

Supramolecular Assembly of Complementary Cyanine Salt J-Aggregates

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Supporting Information Placeholder

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.¹ Among various supramolecular structures, J-aggregates (also called Scheibe aggregates) are particularly interesting,² 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.³

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.⁴ 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**).² 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, $L \leq 3$).^{3a, 3c, 5}

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,⁶ photovoltaics,⁷ and nonlinear optics.⁸ 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.⁹ In addition, the 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.¹⁰ Therefore, it is important to understand the implications of the

varying structural properties in order to design suitable materials.¹¹

Understanding the role of counter ions in the extended structures of cyanines will provide an effective way to manipulate the organization of chromophores towards favorable molecular assemblies.^{11b,12} Because of their ionic nature, it is possible to organize anionic and cationic cyanines into complementary salts for functioning not only as mutually-polarizable counter ions but also as useful building blocks to form favorable supramolecular assemblies in the solid state.¹³ 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 crystalline solids. It enables us to better understand the structural properties of these aggregates at the molecular level.

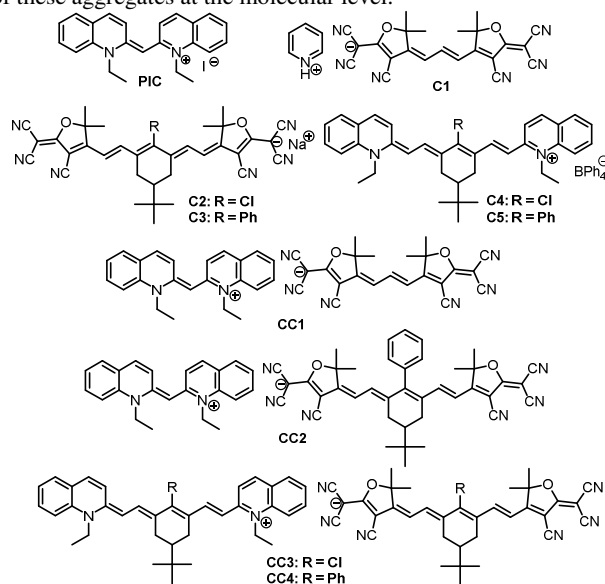


Figure 1. Molecular structure of cyanines and complementary cyanine salts studied.

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 intra-molecular charge transfer properties.¹⁴ TCF-heptamethines, such as **C2** (Figure 1), absorb in the NIR (~900 nm) with a large extinction coefficient ($>3 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$),¹⁵ which enables them to have many possible applications.^{7b,16} For example, **C2** with aromatic counter ions has been demonstrated to have large third-order nonlinearities for AOS applications.^{16c} 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.¹⁵ This deleteriously affects its optical properties. On the other hand, quinolinium-cyanines are known to exhibit diverse aggregations dependent on their conjugated backbone, due to strong π - π interactions between their end groups.^{3c} The PIC compound with $L = 1$ is known to form J-aggregates while the pina-cyanol 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.

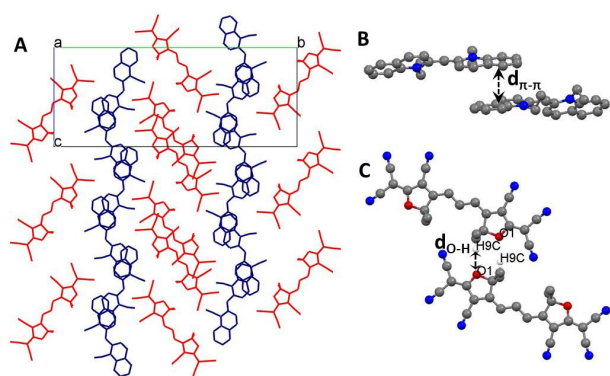


Figure 2. Crystal structure of **CC1**: A) molecular packing of the quinolinium (marked in blue) and TCF (marked in red) - cyanines viewed along the a axis; B) packing mode of the quinolinium-cyanines with a slippage angle ($\theta_{\text{qui}} = 23.8^\circ$) and a π - π interaction distance ($d_{\pi-\pi}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

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 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 π - π stacking mode among PIC molecules with a small slippage angle (θ_{qui}) of 23.8° and a π - π interaction distance of 3.42 \AA . 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 counter ion 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 counter ions 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-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 ($< 0.01 \text{ eV}$) showed a smaller blue shift than those of TCF-cyanines ($\sim 0.03 \text{ eV}$). 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).

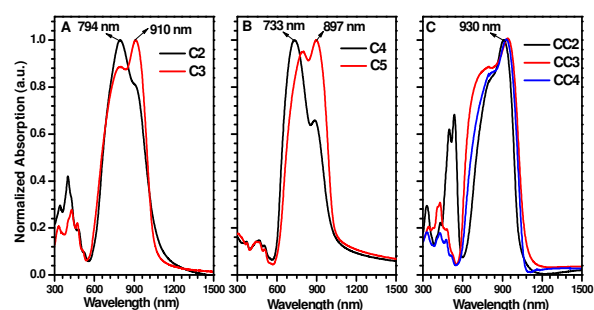


Figure 3. The neat thin-film absorption spectra for cyanine dyes: A) TCF-cyanines **C2** and **C3**; B) quinolinium-cyanines **C4** and **C5**; C) complementary cyanine salts **CC2-CC4**. Note: The absorption maxima in diluted solutions of dyes are listed in Table S1: 900 nm for **C2**; 880 nm for **C3**;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

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 π - π interactions between the end groups still lead to the formation of a highly ordered herringbone-type molecular 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 counter ion to direct the spatial arrangement of an anionic TCF-heptamethine.

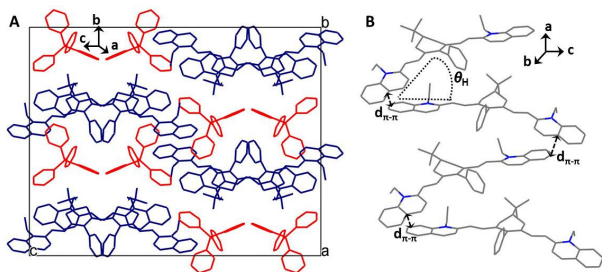


Figure 4. Crystal structure of **C5**: A) unit cell of the quinolinium-cyanines (marked in blue) and borate (marked in red) viewed along the a -axis; B) Extended packing mode of the quinolinium-cyanines with a herringbone angle (θ_H) of 52.0° and a π - π interaction distance ($d_{\pi-\pi} = 3.30 \text{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

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 λ_{\max} and ε_{\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.¹⁰ However, **CC4** exhibits a much sharper absorption band than **CC3** (0.64 eV vs 0.78 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 counter ions 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 π - π interactions between the end groups direct adjacent quinolinium cyanines to pack in a dimeric J-type structure with a small θ_{qui} of 21.3° and a π - π interaction distance of 3.43 \AA (**Figure 5B**). Since the quinolinium-cyanines also act as counter ions, the electrostatic interactions between the cationic and anionic stack dictate the spatial arrangement of the anionic TCF-cyanines, which also form J-aggregate-like stacks along the (011) plane (**Figure 5A**). As shown in **Figure 5C** and **5D**, non-classical 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.

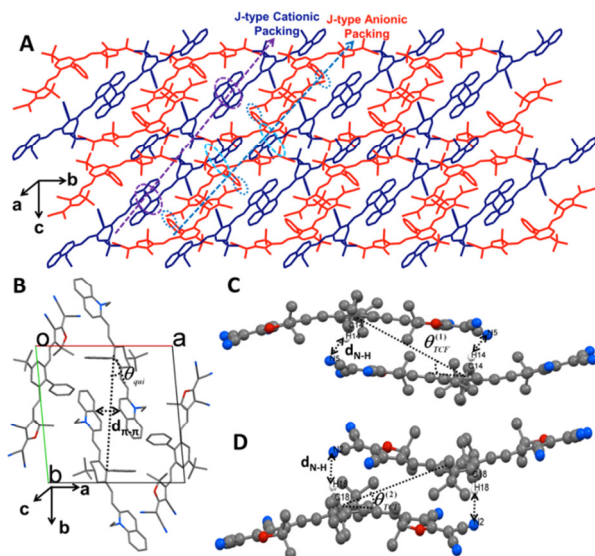


Figure 5. Crystal structure of **CC4**: A) molecular packing of the quinolinium- (marked in blue) and TCF- (marked in red) cyanines viewed along the a axis; B) unit cell viewed along the c axis illustrating the slippage angle ($\theta_{\text{qui}} = 21.3^\circ$) and the π - π interaction distance ($d_{\pi-\pi} = 3.43 \text{ \AA}$); 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 \AA (the C-H \cdots N bond angle is 157°); D) packing of the TCF-cyanines ($\theta_{\text{tcf}}^{(2)} = 24.1^\circ$) through the N2-H18 contact with a distance of 2.59 \AA (C-H \cdots N bond angle of 169°). 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 grey and hydrogen atoms in white.

The average bond-length alternation (BLA) is an important parameter characterizing the geometries and electronic structure of cyanines.⁸ Here, the BLA of **C5** in the crystal structure is only 0.012 \AA (**Table S9**), while those of the complementary TCF-anion and quinolinium-cation in the crystal of **CC4** are found to be 0.015 \AA and 0.020 \AA , respectively (**Table S10**). These values are slightly larger than those obtained from density functional theory (DFT) calculations on the (**Table S2**); however, they remain relatively small when compared to those reported in the literatures.^{12c,15} This can be attributed to the favorable spatial arrangement of cyanines within the fairly symmetric counter-ionic 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

Synthetic Details and characterization Data, Linear optical properties, Computational results, X-ray Crystal Structure and ¹H NMR Spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

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