Article

Zwitterionic Cyanine–Cyanine Salt: Structure and Optical Properties

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ⓢ Supporting Information

Complementary Cyanine Salt → Zwitterionic Cyanine-Cyanine Salt
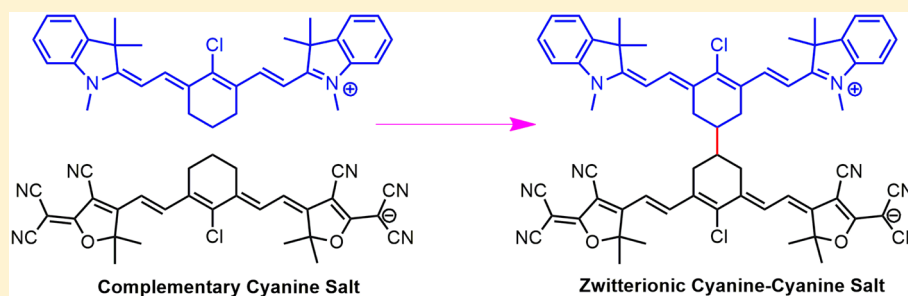
ABSTRACT: Cyanines with long conjugation length such as heptamethines are well known to have strong intramolecular and/or intermolecular interactions (i.e., ion paring and aggregation), which can affect their structures (i.e., symmetry breaking) and optical properties remarkably. In this paper, we report a covalently linked complementary cyanine complex of cationic and anionic heptamethines forming a highly polarizable zwitterionic cyanine–cyanine salt. The effect of the modification was studied in detail on both its electronic structure and its optical properties. This novel zwitterionic salt was found to exhibit a decreased ion-pairing-induced charge localization but with an increased electronic coupling between the excited states of the cyanine cation and the anion, resulting in unusual optical properties compared to closely related noncovalent complementary cyanine salts. The dual-arm Z-scan technique was used to study their third-order NLO properties, suggesting the electronic coupling in such preorganized zwitterionic system has a weak impact on NLO properties, and both cyanines contribute to the large third-order molecular polarizabilities exceeding 4×10^{-32} esu for potential all-optical photonic applications.

INTRODUCTION

Cyanines are a class of ionic organic dyes widely studied over the past century mainly as photosensitizers for photography or bioimaging owing to their very attractive optical properties that include large extinction coefficients and strong fluorescence especially in the near-infrared (NIR) region.[1−3] Recently, their very favorable nonlinear optical (NLO) properties have been demonstrated for organic photonics applications. For example, some heptamethines have been shown to have a very large real part of the third-order polarizabilities, Re(γ), with relatively small two-photon absorption (2PA) loss at the telecommunications wavelengths (1.3−1.55 μm), enabling them to be promising material candidates for all-optical signal processing (AOSP).[4−7] On the other hand, cyanines with large 2PA can be useful for other applications such as optical limiting and microscopy.[8−11]

Typically, an isolated cyanine possesses a well-defined molecular symmetry with a charge fully delocalized over the polymethine backbone, endowing them with the aforementioned attractive optical properties.[1−7] However, the strong Coulombic interactions (i.e., ion pairing) between chromophores and counterions tend to localize the charges close to one side of the end groups, resulting in a significant distortion of the delocalization and subsequent symmetry breaking of

their electronic structures.[12−14] This can adversely affect the favorable NLO properties due to the appearance of undesirable one- and two-photon states, which is more pronounced in particular for those with small and hard (less polarizable) counterions such as halides.[15,16]

To mitigate the ion-pairing effect, both the experimental and the theoretical data have suggested using bulky, soft (easily polarizable) ions as counterions such as tetraaryl–borate anions and –phosphonium cations.[14−17] Another more attractive approach is to chemically lock the position of the counterions at the center of the polymethine backbone to form a highly symmetrical zwitterionic salt. Many rhodamine derivatives,[18] squaraine,[19−21] and quinonoid[22−24] can be regarded as such zwitterionic salts; however, they have limited molecular nonlinearities for AOSP applications due to relatively short conjugation lengths.

Our recent work has demonstrated that organizing anionic and cationic heptamethines with large molecular nonlinearities into complementary cyanine salts can be very advantageous to maintain their highly polarizable and symmetric nature even in

A

Scheme 1. Synthetic Route of Cyanine−Cyanine Salts 1 and 2 Studied Here
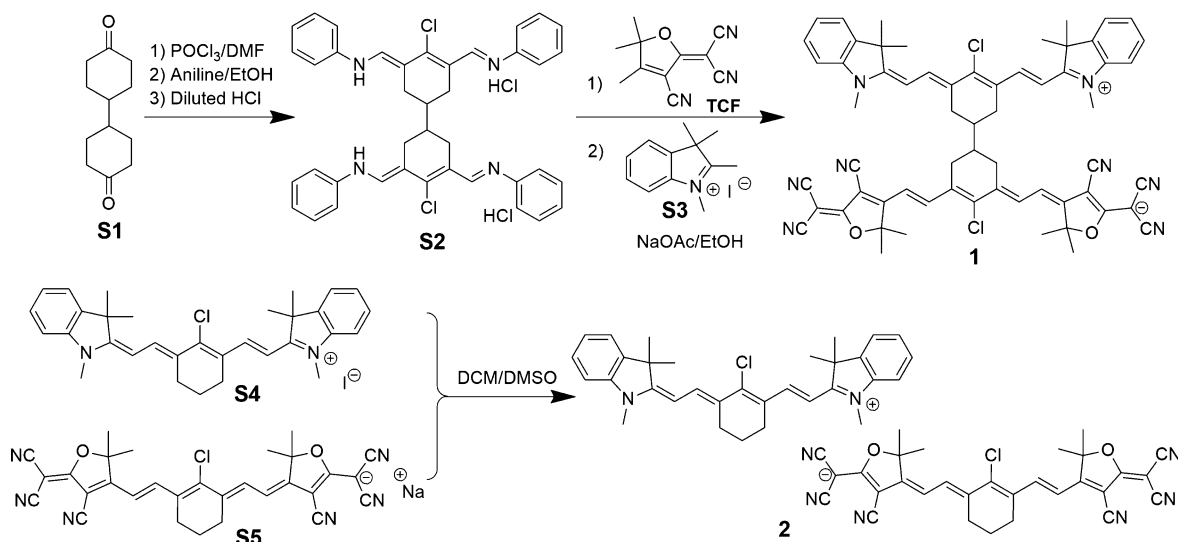
the solid state.[25] This unique structure, on the other hand, suggests an appealing potential building block for zwitterionic "cyanine−cyanine" salts. On this basis, we successfully prepared a highly polarizable zwitterionic salt without breaking the whole molecular symmetry by linking the conjugation bridge of anionic and cationic heptamethines covalently (Scheme 1), which enables a structure−property correlation study of this novel building block that is critically beneficial to rational design and application of cyanine dyes.

■ EXPERIMENTAL SECTION

Materials. The end group of 2-(3-cyano-4,5,5-trimethyl-5H-furan-2-ylidene)malononitrile (TCF),[26] indolium−heptamethine (S4),[27] and TCF−heptamethine (S5)[28,29] were synthesized according to the reported methods. All other reagents were used as received.

Instrumentation. ^1H NMR and ^{13}C NMR were measured using a Bruker 300 and 500 MHz instrument spectrometers. Mass spectroscopy (MS) was performed using a Bruker Esquire LC-Ion Trap at the Department of Chemistry Mass Spectrometry Facilities (UW). Elemental analyses were performed by Intertek QTI Laboratory (Whitehouse, NJ). UV−vis−IR absorption spectra were measured using a PerkinElmer Lambda-9 spectrophotometer. The fluorescence spectra and quantum yields were measured using a PTI Quantamaster spectrofluorometer. Time-resolved photoluminescence (TRPL) spectra were measured by a time-correlated single-photon counting (TCSPC) system (FluoTime 100, PicoQuant GmbH). The samples were photoexcited using a 780 nm laser beam (LDH-P-C-470, PicoQuant GmbH) pulsed at frequencies between 0.25 and 10 MHz with a pulse duration of 60 ps and fluence of ∼10 nJ/cm^2 to avoid nonlinear effects such as exciton-charge annihilation. Cyclic voltammetry was measured on a BAS CV-50W voltammetric analyzer using a conventional three-electrode cell with Pt metal as the working electrode, Pt gauze as the counter electrode, and Ag/Ag$^+$ as the reference electrode at a scan rate of 100 mV/s. The 0.1 M solutions of tetrabutylammonium hexafluorophosphate (TBAPF) in acetonitrile or dichloromethane were used as the electrolytes.

Third-Order Nonlinear Optical Measurement. The dual-arm (DA) Z-scan technique is a differential method and

has been applied to resolve only the nonlinearity of the solute by simultaneously scanning solution and solvent in two equalized Z-scan arms. This can result in a better sensitivity than sequential measurement in a single-arm configuration as the energy, pulse width, and beam pointing fluctuations are correlated and suppressed in parallel in real time.[30] In this experiment we used ∼10 mJ, ∼40 fs (fwhm) pulses at a 1 kHz repetition rate to produce excitation pulses at 1550 nm from a Ti:sapphire amplified laser system (Coherent Legend Elite Duo HE+) pumping an optical parametric amplifier (TOPAS-HE). The salts of **1** and **2** were dissolved in dichloromethane (Sigma-Aldrich, 650463, 99.9%), and all measurements were conducted using 1 mm path length quartz cuvettes.

Synthesis of Double Bridge (S2). To a solution of compound **S1** (1.94 g, 10.0 mmol) in 50 mL of anhydrous dichloromethane (DCM) and 10 mL of anhydrous dimethylformamide (DMF) was added dropwise 10 mL of phosphorus oxychloride (POCl$_3$) under nitrogen in an ice bath. After stirring at 0 °C for 0.5 h, the reaction mixture was refluxed for 3 days and then cooled to 0 °C using an ice bath. After that a mixture of aniline/ethanol [1:1 (v/v), 30 mL] was added dropwise to the above solution. Upon aniline addition, the solution color turned to red, and after another 30 min stirring, the red solution was poured into 220 mL of 1 N HCl solution. Deep purple crystalline precipitates were filtered, washed with cold water, dimethyl ether, and DCM, and then dried in vacuum to afford the red product **S2** (5.3 g, 74.0%). MS (ESI): M$^+$ = 644.1 (calcd for $C_{40}H_{37}Cl_2N_4^+$, 644.6); M^{2+}/2 = 323.3 (calcd for $C_{40}H_{38}Cl_2N_4^{2+}$, 645.7). Note: Due to the limited solubility of **S2**, no appreciable proton peaks can be observed in the ^1H NMR spectrum.

Synthesis of Zwitterionic Cyanine−Cyanine Salt (1). **S2** (717 mg, 1.0 mmol) and TCF end group (400 mg, 2.0 mmol) were dispersed in anhydrous ethanol (50 mL) under nitrogen, and then anhydrous sodium acetate (168 mg, 2.0 mmol) was added. After the mixture was refluxed for 3 h, 1-methyl-2,3,3-trimethylindolenium iodide **S3** (602 mg, 2.0 mmol) was added under nitrogen. The solution then refluxed overnight and cooled to room temperature (RT). After ethanol was evaporated under a vacuum, DCM (50 mL) was added and the organic layer was washed with water, dried over anhydrous sodium sulfate, and then evaporated under a vacuum. The

Table 1. Absorption Properties of 1 and 2 in Various Organic Solvents

	1				2			
	$\lambda_{max,sol}{}^{a}$ (nm)		$\varepsilon_{max}{}^{b}$ (10^5 M^{-1} cm^{-1})		$\lambda_{max,sol}{}^{a}$ (nm)		$\varepsilon_{max}{}^{b}$ (10^5 M^{-1} cm^{-1})	
	cation	anion	cation	anion	cation	anion	cation	anion
p-dioxane	756	913	10.59	3.47	755	908	3.68	1.44
toluene	767	922	11.24	3.82	772	917	4.52	1.76
chloroform	760	919	11.83	4.28	787	910	6.88	6.48
DCM	757	911	7.82	3.21	786	903	5.70	4.32
acetone	754	898	5.67	3.04	778	894	5.15	3.84
acetonitrile	755	898	5.02	2.30	775	892	5.23	2.96
DMSO	779	913	3.94	2.10	791	907	4.19	2.57

^{a}Absorption maxima wavelengths in dilute solutions with a concentration of 2×10^{-6} M. ^{b}Molar extinction coefficients.
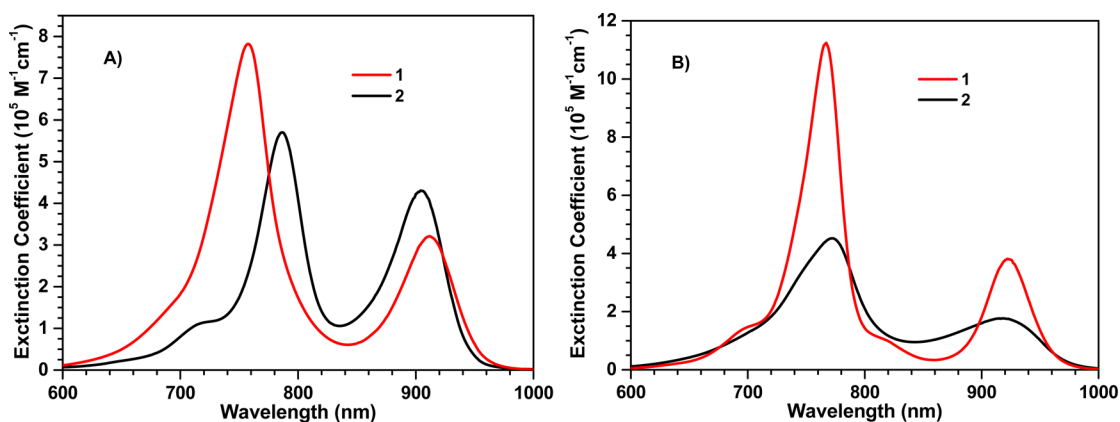

Figure 1. Absorption spectra of **1** and **2** in diluted solutions of DCM (A) and toluene (B) with a concentration of 2×10^{-6} M.

resulting crude solid was purified by flash column chromatography over silica gel twice using DCM/ethyl acetate (20/1, v/v) as eluent solvent to afford the product **1** as green solid (60 mg, 5.9%). ^{1}H NMR (CDCl$_3$, 500 MHz, 293 K) δ (ppm): 1.77 (m, 24H, −C(CH$_3$)$_2$), 1.83 (m, 2H, −CH$_2$−), 2.28−2.39 (m, 4H, −CH$_2$−), 3.11 (t, 4H, J = 5.7 Hz, −CH$_2$−), 3.72 (s, 6H, −NCH$_3$), 6.13 (d, J = 14.0 Hz, 2H, −CH=CH−), 6.27 (d, J = 14.5 Hz, 2H, −CH=CH−), 7.25 (d, J = 8.5 Hz, 2H, ArH), 7.30 (t, J = 7.5 Hz, 2H, ArH), 7.41 (d, J = 7.5 Hz, 2H, ArH), 7.45 (t, J = 7.5 Hz, 2H, ArH), 7.79 (d, J = 14.5 Hz, 2H, −CH=CH−), 8.46 (d, J = 14.0 Hz, 2H, −CH=CH−). ^{13}C NMR (CDCl$_3$, 125 MHz, 293 K) δ (ppm): 27.4, 28.1, 29.7, 30.1, 32.2, 36.6, 48.1, 49.5, 86.6, 94.9, 100.5, 106.3, 111.3, 113.7, 114.6, 115.0, 122.1, 124.2, 124.8, 125.8, 129.1, 140.2, 140.9, 142.6, 145.0, 147.2, 151.0, 169.3, 173.6, 176.1. MS (ESI): M + H$^+$ = 1017.3 (calcd for C$_{62}$H$_{56}$Cl$_2$N$_8$O$_2$, 1016.1). Anal. Calcd: C, 73.32; H, 5.31; N,10.71. Found: C,73.29; H, 5.56; N, 11.03.

Synthesis of Reference Complementary Cyanine Salt (2). Cationic indolium−heptamethine **S4** (305 mg, 0.5 mmol) and anionic TCF−heptamethine **S5** (280 mg, 0.5 mmol) were dissolved in 20 mL of DCM and 1 mL of DMF. The solution was stirred at RT for 0.5 h, washed with distilled water, dried over anhydrous sodium sulfate, and evaporated under a vacuum. The resulting crude solid was purified by flash column chromatography over silica gel using DCM/methanol (49:1, v/v) as eluent solvent to afford the product **2** as green solid (360 mg, 70.9%). ^{1}H NMR (CDCl$_3$, 300 MHz, 293 K) δ (ppm): 1.66 (s, 12H, −C(CH$_3$)$_2$), 1.75 (s, 12 H, −C(CH$_3$)$_2$), 1.83 (m, 2H, −CH$_2$−), 2.0 (t, J = 6.0 Hz, 2H, −CH$_2$−), 2.54 (br, s, 4H, −CH$_2$−), 2.72 (t, J = 6.0 Hz, 2H, −CH$_2$−), 3.67 (s, 6H, -NCH$_3$), 6.02 (d, J = 14.1 Hz, 2H, −CH=CH−), 6.11 (d, J = 14.1 Hz, 2H, −CH=CH−), 7.17 (d, J = 8.4 Hz, 2H, ArH), 7.27 (m, 2H, ArH), 7.40 (m, 4H, ArH), 7.97 (d, J = 14.1 Hz, 2H, −CH=CH−), 8.39 (d, J = 14.1 Hz, 2H, −CH=CH−). ^{13}C NMR (CDCl$_3$, 125 MHz, 293 K) δ (ppm): 20.7, 20.9, 26.4, 27.3, 28.1, 31.6, 47.1, 49.4, 94.7, 100.5, 101.1, 101.7, 110.7, 114.2, 114.9, 115.6, 122.3, 125.6, 127.3, 128.9, 140.9, 142.7, 144.8, 151.2, 168.1, 173.2, 176.6. MS (ESI): M$^+$ = 484.3 (calcd for C$_{32}$H$_{36}$ClN$_2{}^+$, 484.1); M$^-$ = 533.7 (calcd for C$_{30}$H$_{22}$ClN$_6$O$_2{}^-$, 534.0). Anal. Calcd: C, 73.44; H, 5.66; N, 10.99. Found: C, 73.14; H, 5.74; N, 11.01

RESULTS AND DISCUSSION

The synthetic route we have chosen to prepare the zwitterionic cyanine−cyanine salt (**1**) and its reference complementary cyanine salt (**2**) is shown in Scheme 1 with the synthetic details provided in Experimental Section. On the basis of our previous work,[6,25] we used 2-(3-cyano-4,5,5-trimethyl-5H-furan-2-ylidene)malononitrile (TCF) and 1,2,3,3-tetramethyl-3H-indolim iodide (**S3**) as the end groups for anionic and cationic heptamethines, respectively. As shown, 1,1′-bi(cyclohexyl)-4,4′-dione (**S1**) first reacted with the typical Vilsmeier−Haack regent[31] to give a new bifunctional C7-conjugation bridge (**S2**). Salt **1** was then prepared by a simple one-pot, two-step procedure by successive additions of TCF and **S3** into the bridge **S2**, however, with a relatively low yield of 5.9% due to the quite low solubility of **S2** and its limited selectivity of four reaction sites. We have to note that the synthesis of such zwitterionic cyanine−cyanine structure is rather challenging. As shown in Scheme S1, another product for this reaction was the dimeric merocyanine with a purification yield of 14.8%, similar to the results as reported (Scheme S2).[32] Thus, formation of different potential combinatorial isomers needs to be
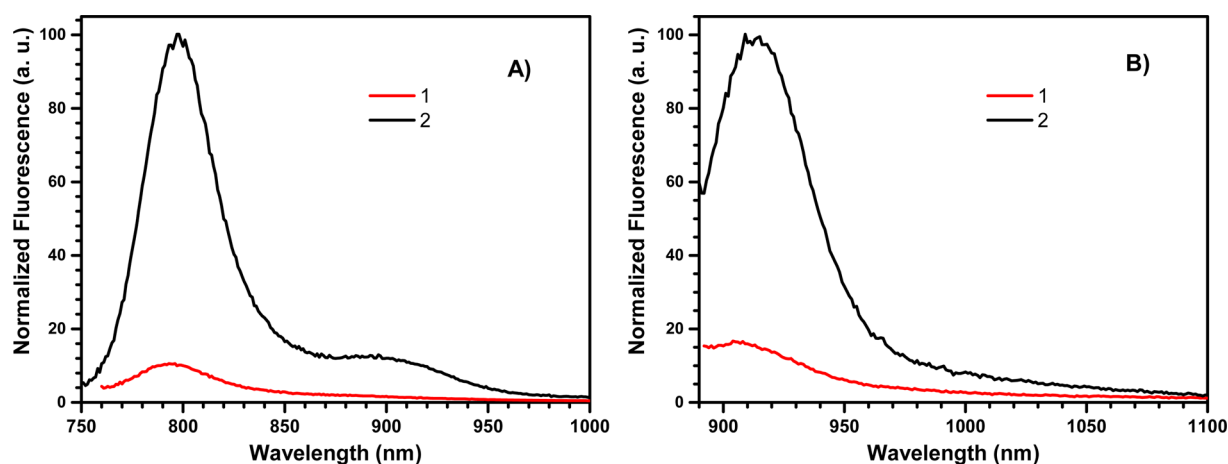
Figure 2. Normalized fluorescent spectra of **1** and **2** in diluted DCM solutions (1.2×10^{-6} M for **1** and 1.7×10^{-6} M for **2**) excited at 740 (A) and 880 nm (B).

controlled. More scalable alternative synthetic routes are being explored currently. Salt **2** was then synthesized via a simple ion exchange between **S4** and **S5** according to the literature method.[33] The chemical structures of both **1** and **2** were fully confirmed by NMR, mass spectrometry, and elemental analysis, with details shown in the Experimental Section and Supporting Information (Figures S12–S17).

We carefully investigated the linear optical properties of **1** and **2** in order to elucidate the effect of the zwitterionic structure on the electronic transition properties, and their UV–vis–IR absorption spectra were measured in various organic solvents with the corresponding absorption data listed in Table 1. As shown in Figures 1 and S1, both **1** and **2** maintain the spectral features of both cationic and anionic heptamethines with two separate absorption bands located at ∼760 and ∼900 nm, respectively, indicating no appreciable electronic coupling in their ground states.[33] When changing solvent from DCM to toluene or *p*-dioxane, we observed a sizable difference on the shape of the absorption band between **1** and **2**. Figure 1B depicts that both the cation and the anion in **2** show much broader absorption bands with significantly reduced extinction coefficients in toluene compared to those of **1**. As is well known, nonpolar solvents like toluene or *p*-dioxane are more likely to force the association of ion pairs, resulting in absorption features that deviate significantly from those of completely solvated cyanines.[14] Another possible reason for such band-broadening phenomena is the formation of aggregates considering the limited solubility in toluene. However, we found that **1** actually has a decreased solubility compared to **2** due to the enhanced structural rigidity when forming a zwitterion. To exclude the aggregation effect, we measured the concentration-dependent absorption spectra for **2** in toluene solutions (Figure S2). As concentration increases from 5×10^{-7} to 2×10^{-5} mol/L, the shape of the absorption band does not change, suggesting the broadening of the absorption band is not due to aggregation. Therefore, the above band-broadening phenomena observed from **2** could come from the ion-pairing-induced charge localization (i.e., symmetry breaking). Given such charge localization is negligible for **1**, our results suggest the relative spatial position of the counterion in the zwitterionic structure can be limited to conserve the molecular symmetry by reducing the deleterious ion-pairing effect.

Moreover, we note here that the terminal end groups also play a role in affecting their optical behaviors. We expect the delocalization strength of end groups can be affected by the surrounding solvent environment differently. TCF–heptamethine is more delocalized compare to indolium–heptamethine. As a result, the oscillator strength of the former may be more sensitive to the change of the surrounding solvent environment. On the other hand, the increased extinction coefficients in nonpolar solvents for indolium–heptamethine in **1** (Table 1) may be attributed to the symmetric geometry of the zwitterionic building block that reinforces the charge delocalization of indolium–heptamethine resulting in a more ideal polymethine geometry. However, the impacts on the oscillator strengths for the already delocalized TCF–heptamethine are smaller than indolium–heptamethine in **1**.

Interestingly, by carefully comparing their absorption maxima ($\lambda_{max,sol}$, Table 1), we found that regardless of solvent polarity, the absorption band of the cation in zwitterionic salt **1** shows a blue shift (≤ 29 nm) while that of the anion gives a red shift (≤ 9 nm) relative to those in reference salt **2**. These unusual absorption characteristics indicate a possible coupling between the excited states of the cation and the anion in the zwitterionic structure. To understand the potential coupling, we studied their fluorescent emission properties. Figure 2 depicts their normalized fluorescent spectra in DCM solutions, where the cation and anion in both salts appear as separate fluorescence species upon excitation at 740 and 880 nm with similar emission maxima (Table 2) and bandwidth. However, as shown, **1** presents a significant fluorescent intensity quenching compared to **2** at both excitation wavelengths. The fluorescence quantum yield of **1** was measured to be only 0.25%, much smaller than that of **2** (14.0%) when excited at 740 nm (Table 2 and see SI details). Additionally, it is worth noting that unlike **1**, a weak emission peak at ∼900 nm was also observed in the fluorescent spectrum of **2** when excited at 740 nm, which overlaps with the absorption of TCF anion (Figure S5). To find the origin of this peak at ∼900 nm, we then measured the fluorescent spectrum of the individual **S4** also excited at 740 nm for comparison (Figure S6), which indicated this should be due to the mirror reflection of the vibronic structure of the cation absorption.

By changing solvent from DCM to toluene, **1** similarly exhibits a reduced emission compared to **2**. In toluene solution, **1** becomes nonfluorecent while weak emissions can still be

Table 2. Fluorescent and Electrochemical Properties of 1 and 2 in DCM Solutions

	$\lambda_{em,sol}$ (nm)		Φ^c (%)	τ^d (ns)	HOMO^e (eV)	LUMO^f (eV)	$E_g{}^g$ (eV)
	cation^a	anion^b					
1	793	906	0.25	0.38	−4.74	−3.74	1.00
2	798	914	14.0	1.31	−4.78	−3.71	1.07

^{a}The emission peak maxima excited at 740 nm. ^{b}The emission peak maxima excited at 880 nm. ^{c}Quantum yield excited at 740 nm. ^{d}The PL lifetime measured by time-resolved photoluminescence (TRPL) measurements excited at 780 nm. ^{e}According to the equation of $E_{HOMO} = -(E_{ox\ vs\ Fc/Fc+} + 4.80)$ (eV). ^{f}According to the equation of $E_{LUMO} = -(E_{Red\ vs\ Fc/Fc+} + 4.80)$ (eV). ^{g}According to the equation of $E_g = E_{LUMO} - E_{HOMO}$. Note: $E_{ox\ vs\ Fc/Fc+}$ and $E_{Red\ vs\ Fc/Fc+}$ correspond to the first oxidation and reduction onset, respectively, versus Fc/Fc$^+$ (0.53 V).

measured for **2** (Figure S7). As a result, the lower emission efficiency observed in both DCM and toluene for **1** suggests the aforementioned electronic coupling between the excited states in fact plays a role as a result of the tight molecular contact between cation and anion in the zwitterionic structure.[28,34] Moreover, it is worth noting the fluorescent quenching for **2** in toluene solution relative to DCM solution is due to the ion-pairing-induced symmetry breaking as described above. The time-resolved photoluminescence (TRPL) measurements were also conducted, while the spectra are shown in Figure S8 with results summarized in Table 2. The PL lifetime (τ) of **1** is found to be only 0.38 ns, much shorter than that of **2** (1.31 ns), which is consistent with the results from quantum yields and indicates a significant electronic coupling in the zwitterionic salt. However, the difference between **1** and **2** in terms of electronic coupling becomes negligible in the solid state since strong intermolecular interactions (i.e., aggregation) now play a more pronounced role, as evident in the thin film absorption spectra of **1** and **2** (Figure S3) which show large bathochromic shifts (over 80 nm) compared to those in solutions. Moreover, no appreciate emission signal can be detected in their thin films.

The electrochemical properties of **1** and **2** were evaluated by cyclic voltammetry (CV) using an Ag/Ag$^+$ electrode as the reference electrode, and the curves are shown in Figure 3. Similar to those described in the typical complementary cyanine salts,[33] here **2** also reveals two reversible oxidative onsets (E_{ox}) at 0.51 and 0.75 V corresponding to the first
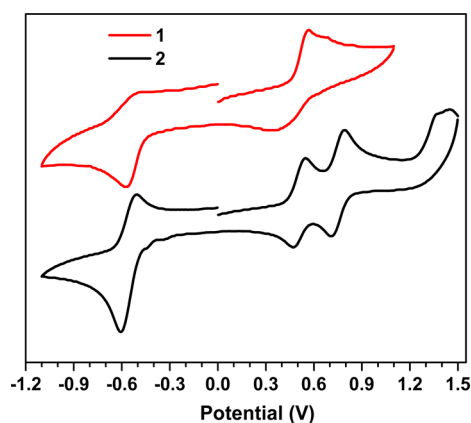
oxidation of the TCF anion and indolium cation, respectively (Figure S9). A third irreversible oxidation at 1.11 V, assigned to the second oxidation of the TCF anion, was also observed. In sharp contrast, a broad signal during the oxidation process was shown in the CV curve of **1**, with only one partially reversible E_{ox} at 0.47 V. According to the first E_{ox} versus Fc/Fc$^+$ (0.53 V), we can calculate the highest occupied molecular orbital (HOMO) levels of **1** and **2** to be −4.74 and −4.78 eV, respectively (Table 2). On the other hand, both cases only show one reduction peak with an onset (E_{Red}) at −0.53 V for **1** and −0.56 V for **2**, suggesting that the lowest occupied molecular orbitals (LUMOs) of the TCF anion and indolium cation are energetically close. The LUMO levels of **1** and **2** were estimated to be −3.74 and −3.71 eV, respectively (Table 2).

It is worth noting that similar to those shown in the literature,[33] our data (Table S1) also demonstrated that the anionic TCF−heptamethine has a higher lying HOMO level than that of the cationic indolium−heptamethine, indicating the former has more electron-rich character compared to the latter. As a result, the contrasting shift in the solution absorption band for the zwitterionic salt of **1** (a blue-shifted band for the cation and a red-shifted band for the anion) can be rationalized by the difference of their HOMO levels, which enables them to play different roles during the electronic coupling.

Motivated by the interesting electronic coupling properties, we further studied the effect of electronic coupling on the molecular third-order NLO properties including two-photon absorption (2PA) and third-order nonlinear refraction (NLR) coefficients using a femtosecond pulsed dual-arm (DA) Z-scan technique at 1.55 μm,[6,30] the wavelength of interest in the telecommunication band for AOSP applications. The measured values of Re(γ) and Im(γ) are shown in Table 3 with ∼20%

Table 3. Third-Order Microscopic Nonlinearities Measured in Concentrated DCM Solutions^a Using the Femtosecond Pulsed Dual-Arm Z-Scan Method at 1.55 μm

	Re(γ)^b (10^{-32} esu)	Im(γ)^c (10^{-32} esu)	$|\gamma|^d$ (10^{-32} esu)	$|$Re(γ)/Im(γ)$|$
1	−3.8	1.9	4.2	2.0
2	−4.2	2.3	4.8	1.8

^{a}Concentration of solutions: 0.17 mM for **1** and 0.4 mM for **2**. ^{b}Real part of the third-order polarizability. ^{c}Imaginary part of the third-order polarizability. $^d|\gamma| = [\text{Re}(\gamma)^2 + \text{Im}(\gamma)^2]^{1/2}$.

errors due to irradiance uncertainties and data noise. In general, Z-scans to determine the nonlinearities of an active chromophore require rather high concentrations for reliable data. Since the solubility of **1** and **2** in toluene is too low for measurement, here we only focused on performing measurements in DCM solutions. Nonetheless, a much higher $|$Re(γ)/Im(γ)$|$ ratio can be anticipated for **1** in toluene, considering the mitigated ion-pairing effect as suggested by the linear optical properties. Figures S10 and S11 present their open aperture (OA) and closed aperture (CA) DA Z-scan signals in concentrated DCM solutions, where OA signals of **1** (Figure S10A) yield 2PA cross sections with no discernible dependence on pulse energy, indicating the absence of higher order nonlinear absorption. For **2**, however, we see a small saturation of the 2PA with higher irradiance (Figure S11A). Higher order nonlinear refraction appears to be present for both salts, as values of the Re(γ) measured from the lowest energy (Table 3)

Figure 3. Cyclic voltammograms of **1** and **2** versus Fc/Fc$^+$ (0.53 V) in diluted DCM solutions.

clearly underestimate the signals with higher energies. As suggested by theoretical calculations,[15,16] the electronic coupling between adjacent cyanine molecules can broaden the excited state spectrum, resulting in an enhancement of $\text{Im}(\gamma)$ and a sequential reduction of the $|\text{Re}(\gamma)/\text{Im}(\gamma)|$ ratio. However, it can be seen that both $\text{Re}(\gamma)$ and $\text{Im}(\gamma)$ values of **1** are quite similar to those of **2**, in spite of the former having demonstrated electronic coupling. This therefore suggests, to some degree, the different types and/or levels of electronic coupling in a preorganized zwitterionic system have less impact on the excited state properties

CONCLUSION

In summary, we demonstrated the first example of a heptamethine-based zwitterionic cyanine−cyanine salt by covalently linking the conjugation bridge of anionic TCF− and cationic indolium−heptamethines. By comparing with a closely related complementary cyanine salt, we have shown how such structural modification affects their electronic structure and photophysical and NLO properties, which will increase our fundamental understanding of the structural properties of highly polarizable cyanines. Our results demonstrate that rational mitigation of the ion-pairing-induced charge localization can be achieved in the zwitterionic structure, which also results in increased intramolecular electronic coupling between the excited states of the cationic and anionic cyanines.

ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b03037.

> Absorption, fluorescent, and lifetime spectra of **1** and **2**, electrochemical properties of **S4** and **S5**, third-order NLO characterization spectra of **1** and **2**, ^{1}H NMR and mass spectra of **1** and **2** (PDF)

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Notes
The authors declare no competing financial interest.

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