Electronic Supplementary Information

Atomistic simulation studies of ionic cyanine dyes: self-assembly and aggregate formation in aqueous solution

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Table 1: Optimised Ryckaert-Bellemans coefficients, C_n (kJ mol^{-1}), obtained from fitting to DFT data for PIC.

Dihedral	C_0	C_1	C_2	C_3	C_4	C_5
ϕ	42.00000	-26.00000	-74.00000	16.00000	57.00000	-11.00000

Table 2: Optimised Ryckaert-Bellemans coefficients, C_n (kJ mol^{-1}), obtained from fitting to DFT data for PCYN.

Dihedral	C_0	C_1	C_2	C_3	C_4	C_5
ϕ_1	58.00000	16.00000	-116.00000	-21.00000	74.00000	21.00000
ϕ_2	88.00000	28.00000	-158.00000	-60.00000	82.00000	23.00000

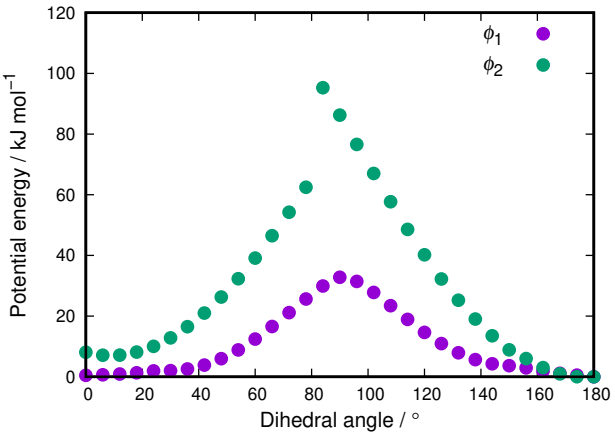

Figure 1: Calculated dihedral potentials (DFT, B3LYP/6-31+G*) for TTBC.

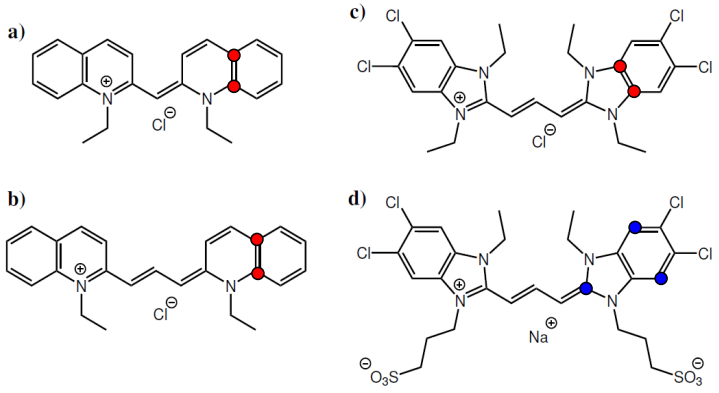

Figure 2: Atoms used to define the vector (red) and the plane (blue) for analysis of the aggregates for (a) PIC, (b) PCYN, (c) TTBC and (d) BIC.

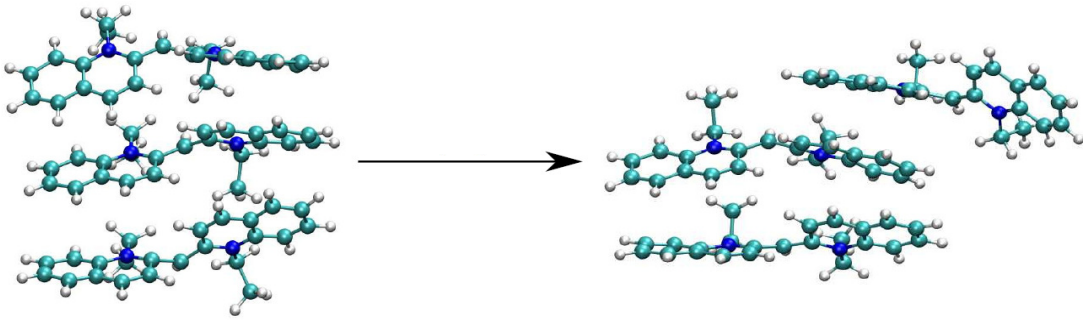

Figure 3: Snapshots of trimer structures along the reaction coordinate for PIC. Tetramer structures are identical where an additional molecule is present in the stack.

Table 3: Atomic charges obtained by the CHELPG method for PIC.

Atom	Charge	Atom	Charge
C	0.406421	C12	0.431797
C1	-0.175063	N1	-0.321220
C2	-0.110457	C13	0.241331
C3	0.085208	C14	0.090561
C4	0.248879	C15	-0.090746
N	-0.315935	C16	-0.204636
C5	-0.213924	H11	0.112617
C6	-0.053032	H12	0.254901
C7	-0.063033	C17	0.232796
C8	-0.154096	H13	-0.012589
H	0.154937	C18	-0.030561
H1	0.115214	H14	0.003643
H2	0.116736	H15	-0.003272
H3	0.125131	H16	0.011856
H4	0.109734	H17	0.037411
H5	0.147987	H18	0.139614
C9	0.240836	C19	-0.183815
H6	0.006068	C20	-0.214720
C10	-0.067320	C21	-0.033501
H7	-0.015132	H19	0.132365
H8	0.022332	C22	-0.056758
H9	0.010087	H20	0.154884
H10	0.046111	H21	0.111670
C11	-0.576261	H22	0.104943

Table 4: Atomic charges obtained by the CHELPG method for PCYN.

Atom	Charge	Atom	Charge
C	-0.064556	C14	0.376907
C1	-0.028564	C15	-0.244071
C2	-0.161221	N1	-0.275841
C3	0.055492	C16	-0.062166
C4	0.255572	C17	0.053702
C5	-0.244007	C18	0.258436
C6	-0.064506	C19	-0.160877
C7	-0.240908	C20	-0.064786
C8	0.374592	C21	-0.028482
N	-0.271749	C22	-0.244595
C9	0.168669	C23	0.170746
C10	-0.107179	C24	-0.106432
H	0.112704	H11	0.178015
H1	0.106351	H12	0.088207
H2	0.131636	H13	0.175042
H3	0.162467	H14	0.148085
H4	0.128518	H15	0.128144
H5	0.147484	H16	0.131598
H6	0.014912	H17	0.112766
H7	0.021882	H18	0.106399
H8	0.035487	H19	0.162540
H9	0.028888	H20	0.014810
H10	0.056610	H21	0.021314
C11	-0.365182	H22	0.035024
C12	0.048526	H23	0.028948
C13	-0.361720	H24	0.056369

Table 5: Atomic charges obtained by the CHELPG method for TTBC.

Atom	Charge	Atom	Charge
C	0.058872	H11	0.056588
C1	-0.157108	H12	0.054750
C2	0.090726	N2	-0.323413
C3	0.204938	N3	-0.243968
C4	-0.219045	C15	0.090633
C5	0.093157	C16	0.204977
CL	-0.061145	C17	0.216069
H	0.140494	C18	0.275597
H1	0.153738	C19	-0.078444
CL1	-0.062598	H13	-0.019097
N	-0.243900	H14	0.022861
N1	-0.323515	H15	0.016363
C6	0.422504	H16	0.030875
C7	0.215884	C20	-0.157073
H2	-0.009895	C21	-0.219096
C8	-0.124416	C22	0.058825
C9	0.275791	C23	0.093251
C10	-0.078355	H17	0.140490
H3	0.022798	CL2	-0.061137
H4	-0.019154	H18	0.153751
H5	0.030856	CL3	-0.062642
H6	0.016352	H19	0.022542
C11	-0.476898	H20	0.042349
C12	0.137129	H21	0.042400
C13	-0.476894	C24	-0.124347
C14	0.422501	H22	-0.009995
H7	0.202191	H23	0.030340
H8	0.145142	H24	0.056538
H9	0.202205	H25	0.054716
H10	0.030370	H26	0.022572

Table 6: Atomic charges obtained by the CHELPG method for BIC.

Atom	Charge	Atom	Charge
C	0.067397	H12	0.009304
C1	-0.181154	H13	0.091486
C2	0.151632	H14	0.031045
C3	0.155981	N2	-0.304602
C4	-0.195142	N3	-0.326748
C5	0.066943	C16	0.127943
CL	-0.105440	C17	0.193224
H	0.149297	C18	0.360675
H1	0.152082	H15	0.005199
CL1	-0.107032	H16	-0.032853
N	-0.307166	C19	-0.180015
N1	-0.302551	H17	0.007264
C6	0.463820	H18	0.005199
C7	0.296191	C20	0.125904
H2	0.018913	C21	0.227289
C8	-0.178705	C22	-0.282220
C9	0.143862	S1	1.065557
C10	0.185190	O3	-0.650114
C11	-0.324051	O4	-0.611391
S	1.065534	O5	-0.624066
O	-0.618861	H19	0.011372
O1	-0.654074	H20	0.028908
O2	-0.612995	H21	-0.029283
H3	0.022031	H22	-0.064671
H4	0.014689	H23	0.066456
H5	-0.007247	H24	0.068285
H6	-0.038304	C23	-0.171408
H7	0.078357	C24	-0.223350
H8	0.081887	C25	0.052632
C12	-0.494158	C26	0.082514
C13	0.376963	H25	0.152482
C14	-0.509125	CL2	-0.102736
C15	0.462581	H26	0.158037
H9	0.174693	CL3	-0.109103
H10	0.017539	H27	0.071267
H11	0.177585	H28	0.083356