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

Supplementary information of Disaggregation-induced fluorescence enhancement of NIAD-4 upon interacting with amyloid-β fibrils

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Figures

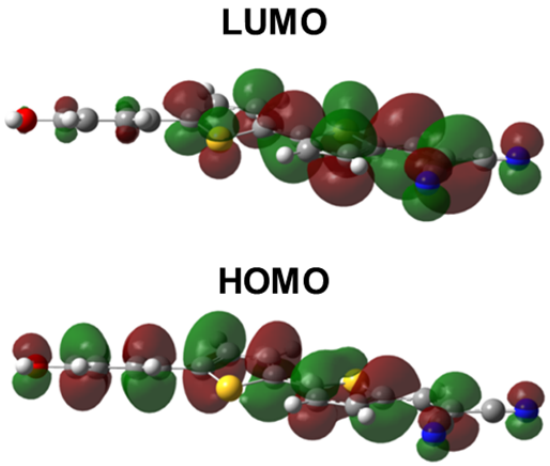

Figure S1. Molecular orbitals of NIAD-4 involved in the excitation responsible for fluoresce emission (HOMO and LUMO).

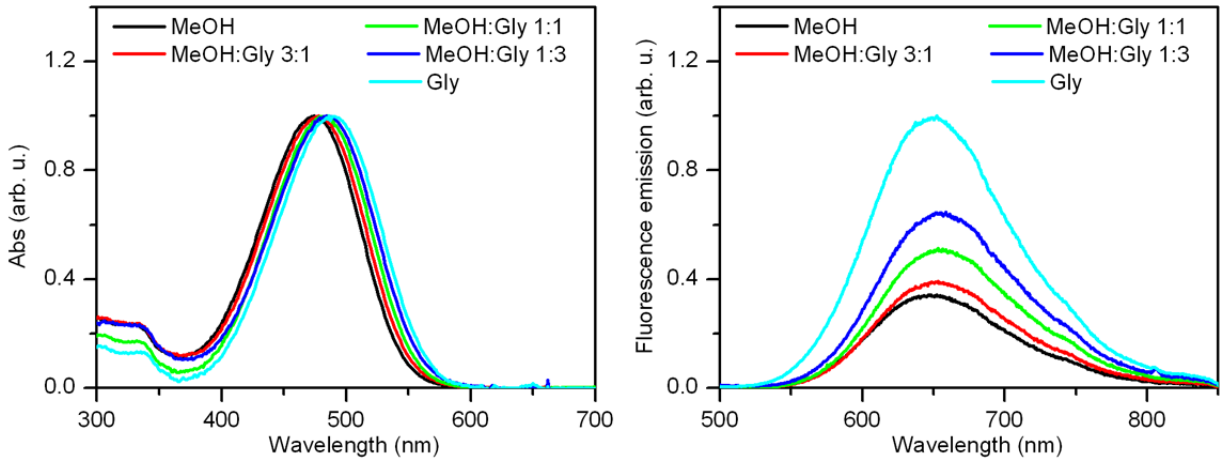

Figure S2. Absorption and fluorescence emission spectra of NIAD-4 in mixtures of MeOH and glycerol of increasing viscosity (c_{NIAD-4} = 5 µM). All absorption spectra are normalized to their absorption maximum. Each fluorescence spectrum is normalized by the absorption at the excitation wavelength.

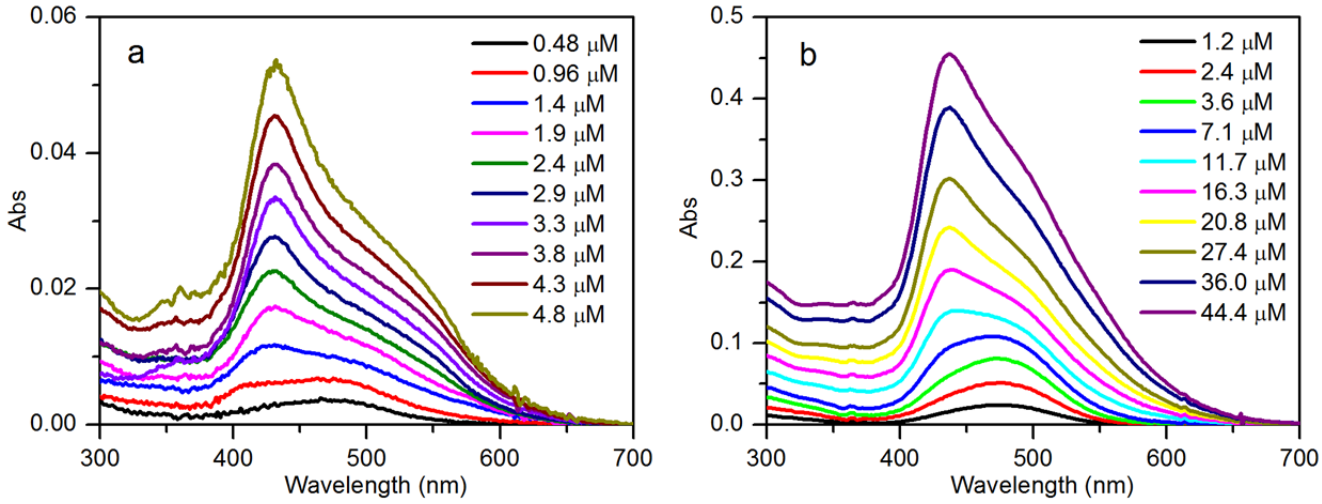

Figure S3. Concentration dependence of the absorption spectrum of NIAD-4 in (a) H_2O and (b) H_2O:MeOH 2:1.

Tables

Table S1. Excitation wavelengths (nm) corresponding to the first singlet excited state of the dye NIAD-4 calculated with different functionals and basis sets in gas phase and in aqueous solution (non-equilibrium LR-PCM).[a] Experimental value: 475 nm.[b]

Method	6-31+G(d,p) gas phase	6-31+G(d,p) aq. sol.	6-311+G(2d,p) gas phase	6-311+G(2d,p) aq. sol.
PBE	586	651	583	647
PBE0	470	516	469	515
LC-PBE	344	365	345	367
B3LYP	493	543	490	540
CAM-B3LYP	405	438	404	438
BLYP	591	655	587	650
BHandH	408	442	409	442
M06	476	521	472	516
M06-L	550	606	545	599
M06-2X	406	436	406	439

[a] Values corresponding to the excitation of the optimized geometry. [b] The experimental value refers to low concentration solutions, where the dye is predominantly in its monomeric form.

Table S2. State Specific (SS) correction to computed absorption and emission wavelengths (nm) of the most stable isomer A considering equilibrium (EQ) and non-equilibrium solvation regime (NEQ).

		water	methanol	dichlormethane	diethylether
Absorption[a]	LR NEQ	439	438	440	435
	SS NEQ	447	446	449	443
Emission[b]	LR EQ	625	620	598	572
	SS NEQ	554	553	534	535

[a] Computed at the optimized S_0 geometry.
[b] Computed at the optimized S_1 geometry.

Table S3. S_1 and T_2 energies at the S_1 optimized geometry (isomer **A**).

	TD	TDA	CAS(12,12)	CASPT2	MS-CASPT2
S_1	2.43	2.64	2.91	2.49	2.57
T_2	2.05	2.34	2.57	2.79	2.99

Table S4. Gas phase CASSCF and MS-CASPT2 relative energies (eV) of singlet and triplet states of four geometries having different values of dihedral Φ_2. The first singlet is the ground state.

Φ_2=0˚				Φ_2=20˚			
CAS singlets	**CAS triplets**	**MS-CASPT2 singlets**	**MS-CASPT2 triplets**	**CAS singlets**	**CAS triplets**	**MS-CASPT2 singlets**	**MS-CASPT2 triplets**
0.00	1.24	0.00	1.81	0.00	1.33	0.00	1.88
2.91	2.57	2.57	2.99	3.01	2.55	2.68	2.97
3.66	3.79	3.41	4.12	3.73	3.79	3.43	4.13
4.25	3.97	3.67	4.50	4.33	4.01	3.65	4.53
4.91	4.37	4.55	4.72	4.97	4.35	4.61	4.68
5.27	4.88	4.79	5.27	5.32	4.89	4.85	5.31
5.43		5.16		5.46		5.14	
5.66		5.42		5.67		5.46	
5.85		5.85		5.87		5.86	
6.28		6.03		6.29		6.05	
6.48		6.31		6.52		6.29	
6.54		6.65		6.56		6.67	
Φ_2=30˚				Φ_2=40˚			
CAS singlets	**CAS triplets**	**MS-CASPT2 singlets**	**MS-CASPT2 triplets**	**CAS singlets**	**CAS triplets**	**MS-CASPT2 singlets**	**MS-CASPT2 triplets**
0.00	1.33	0.00	1.88	0.00	0.99	0.00	2.05
3.01	2.55	2.68	2.97	3.26	1.92	2.61	2.88
3.73	3.79	3.43	4.13	3.75	3.22	3.50	4.09
4.33	4.01	3.65	4.53	4.77	3.53	3.85	4.54
4.97	4.35	4.61	4.68	5.24	3.72	4.43	4.61
5.32	4.89	4.85	5.31	5.59	4.34	4.86	5.37
5.46		5.14		5.71		5.10	
5.67		5.46		5.90		5.21	
5.87		5.86		6.03		5.52	
6.29		6.05		6.13		5.95	
6.52		6.29		6.23		6.31	
6.56		6.67		6.65		6.49	

Table S5. Dependence of the optical properties of NIAD-4 with solvent viscosity in mixtures of methanol and glycerol.

Solvent	Viscosity (cP)[a]	ε	$\lambda_{max, abs}$ (nm)	$\lambda_{max, fl}$ (nm)	Φ_{fl}
MeOH	0.59	31.0	474	646	0.14
MeOH:Gly 3:1	4.0	33.9	478	653	0.16
MeOH:Gly 1:1	28	36.2	484	653	0.21
MeOH:Gly 1:3	170	38.0	485	653	0.27
Gly	1182	39.4	486	652	0.427

[a] Levitt, J. A.; Kuimova, M. K.; Yahioglu, G.; Chung, P.-H.; Suhling, K.; Phillips, D. *J. Phys. Chem. C* **2009**, *113*, 11634