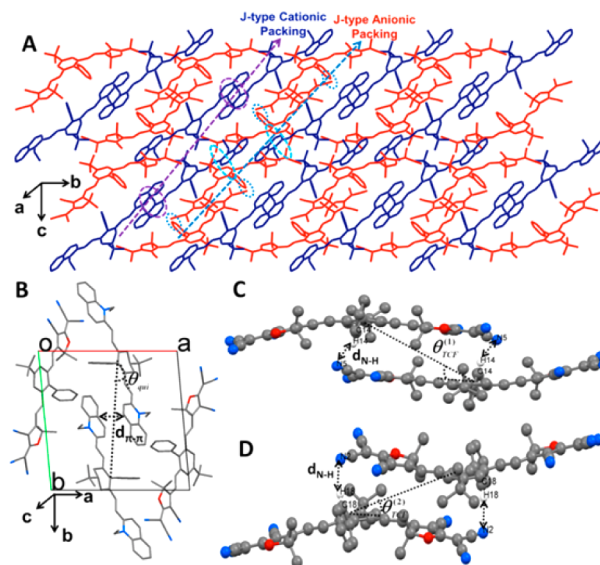
**Figure 4.** Crystal structure of C5: (A) unit cell of the quinolinium-cyanines (marked in blue) and borate (marked in red) viewed along the *a*-axis; (B) extended packing mode of the quinolinium-cyanines with a herringbone angle ( $\theta_{\text{H}}$ ) of  $52.0^\circ$  and a  $\pi$ - $\pi$  interaction distance ( $d_{\pi-\pi} = 3.30 \text{ \AA}$ ) viewed along the *b*-axis. For clarity, the hydrogen atoms are omitted. The nitrogen atoms are marked in blue and carbon atoms in gray.

packing structure along the (020) plane. This can be attributed to the twisted phenyl ring at the center of the bridge serving as an effective “spacer” to mitigate the deleteriously random intermolecular interactions, as demonstrated in the film absorption spectra. Thus, the above observations indicate that C5 has the potential to be used as a templating counterion to direct the spatial arrangement of an anionic TCF-heptamethine.

By mixing quinolinium and TCF-heptamethines through a simple ion exchange, the complementary salts CC3 and CC4 have been prepared (Figure 1 and Scheme S2). The close  $\lambda_{\text{max}}$  and  $\epsilon_{\text{max}}$  (Table S1) between the quinolinium and TCF-heptamethines causes some overlap of their solution absorption bands; therefore, only one slightly broader combined transition peak can be observed (Figure S3). Their neat thin-film absorption spectra are shown in Figure 3C, all of which show a red-shifted ( $>0.06 \text{ eV}$ ) and broadened absorption band as compared to those obtained from the solution spectra, which suggest a strong ion-pairing and/or aggregation in the solid state.<sup>10</sup> However, CC4 exhibits a much sharper absorption band than CC3 ( $0.64 \text{ eV}$  vs  $0.78 \text{ eV}$ ), indicating somewhat narrower distribution of conformational variation of aggregates for the CC4 as a result of the spacing effect from the twisted phenyl ring at the center of the bridge.

The single-crystal structure (triclinic,  $P\bar{1}$  space group) of the complementary cyanine salt CC4 has been determined and is presented in Figure 5 (see SI for details). To the best of our knowledge, this is the first crystal structure reported for a complementary cyanine salt with a highly polarizable heptamethine backbone. Interestingly, Figure 5A shows that the oppositely charged cyanines in the salt form a cooperative self-assembly and individually pack in alternating J-type fashion, similar to the packing observed in CC1. This is consistent with our initial concept of using complementary cyanines as counterions to control the spatial arrangements and interactions of highly polarizable dyes in the solid state.

The unit cell is shown in Figure 5B, and both cationic and anionic cyanines in the salt maintain overall symmetric geometries, without significant twisting of the cyanine cores (Figure S6). Unlike in the crystal structure of C5, here, the strong  $\pi$ - $\pi$  interactions between the end groups direct adjacent quinolinium cyanines to pack in a dimeric J-type structure with a small  $\theta_{\text{qui}}$  of  $21.3^\circ$  and a  $\pi$ - $\pi$  interaction distance of  $3.43 \text{ \AA}$  (Figure 5B). Since the quinolinium-cyanines also act as counterions, the electrostatic interactions between the cationic and anionic stack dictate the spatial arrangement of the anionic



**Figure 5.** Crystal structure of CC4: (A) molecular packing of the quinolinium- (marked in blue) and TCF- (marked in red) cyanines viewed along the *a* axis; (B) unit cell viewed along the *c* axis illustrating the slippage angle ( $\theta_{\text{qui}} = 21.3^\circ$ ) and the  $\pi$ - $\pi$  interaction distance ( $d_{\pi-\pi} = 3.43 \text{ \AA}$ ); (C) packing mode of the TCF-cyanines ( $\theta_{\text{TCF}}^{(1)} = 26.4^\circ$ ) through the N5–H14 contact with a distance of  $2.71 \text{ \AA}$  (the C–H $\cdots$ N bond angle is  $157^\circ$ ); (D) packing of the TCF-cyanines ( $\theta_{\text{TCF}}^{(2)} = 24.1^\circ$ ) through the N2–H18 contact with a distance of  $2.59 \text{ \AA}$  (C–H $\cdots$ N bond angle of  $169^\circ$ ). For clarity, most of the hydrogen atoms and the solvent molecules are omitted. The oxygen atoms are marked in red, nitrogen atoms in blue, carbon atoms in gray, and hydrogen atoms in white.

TCF-cyanines, which also form J-aggregate-like stacks along the (011) plane (Figure 5A). As shown in Figure 5C,D, nonclassical C–H $\cdots$ N bonding, in two different configurations, between the phenyl rings on the bridge and the TCF end groups, plays a significant role in reinforcing the stability of such structures.

The average bond-length alternation (BLA) is an important parameter characterizing the geometries and electronic structure of cyanines.<sup>8</sup> Here, the BLA of C5 in the crystal structure is only  $0.012$  (Table S9), while those of the complementary TCF-anion and quinolinium-cation in the crystal of CC4 are found to be  $0.015$  and  $0.020 \text{ \AA}$ , respectively (Table S10). These values are slightly larger than those obtained from density functional theory (DFT) calculations (Table S2); however, they remain relatively small when compared to those reported in the literature.<sup>12c,15</sup> This can be attributed to the favorable spatial arrangement of cyanines within the fairly symmetric counterionic environment. In CC4, the highly polarizable and delocalized cyanine pairs with mutually compatible size and complementary charges clearly facilitate the symmetrical distribution of electrons between heptamethines, as shown in Figure S8.

In conclusion, through rational molecular design, complementary salts of quinolinium- and TCF-cyanines have been prepared to modulate the molecular packing of heptamethine dyes in the solid state while maintaining their highly polarizable and symmetric nature. We demonstrated that well-known J-aggregating cationic cyanines such as PIC can be used as structure-directing counter cations for anionic cyanines. Our results revealed that the phenyl substitution at the center of conjugation backbone not only suppresses the potential H-type aggregation efficiently but also plays an important role in reinforcing the stability of J-type supramolecular aggregate structures. We also reported the first crystal structure of a

complementary cyanine salt with a highly polarizable heptamethine backbone, which shows that both cationic and anionic cyanines in the complementary salt form a cooperative self-assembly, resulting in highly ordered J-aggregate-like molecular packing. This study provides a molecular design strategy useful to modulate the aggregation and ion-pairing properties of highly polarizable cyanines with long conjugation length. Such rational design can prove highly beneficial for application of cyanine dyes in biomedicine, optics, and other technologies.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b08072.

Synthetic details and characterization data, linear optical properties, computational results, X-ray crystal structure, and <sup>1</sup>H NMR spectra (PDF)

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### Notes

The authors declare no competing financial interest.

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