SUPPORTING INFORMATION

Polymethine dyes for all-optical switching applications:

A quantum-chemical characterization of counter-ion and aggregation effects

on the third-order nonlinear optical response

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Figure S1: A) Representative dimer configuration of the 5C cyanine-Cl⁻ complex with definition of the x-, y- and z-axes; d represents the distance between monomers (used in Figures S2, S4 and S5) and d_{p-p} , the plane-to-plane distance. B) Dimer binding energy with respect to translations along the y-axis (indicated in red) and z-axis (indicated in black) at the ω B97X-D/6-31G** level of theory.

For the binding energy calculations, 5C is used as the reference. The variations in binding energies for a pair of 5C cyanine-Cl⁻ complexes (that is, a pair of monomers) with respect to translations along the y- and z-axes are calculated at the ω B97X-D/6-31G** level of theory (Figure S1). The variations in binding energies with respect to translations along the z-axis are given at the ω B97X-D/aug-cc-pVDZ, ω B97X-D/cc-pVDZ and MP2/cc-pVDZ levels of theory in Figure S2.



Figure S2: Dimer binding energies with respect to translation along the z-axis at the ω B97X-D/6-31G**, ω B97X-D/cc-pVDZ, MP2/cc-pVDZ, and ω B97X-D/aug-cc-pVDZ levels.



Figure S3: Dimer configuration where the cyanine monomers are parallel to each other and are separated along the z-axis by 2.4 Å (plane-to-plane distance is about 4.2 Å).

Figures S1 and S2 show that calculations at the ω B97X-D/ cc-pVDZ level provide binding energies that are about 1 kcal/mol larger than that given by MP2/ cc-pVDZ. Furthermore, the calculations using aug-cc-pVDZ basis set provide the strongest binding energy, which is related to the presence of diffuse functions. The PES calculations (Figure S1) also indicate that the dimer configuration, when displaced along the z-direction, has a lower energy compared to the configurations where the individual monomers are displaced along the y-direction. In the minimum energy configuration, the cyanine molecules are separated along the z-axis by about 2.4 Å (in Figure S1, the variation in binding energies are plotted with respect to the minimum distance between the monomers, which is smaller than the plane-to-plane distances by ~ 1.8 Å due to the presence of the terminal bulky methyl substituents). The lower energies of the zdisplaced configurations are due to the π - π interactions between the two cyanines, which strongly decrease in the case of the y-displaced configurations. The minimum energy structure obtained under these conditions are depicted in Figure S3. Taking this minimum energy configuration as the initial structure, we further optimize the structure at the ω B97X-D/6-31G** and ω B97X-D/aug-cc-pVDZ levels, by displacing one monomer with respect to the other along the x- and y-axes, see Figure S4. The lowest energy configuration is obtained by displacing one of the monomer units along the x-direction.



Figure S4: Variation of binding energies of a pair of monomers with respect to the translation along x- (marked in black) and y-axis (marked in red) using ω B97X-D/6-31G** (marked with solid line), and ω B97X-D/aug-cc-pVDZ (marked in dotted line) methods.

Again taking the configuration in Figure S3 as the initial structure, we now optimize the structure by rotating one of the monomers around the z-axis. In addition, we perform this rotation as well starting from a "flipped" geometry (Figure S5), where the chloride ion of one of the monomers is

placed along the negative y-direction. The computed binding energies for these dimer configurations, using the ω B97X-D/6-31G** level of theory, are presented in Figure S5.

Figure S5: Variation in binding energies with respect to rotation about the z-axis, starting from the parallel configuration (marked in black solid line) and the parallel-flipped configuration (marked in red dashed line), using the ω B97X-D/6-31G** method.

Figure S5 shows that the flipped geometry is the lowest energy configuration. Furthermore, the rotations of the parallel and flipped structures provide for multiple minima that serve as initial

guesses for further geometry optimizations of the dimers. We performed a similar set of binding energy calculations to obtain the initial geometries of the 7C and 9C cyanine dimers.

S-2 SAC-CI Methodology

In the SAC-CI method, we define a symmetry-adapted excitation operator (S_i^+) that operates on the Hartree-Fock (HF) ground state $(\!|\Psi_g^{HF}\rangle\!)$, resulting in symmetry-adapted configurations. These symmetry-adapted configurations are the basis functions that span the Hilbert space for the ground and excited states. The symmetry adapted ground state $(\!|\Psi_g^{SAC}\rangle\!)$ can be expressed as,

$$\left|\Psi_{g}^{SAC}\right\rangle = \exp(S)\left|\Psi_{g}^{HF}\right\rangle \tag{S1}$$

where $S = \sum_{i} C_{i}S_{i}^{+}$. Thus, the SAC expansion involves as many variables (C_{i} 's) as required to describe a state with certain symmetry. Such symmetry constraints include both spatial and spin symmetries. The coefficients (C's) can be obtained variationally using a procedure similar to any configuration interaction method. Thus, the SAC-CI method incorporates doubles, triples and quadruples particle-hole excitations over the HF ground state and incorporates correlation effects on the ground and excited states at the same level. We recall that single CI methods cannot correctly predict the 2PA cross sections because of the absence of two particle-hole excitations over the HF ground state. The cluster expansion (Eq. S1) guarantees that the SAC-CI method is size consistent and can be used to accurately determine the ground and excited state electronic properties of cyanine dimers in various configurations. This is the primary advantage of the

SAC-CI method over the often used INDO/MRD-CI method, which is size inconsistent and thus cannot be used to compare the electronic properties of cyanine monomers with their corresponding dimers. In our calculations, we incorporate all single particle-hole excitations and only those double excitations whose second-order contributions to the energy are larger than 10^{-6} a.u. in the linear part of the excitation operators (linked terms). For the higher-order terms (unlinked terms), we only include those excitations whose coefficients in a particular state are larger than 10^{-7} a.u.

S-3 Structural Parameters of Cyanine Monomers

Figure S6: Molecular structures of (I) 5C and (II) 7C and (III) 9C cyanine molecules with chloride as a counterion. The x-axis is along the long axis of the cyanine molecules, the y-axis is

directed towards the chloride counterion, and the z-axis is perpendicular to the plane of the paper.

Table T1: Representative bond lengths of 5C, 7C, and 9C cyanine-Cl⁻ complexes (monomers) either isolated ($\varepsilon = 1$) or in a dielectric continuum ($\varepsilon = 37.5$, acetonitrile), as determined at the ω B97X-D/cc-pVDZ level. The atom labels are shown in Figure S6.

Atomic	5C-cyanine		7C-0	cyanine	9C-cyanine	
Index	Isolated	ACN	Isolated	ACN	Isolated	ACN
C ₁ -C ₂	1.402	1.399	1.411	1.400	1.414	1.394
C ₂ -C ₃	1.387	1.391	1.378	1.391	1.375	1.396
C ₃ -C ₄	1.406	1.399	1.419	1.401	1.423	1.396
C ₄ -C ₅	1.383	1.391	1.369	1.387	1.366	1.392
C ₅ -C ₆	-	-	1.423	1.403	1.429	1.401
C ₆ -C ₇	-	-	1.370	1.389	1.362	1.387
C ₇ -C ₈	-	-	-	-	1.430	1.403
C ₈ -C ₉	-	-	-	-	1.366	1.388
N ₁₀ -Cl ₁₂	4.218	4.285	3.973	4.367	3.932	5.720
N ₁₁ -Cl ₁₂	5.547	6.628	8.205	8.300	10.398	8.272

Table T2: Mean BLA (mBLA, Å) for the cyanines, with and without a chloride counterion, and minimum distance between the nitrogen and chloride counterion (Å) both for the isolated monomer (cyanine-Cl⁻ complex) and when considering an implicit dielectric medium as determined at the ω B97X-D/cc-pVDZ level of theory.

		In absence of Cl ⁻			
Cyanine	Isolated		Dielectric medium		Isolated
	mBLA	N-Cl distance	mBLA	N-Cl distance	mBLA
5C	0.009	4.218	0.008	4.285	0.001
7C	0.046	3.973	0.013	4.367	0.006
9C	0.058	3.932	0.019	4.347	0.010

Bond	5C	7C	9C				
C ₁ -C ₂	1.393	1.384	1.377				
C ₂ -C ₃	1.396	1.404	1.411				
C ₃ -C ₄	1.396	1.392	1.385				
C ₄ -C ₅	1.393	1.392	1.399				
C ₅ -C ₆	-	1.404	1.399				
C ₆ -C ₇	-	1.384	1.385				
C ₇ -C ₈	-	-	1.411				
C ₈ -C ₉	-	-	1.377				
	mBLA						
0.001 0.016 0.0							

Table T3: Representative monomer bond lengths (Å) determined with C_2 symmetry and $\epsilon = 1$ at the $\omega B97X$ -D/cc-pVDZ level of theory. The atomic indices are shown in Figure S6.

S-4 Structural Parameters of Cyanine Dimers

Figure S7: Optimized geometries of the 7C-dimer (I) perpendicular, (II) cofacial-x, (III) cofacial-z, and (IV) parallel-displaced configurations, as determined at the ω B97X-D/cc-pVDZ level. Carbon is grey, hydrogen white, nitrogen blue, and chloride green.

Figure S8: Optimized geometries of the 9C-dimer (i) perpendicular, (II) cofacial-x, (III) cofacial-z, and (IV) parallel-displaced configurations, as determined at the ω B97X-D/cc-pVDZ level. Carbon is grey, hydrogen white, nitrogen blue, and chloride green.

Figure S9: Atom labels for the 5C cyanine-Cl⁻ dimer.

Units	Bond	Perpendicular	Cofacial-x	Cofacial-z	Parallel-displaced
II.'. 1	C_1 - C_2	1.415	1.417	1.389	1.396
	C ₂ -C ₃	1.371	1.366	1.401	1.394
	C ₃ -C ₄	1.419	1.427	1.391	1.395
Unit I	C ₄ -C ₅	1.370	1.365	1.390	1.394
	N ₁₀ -Cl ₁₂	4.466	3.883	4.138	4.041
	N ₁₁ -Cl ₁₂	5.533	7.124	6.048	6.419
	C ₃₆ -C ₃₇	1.399	1.404	1.389	1.396
	C ₃₇ -C ₃₈	1.389	1.376	1.401	1.394
Linit O	C ₃₈ -C ₃₉	1.400	1.415	1.391	1.395
Unit 2	C ₃₉ -C ₄₀	1.390	1.371	1.390	1.394
	N ₄₅ -Cl ₄₇	3.830	4.135	4.138	4.041
	N ₄₆ -Cl ₄₇	7.440	6.166	6.048	6.419

Table T4: Representative bond lengths (Å) of 5C dimers in four optimized configurations obtained at the ω B97X-D/cc-pVDZ level of theory. The atom labels are given in Figure S9.

Table T5: Representative bond lengths (Å) of 7C dimers in four optimized configurations obtained at ω B97X-D/cc-pVDZ level of theory.

Units	Bond	Perpendicular	Cofacial-x	Cofacial-z	Parallel-displaced
	C_1-C_2	1.396	1.419	1.398	1.398
	C ₂ -C ₃	1.391	1.365	1.389	1.391
	C ₃ -C ₄	1.398	1.431	1.402	1.400
Unit 1	C_4-C_5	1.384	1.359	1.381	1.387
	C_5-C_6	1.404	1.435	1.406	1.400
	C_6-C_7	1.381	1.361	1.378	1.391
	N_{10} - Cl_{12}	3.899	3.850	3.844	3.985
	N_{11} - Cl_{12}	8.896	9.405	9.336	8.575
	$C_{36}-C_{37}$	1.396	1.419	1.398	1.398
-	C_{37} - C_{38}	1.391	1.365	1.389	1.391
	$C_{38}-C_{39}$	1.398	1.431	1.402	1.400
Unit 2	C_{39} - C_{40}	1.384	1.359	1.381	1.387
	C_{40} - C_{41}	1.404	1.435	1.406	1.400
	C_{41} - C_{42}	1.381	1.361	1.378	1.391
	$\overline{N_{45}}$ - Cl_{47}	3.899	3.850	3.844	3.983
	$\overline{N_{46}-Cl_{47}}$	8.896	9.403	9.336	8.591

Table T6: Representative bond lengths (Å) of 9C dimers in four optimized configurations obtained at the ω B97X-D/cc-pVDZ level of theory.

Units	Bond	Perpendicular	Cofacial-x	Cofacial-z	Parallel-displaced
	C_1 - C_2	1.396	1.425	1.401	1.421
	C_2-C_3	1.393	1.364	1.387	1.364
	C_3-C_4	1.397	1.432	1.404	1.432
	C_4-C_5	1.386	1.357	1.381	1.359
Unit 1	C_5-C_6	1.402	1.438	1.409	1.436
Unit I	C_6-C_7	1.384	1.355	1.376	1.359
	C ₇ -C ₈	1.406	1.439	1.412	1.435
	C_8-C_9	1.380	1.360	1.372	1.362
	N_{10} - Cl_{12}	3.918	4.059	3.841	3.901
	N_{11} - Cl_{12}	10.840	11.007	11.563	10.761
-	$C_{36}-C_{37}$	1.396	1.422	1.401	1.421
	C_{37} - C_{38}	1.393	1.363	1.387	1.364
	C ₃₈ -C ₃₉	1.397	1.432	1.404	1.432
	C_{39} - C_{40}	1.386	1.357	1.381	1.359
Unit 2	C_{40} - C_{41}	1.402	1.436	1.409	1.436
Unit 2	C_{41} - C_{42}	1.384	1.356	1.376	1.359
	C_{42} - C_{43}	1.406	1.438	1.412	1.435
	C_{43} - C_{44}	1.380	1.359	1.372	1.362
	$\overline{N_{45}}$ - Cl_{47}	3.918	3.877	3.841	3.901
	N46-Cl47	10.840	11.769	11.563	10.761

Table T7: mBLA (Å) obtained for the 5C, 7C, and 9C molecules in the dimer configurations.

	Optimized Geometry							
	Ι	II	III	IV				
	(perpendicular)	(cofacial-x)	(cofacial-z)	(parallel-displaced)				
5C	0.029	0.048	0.008	0.001				
7C	0.014	0.068	0.019	0.010				
9C	0.014	0.076	0.027	0.072				

Figure S10: Frontier molecular orbitals of the 5C, 7C, and 9C monomers with $\epsilon = 1$ as determined at the ω B97X-D/cc-pVDZ level.

Figure S11: Frontier molecular orbitals of the 5C, 7C, and 9C monomers with $\varepsilon = 37.5$ as determined at the ω B97X-D/cc-pVDZ level.

Figure S12: Frontier molecular orbitals of the 5C, 7C, and 9C monomers with $\varepsilon = 1$ as determined at the HF/cc-pVDZ level of theory.

Figure S13: Frontier molecular orbitals of 5C, 7C, and 9C monomers with $\varepsilon = 37.5$ obtained at HF/cc-pVDZ level.

Table T8: Frontier orbital energies (eV) as determined at the HF/cc-pVDZ and ω B97X-D/cc-pVDZ levels.

Cuanina	HF/cc-pVDZ			ωB97X-D/cc-pVDZ			
Cyannie	HOMO-1*	HOMO	LUMO	HOMO-3	HOMO*	LUMO	
5C	-7.90	-7.89	1.81	-7.59	-6.52	-0.21	
7C	-7.80	-7.49	1.22	-7.20	-6.48	-0.65	
9C	-7.81	-7.15	0.89	-6.94	-6.50	-0.94	

*For the HF/cc-pVDZ calculations, the HOMO-1 wave functions are primarily localized on the Cl⁻ counterion, whereas for the ω B97X-D/cc-pVDZ calculations the HOMO wave functions are Cl⁻ localized.

The highest-occupied (HOMO) and lowest-unoccupied (LUMO) molecular orbitals for the isolated 5C monomer (cyanine dye plus counterion) as determined at the HF/cc-pVDZ level are presented in Figure S12. The 5C HOMO is delocalized over the cyanine chain and the chloride ion, while the HOMO-1 and HOMO-2 wave functions are principally localized on the chloride

counterion (with negligible overlap on the cyanine molecule). The LUMO, on the other hand, is distributed solely on the cyanine molecules and its nature is similar to that of the individual cyanine molecule without the counterion. These results indicate significant electronic mixing between the cyanine upper occupied MOs and the chloride lone pair orbitals. Such a mixing is related to the closely spaced frontier orbital energies of these two systems. The frontier molecular orbitals of 7C and 9C are also depicted in Figure S12. Similar to 5C, the HOMO of 7C is delocalized over both the chloride and cyanine units. On the contrary, the HOMO of 9C is localized on the cyanine chain because of a larger difference in orbital energies between the chloride p-orbitals and cyanine π -orbitals. The LUMOs in 7C and 9C are found solely only on the cyanine chain.

A considerably different outcome in the nature of frontier orbitals is observed in the presence of a dielectric continuum ($\epsilon = 37.5$). Both the HOMO and LUMO are primarily localized on the cyanine chain, with the HOMO resembling the HOMO of isolated cyanines without the chloride counterion; the LUMOs in both structures are the same. In the dielectric medium, the chloride orbitals become energetically stabilized as the positive poles of the dielectric orient towards the localized, negatively-charged chloride ion.

Table T9 collects the SAC-CI results for the cyanine molecules kept in their optimal geometry with the chloride counter-ions.

Table T9: SAC-CI vertical excitation energy (E_{ge}), oscillator strength (f_{ge}), excited-state transition moment ($\mu_{ee'}$, Debye), difference in state dipole moment ($\Delta\mu$, Debye), and two-photon cross section (δ_{2P}) of the monomers (based on the optimized geometries in the presence of chloride counterions).

Cyanine	Ege	11 (Δu	δαρ
Chain	(f_{ge})	pree	Δμ	02P
	2.97 (1.13)	-	0.79	0.6
5C	5.84 (0.02)	5.25	1.38	18.1×10^4
	5.97 (0.00)	0.20	5.16	7.1×10^3
	2.14 (1.22)	-	3.52	37.3
7C	4.66 (0.06)	6.84	4.88	22.3×10^{3}
	4.99 (0.04)	3.52	4.68	1.9×10^{3}
	1.77 (1.31)	-	6.74	1.8×10^2
9C	4.05 (0.14)	8.13	9.11	16.3×10^{3}
	4.42 (0.08)	4.33	7.77	1.9×10^{3}

S-6 Frontier Molecular Orbitals of Cyanine Dimers

Figure S15: Frontier molecular orbitals of 7C-cyanine dimers in the (I) perpendicular, (II) cofacial-x, (III) cofacial-z, and (IV) parallel-displaced configurations, as determined at the HF/cc-pVDZ level.

Figure S16: Frontier molecular orbitals of 9C-cyanine dimers in the (I) perpendicular, (II) cofacial-x, (III) cofacial-z, and (IV) parallel-displaced configurations as determined at the HF/cc-pVDZ level

Figure S14 depicts select frontier molecular orbitals of the 5C aggregate dimers in the four optimized configurations. The HOMO for the perpendicular configuration is primarily localized on one cyanine chain, while the HOMO-1 is localized on the other cyanine moiety; the energetic splitting between the HOMO and HOMO-1 is 0.15 eV. This small splitting reveals that the interchain interaction is weaker in the perpendicular configuration versus the cofacial configurations, where the HOMO-HOMO-1 splitting varies between 0.25 eV - 0.30 eV. Similar to the perpendicular configurations, the splitting between the HOMO and HOMO-1 is small (~0.1 eV) in the parallel-displaced configuration, due to the relative displacement of the two cyanine chains along the *x*-axis. The dimer LUMOs are delocalized over both cyanine chains, revealing strong overlap between the two chains. This is not the case for perpendicular configuration, however, as the LUMO and LUMO+1 orbital are localized on individual cyanine units. For 7C and 9C, the characteristics of the frontier orbitals closely match those of the 5C dimer.

S-7 Parallel-displaced Configurations of the 5C and 7C Dimers

Table T10 lists the vertical excitation energies and oscillator strengths of the parallel-displaced structures for both the 5C and 7C dimers, which were optimized at the ω B97X-D/cc-pVDZ level. In order to understand the effect of geometry on the excitation energies, we omit the chloride ions from the calculations of excited states. In the optimized geometry, the center-to-center (c-c) distance is 6.31 Å and 6.40 Å, respectively, and the slip angles are 39° and 37° for the 5C and 7C dimers, respectively. The (SAC-CI) first excited state of the optimized parallel-displaced structure (for both 5C and 7C) is optically forbidden, whereas the second excited state is optically allowed, indicating that the structure corresponds to an H-type aggregate.

Table T10: Vertical excitation energies (E_{ge} , eV) and oscillator strengths (f_{ge}) of cyanine dimers without the chloride counterions calculated using the SAC-CI method with the cc-pVDZ basis set.

Cyanine	Optimized- Parallel-displaced
Dimer	E_{ge} (f_{ge})
5C	2.95 (0.00)
	3.01 (2.28)
7C	2.20 (0.00)
	2.34 (2.65)

S-8 Symmetric Configurations of Cyanine Monomers

Table T11: Vertical excitation energy (E_{ge} , eV), oscillator strength (f_{ge}), excited state transition moment ($\mu_{ee'}$), difference in state dipole moment ($\Delta\mu$), two-photon cross section (δ_{2P}), and third-order polarizability ($\gamma(\omega; \omega, -\omega, \omega)$) of the symmetric cyanine molecules. Geometry optimizations were performed using the ω B97X-D/cc-pVDZ method with the chloride counterion present but with the geometry constrained to C₂ symmetry.

	E _{ge} (f _{ge})	μ_{ee}	Δμ	δ_{2P}	γ_{stat} (esu×10 ³³)	γ_{1550}^{dyn} (esu×10 ³³)	γ_{1300}^{dyn} (esu×10 ³³)
5C	3.52 (1.17) 6.61 (0.00) 6.74 (0.05)	- 0.46 3.57	0.94 0.21 0.38	$0.53 \\ 88.6 \\ 1.1 \times 10^4$	-0.19	-0.23	-0.24
7C	2.77 (1.40) 5.34 (0.00) 5.70 (0.06)	- 2.63 3.64	0.97 0.86 0.59	$0.86 \\ 1.3 \times 10^4 \\ 5.2 \times 10^4$	-0.87	-1.2	-1.3
9C	2.42 (1.62) 4.51 (0.03) 5.06 (0.11)	- 6.09 3.92	0.68 1.15 0.26	$0.56 \\ 2.6{\times}10^4 \\ 3.0{\times}10^4$	-2.1	-3.1	-3.7