Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

About the Origin of the Large Stokes Shift in Aminoalkyl Substituted Heptamethine Cyanine Dyes

Cristina Sissa[a *], Anna Painelli[a], Francesca Terenziani[a], M. Trotta[b], R. Ragni[c*]

[a] Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università di Parma, Parco Area delle Scienze 17/A, 43124, Parma, Italy

[b] CNR-IPCF, Institute for Physical and Chemical Processes, Bari unit, Via Orabona 4, 70125 Bari, Italy

[c] Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro", via Orabona 4, I-70126 Bari, Italy

1. Results obtained with different functionals

a. Functional: B3LYP

Molecule	Solvent	δ_1(°)	δ_2(°)	BLA_1 (Å)	BLA_2 (Å)	ℓ_4 (Å)	ℓ_5 (Å)
IR780 (GS)	DMSO	175	-175	0.014	0.014	1.412	1.412
HCY2 (GS)	DMSO	-169	-155	0.071	0.065	1.436	1.434
IR780 (1EX)	DMSO	175	-175	0.025	0.025	1.418	1.418
HCY2 (1EX)	DMSO	-175	-163	0.046	0.045	1.430	1.431

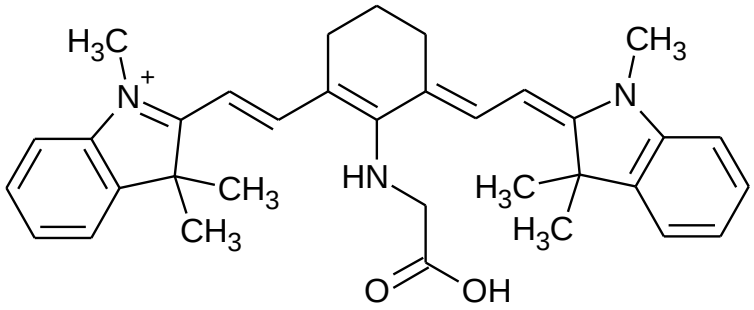
Table S1: Selected ground state (GS) and first excited state (1EX) properties of IR780 and HCy2 in DMSO. Dihedral angles, BLAs and bond lengths are defined in Figure 3 of the main text.

b. Functional: M062X

Molecule	Solvent	δ_1(°)	δ_2(°)	BLA_1 (Å)	BLA_2 (Å)	ℓ_4 (Å)	ℓ_5 (Å)
IR780 (GS)	DMSO	174	-174	0.012	0.012	1.407	1.407
HCY2 (GS)	DMSO	-163	-155	0.109	0.084	1.445	1.435
IR780 (1EX)	DMSO	174	-174	0.013	0.013	1.413	1.413
HCY2 (1EX)	DMSO	-174	-171	0.026	0.024	1.420	1.422

Table S2: Selected ground state (GS) and first excited state (1EX) properties of IR780 and HCy2 in DMSO. Dihedral angles, BLAs and bond lengths are defined in Figure 3 of the main text.

2. Results obtained on a modified HCy2 dye



Scheme S1: Molecular structure of the modified HCy2 dye with the carboxylic group

Molecule	Solvent	δ_1(°)	δ_2(°)	BLA_1 (Å)	BLA_2 (Å)	ℓ_4 (Å)	ℓ_5 (Å)
HCY2 (GS)	DMSO	-163	-154	0.100	0.070	1.440	1.429
HCY2 (1EX)	DMSO	-174	-169	0.023	0.022	1.419	1.422

Table S3: Selected ground state (GS) and first excited state (1EX) properties of IR780 and HCy2 in DMSO. Dihedral angles, BLAs and bond lengths are defined in Figure 3 of the main text.

Molecule	Solvent	Absorption [nm/eV]	Emission [nm/eV]	Stokes Shift [eV]
HCY2	DMSO	492/2.52 (H-L 0.68; H-1-> L+1 -0.15)	554/2.24 (H-L 0.69; H-1-> L+1 -0.13)	0.28

Table S4: Calculated spectroscopic properties

3. Calculation results in Toluene

Molecule	Solvent	δ_1(°)	δ_2(°)	BLA_1 (Å)	BLA_2 (Å)	ℓ_4 (Å)	ℓ_5 (Å)
IR780 (GS)	Toluene	173	-173	0.016	0.16	1.408	1.408
HCY2 (GS)	Toluene	-163	-154	0.103	0.080	1.442	1.433
IR780 (1EX)	Toluene	174	-174	0.016	0.016	1.414	1.414
HCY2 (1EX)	Toluene	-173	-168	0.032	0.029	1.421	1.423

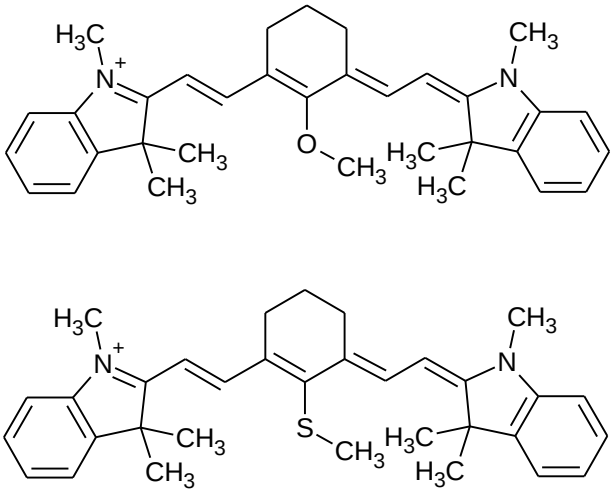
Table S5: Selected ground state (GS) and first excited state (1EX) properties of IR780 and HCy2 in Toluene.

Dihedral angles, BLAs and bond lengths are defined in Figure 3 of the main text.

Molecule	Solvent	Absorption [nm/eV]	Emission [nm/eV]	Stokes Shift [eV]
IR780	Toluene	554/2.24 (H-L 0.69; H-1-> L+1 -0.13)	569/2.18 (H-L 0.69; H-1-> L+1 0.13)	0.06
HCY2	Toluene	490/2.53 (H-L 0.68; H-1-> L+1 -0.16)	514/2.26	0.27

Table S6: Calculated spectroscopic properties

4. Computational results on modified molecular structures with -OCH_3 and -SCH_3 substituents in the central position



Scheme S2: Molecular structure of the modified dye with the -OCH_3 and -SCH_3 substituents.

Ground state optimization was performed in gas phase at the DFT level, using the ωB97xD functional and the 6-31g(d) basis set. Results are reported in Figure S1. The bond lengths of the C-O and C-S bonds are 1.368Å and 1.802Å, respectively (the C carbon belongs to the polymethine chain).

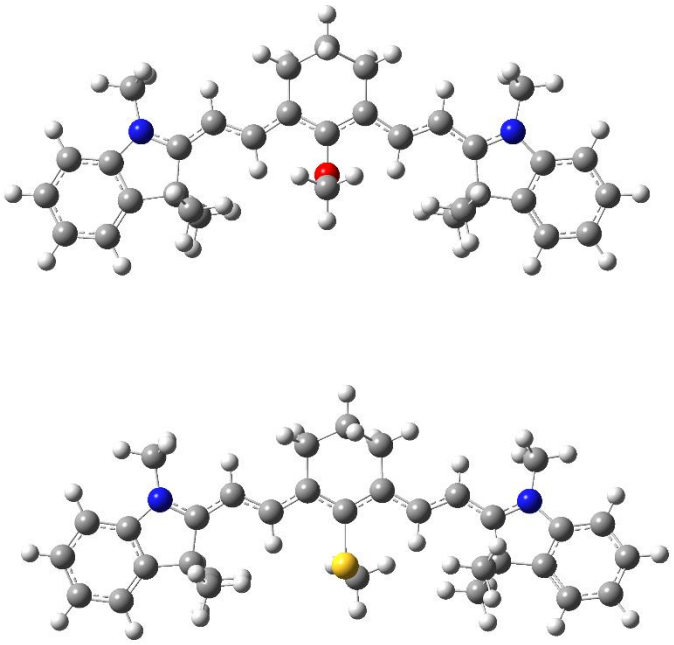


Figure S1: Ground state optimized geometries.