Supporting Information

The photoprocesses effects of amino group located at different positions along the polymethine chain in indodicarbocyanine dyes

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Table S1 The calculated bond lengths (Å), bond angles (°) and dihedral angles (°) of Cy3 aminocyanine dyes calculated by Gaussian 09 software based on DFT and TDDFT//B3LYP/6-31G(d,p) basis set.

Dyes		Atomic Number	Ground State	Excited State
Cy3-NH_2-1	Bond Length (Å)	N1- H1	1.016	1.009
		N1- H2	1.012	1.011
		N1- C1	1.418	1.346
	Bond angle (°)	H1-N1-C1	113.627	120.133
		H2-N1-C1	113.390	123.213
		H1-N1-H2	109.670	116.655
	dihedral angle (torsional angle) (°)	H1-N1-C1-C2	71.034	-2.490
		H2-N1-C1-C3	16.016	-0.887
Cy3-NH_2-2	Bond Length (Å)	N1- H1	1.004	1.008
		N1- H2	1.006	1.012
		N1- C1	1.346	1.384
	Bond angle (°)	H1-N1-C1	121.980	116.614
		H2-N1-C1	120.216	114.323
		H1-N1-H2	116.482	110.830
	dihedral angle (torsional angle) (°)	H1-N1-C1-C2	-4.759	15.410
		H2-N1-C1-C3	-18.016	-35.895

Table S2 The calculated bond lengths (Å), bond angles (°) and dihedral angles (°) Cy7 aminocyanine dyes calculated by Gaussian 09 software based on DFT and TDDFT//B3LYP/6-31G(d,p) basis set.

Dyes		Atomic Number	Ground State	Excited State
Cy7-NH_2-1	Bond Length (Å)	N1- H1	1.016	1.012
		N1- H2	1.012	1.009
		N1- C1	1.418	1.387
	Bond angle (°)	H1-N1-C1	113.250	117.776
		H2-N1-C1	112.981	117.149
		H1-N1-H2	109.252	113.610
	dihedral angle (torsional angle) (°)	H1-N1-C1-C2	66.759	42.824
		H2-N1-C1-C3	10.286	2.773
Cy7-NH_2-2	Bond Length (Å)	N1- H1	1.004	1.007
		N1- H2	1.007	1.011
		N1- C1	1.350	1.380
	Bond angle (°)	H1-N1-C1	121.874	117.298
		H2-N1-C1	120.562	115.792
		H1-N1-H2	115.573	111.587
	dihedral angle (torsional angle) (°)	H1-N1-C1-C2	-10.157	-22.657
		H2-N1-C1-C3	7.673	25.608
Cy7-NH_2-3	Bond Length (Å)	N1- H1	1.013	1.009
		N1- H2	1.012	1.009
		N1- C1	1.401	1.373
	Bond angle (°)	H1-N1-C1	113.652	118.419
		H2-N1-C1	113.927	118.370
		H1-N1-H2	108.908	113.197
	dihedral angle (torsional angle) (°)	H1-N1-C1-C2	36.933	22.984
		H2-N1-C1-C3	-21.666	-16.169
Cy7-NH_2-4	Bond Length (Å)	N1- H1	1.006	1.011
		N1- H2	1.006	1.011
		N1- C1	1.349	1.385
	Bond angle (°)	H1-N1-C1	121.934	115.674
		H2-N1-C1	121.933	115.671
		H1-N1-H2	116.113	110.713
	dihedral angle (torsional angle) (°)	H1-N1-C1-C2	-0.835	-25.847
		H2-N1-C1-C3	0.979	25.911

Table S3 The calculated bond lengths (Å), bond angles (°) and dihedral angles (°) of Cy9 aminocyanine dyes calculated by Gaussian 09 software based on DFT and TDDFT//B3LYP/6-31G(d,p) basis set.

Dyes		Atomic Number	Ground State	Excited State
Cy9-NH_2-1	Bond Length (Å)	N1- H1	1.016	1.012
		N1- H2	1.012	1.010
		N1- C1	1.418	1.392
	Bond angle (°)	H1-N1-C1	113.283	116.812
		H2-N1-C1	113.008	116.290
		H1-N1-H2	109.274	112.680
	dihedral angle (torsional angle) (°)	H1-N1-C1-C2	66.180	46.400
		H2-N1-C1-C3	9.710	1.993
Cy9-NH_2-2	Bond Length (Å)	N1- H1	1.004	1.007
		N1- H2	1.007	1.011
		N1- C1	1.349	1.377
	Bond angle (°)	H1-N1-C1	121.980	117.674
		H2-N1-C1	120.871	116.300
		H1-N1-H2	115.896	111.964
	dihedral angle (torsional angle) (°)	H1-N1-C1-C2	-11.807	-22.467
		H2-N1-C1-C3	2.214	23.811
Cy9-NH_2-3	Bond Length (Å)	N1- H1	1.013	1.010
		N1- H2	1.012	1.009
		N1- C1	1.400	1.375
	Bond angle (°)	H1-N1-C1	113.786	117.878
		H2-N1-C1	113.992	117.670
		H1-N1-H2	108.993	112.630
	dihedral angle (torsional angle) (°)	H1-N1-C1-C2	35.728	23.102
		H2-N1-C1-C3	-22.552	-19.295
Cy9-NH_2-4	Bond Length (Å)	N1- H1	1.007	1.011
		N1- H2	1.007	1.011
		N1- C1	1.350	1.384
	Bond angle (°)	H1-N1-C1	121.670	115.953
		H2-N1-C1	121.473	116.146
		H1-N1-H2	116.037	111.122
	dihedral angle (torsional angle) (°)	H1-N1-C1-C2	-10.231	-29.056
		H2-N1-C1-C3	1.324	21.065
Cy9-NH_2-5	Bond Length (Å)	N1- H1	1.012	1.009
		N1- H2	1.012	1.009
		N1- C1	1.399	1.372
	Bond angle (°)	H1-N1-C1	114.050	118.329
		H2-N1-C1	114.050	118.328
		H1-N1-H2	109.275	113.324
	dihedral angle (torsional angle) (°)	H1-N1-C1-C2	28.790	19.581
		H2-N1-C1-C3	-28.796	-19.593

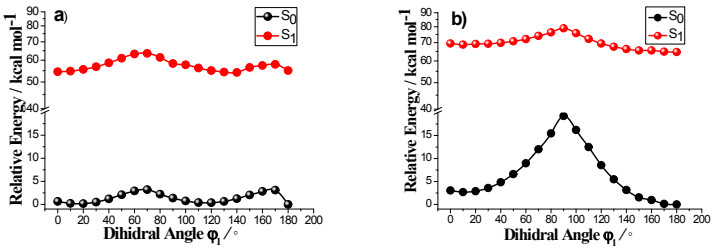

Fig. S1 Energy levels of the S_0 (black) and S_1 (red) states of Cy3-NH_2-1(a) and Cy3-NH_2-2(b) rotation around chemical bond (dihedral angle φ_1)calculated at the TD-DFT/B3LYP/6-31G(d,p) level with PCM salvation model.

Table S4 Energy barrier E_a and energy gap E_{gap} between the S_0 and S_1 states of Cy3-NH_2-1(a) and Cy3-NH_2-2(b) rotation around chemical bond C_1-N_1 (dihedral angle φ_1) in the S_0 and S_1 states.

	Cy3-NH_2-1	Cy3-NH_2-2
	φ_1	φ_1
E_a (kcal•mol^{-1})	2.95	7.30
E_{gap} (kcal•mol^{-1})	52.92	47.41

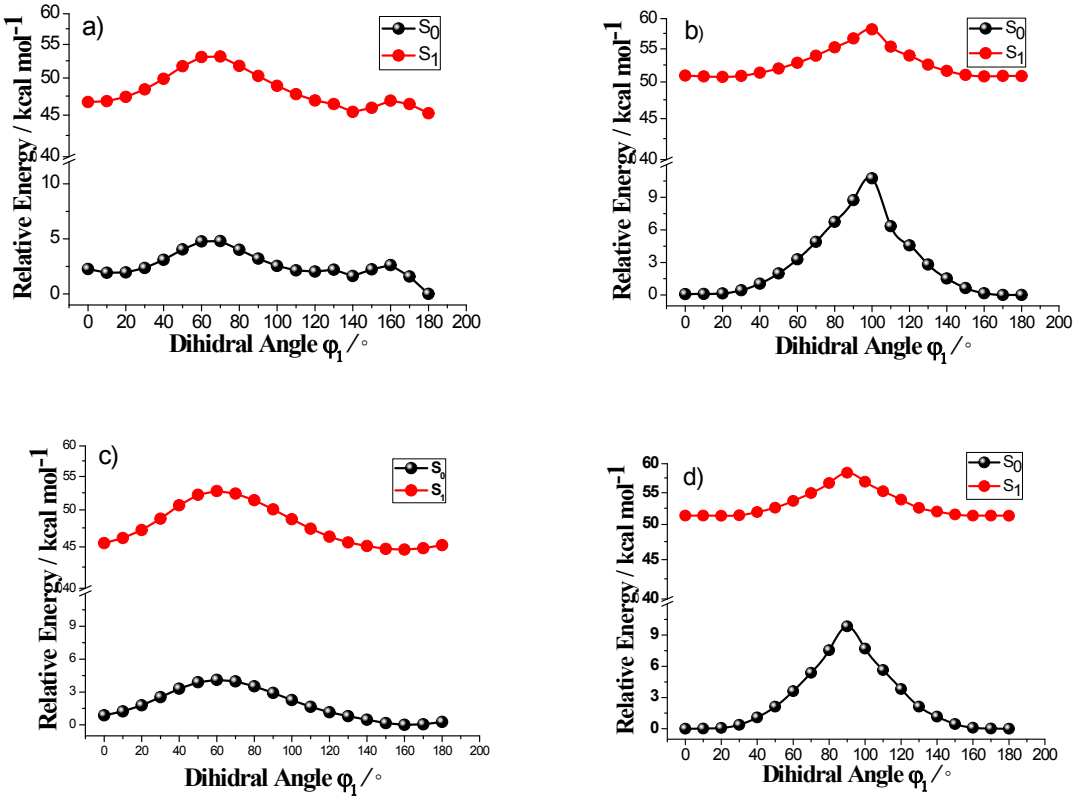

Fig. S2 Energy levels of the S_0 (black) and S_1 (red) states of Cy7-NH2-1(a), Cy7-NH2-2(b), Cy7-NH2-3(c) and Cy7-NH2-4(d) rotation around chemical bond (dihedral angle φ_1)calculated at the TD-DFT/B3LYP/6-31G(d,p) level with PCM salvation model.

Table **S5** Energy barrier E_a and energy gap E_{gap} between the S_0 and S_1 states of Cy7-NH_2-1, Cy7-NH_2-2, Cy7-NH_2-3 and Cy7-NH_2-4 rotation around chemical bond C_1-N_1 (dihedral angle φ_1) in the S_0 and S_1 states.

	Cy7-NH_2-1	Cy7-NH_2-2	Cy7-NH_2-3	Cy7-NH_2-4
	φ_1	φ_1	φ_1	φ_1
E_a (kcal•mol^{-1})	0.06	7.30	0.10	7.09
E_{gap} (kcal•mol^{-1})	43.71	47.41	49.52	48.57

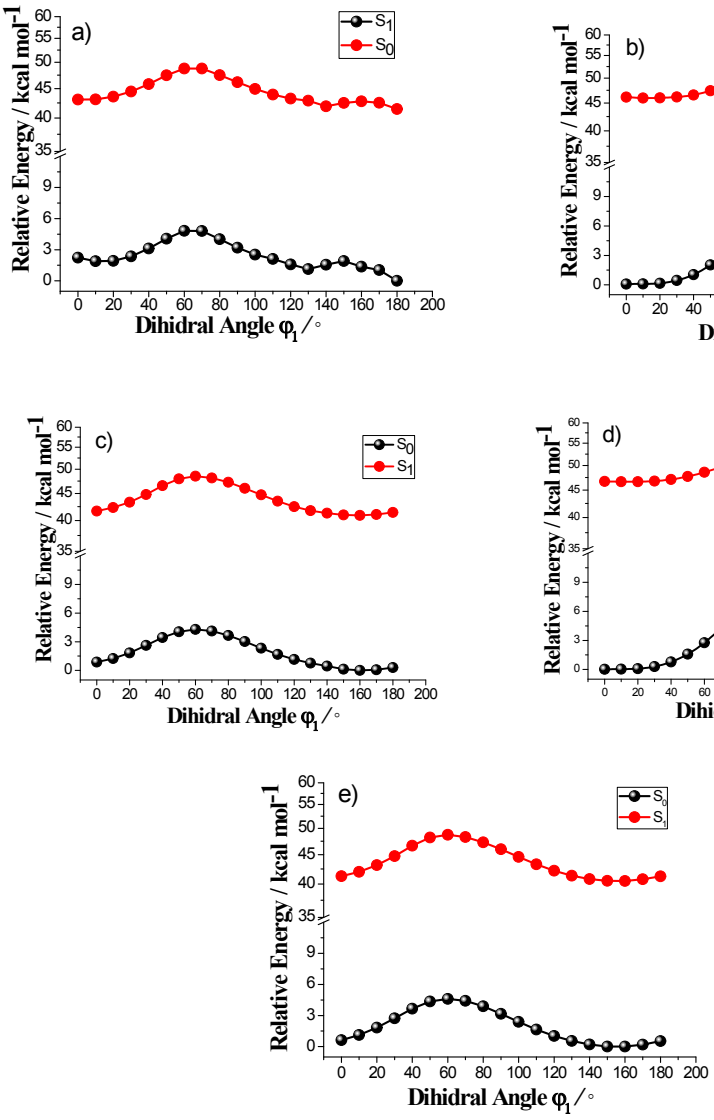

Fig. S3 Energy levels of the S_0 (black) and S_1 (red) states of Cy9-NH_2-1(a), Cy9-NH_2-2(b), Cy9-NH_2-3(c), Cy9-NH_2-4(d) and Cy9-NH_2-5(e) rotation around chemical bond (dihedral angle φ_1)calculated at the TD-DFT/B3LYP/6-31G(d,p) level with PCM salvation model.

Table S6 Energy barrier E_a and energy gap E_{gap} between the S_0 and S_1 states of Cy9-NH_2-1, Cy9-NH_2-2, Cy9-NH_2-3, Cy9-NH_2-4 and Cy9-NH_2-5 rotation around chemical bond C_1-N_1 (dihedral angle φ_1) in the S_0 and S_1 states.

	Cy9-NH_2-1	Cy9-NH_2-2	Cy5-NH_2-3	Cy5-NH_2-4	Cy5-NH_2-5
	φ_1	φ_1	φ_1	φ_1	φ_1
E_a (kcal•mol^{-1})	0.95	7.65	0.07	6.56	0.01
E_{gap} (kcal•mol^{-1})	40.36	46.06	40.85	43.84	40.50