SUPPLEMENTARY INFORMATION

Graphene Oxide Promotes Aggregation-Induced Emission in Binary Solvents Mixtures

Souvik Pandit, Sanyukta Bhattacharjee, Debabrata Seth*

Department of Chemistry, Indian Institute of Technology Patna, Patna 801103, Bihar, India, E-mail: debabrata@iitp.ac.in; Phone: +91-6115-233028

Contents.

S1. Absorption Spectral Studies on Interaction of NaFlu with GO in ACN, DMF, DMSO and THF:

In ACN, the absorption peak of NaFlu is generated at 510 nm i.e. w.r.t water, the dianion form of NaFlu is experiences a red shift by 23 nm. On gradual addition of GO, till 4 μg/mL of GO, the peak position remains the same followed by a decrease in the absorption intensity. In neat DMF, the absorption maximum is observed at 524 nm i.e. a red shift by 37 nm w.r.t to water followed by decrease in intensity value. In case of DMSO, the absorption peak of NaFlu is generated at 521 nm i.e a red shift by 34 nm. On addition of GO, the absorption intensity decreases but the peak position remains the same. In case of neat THF, no absorption peak of NaFlu was observed. For emission studies we have chosen two excitation wavelengths. We have excited samples at 405 nm to monitor the lower absorbing species if present in the system, and another is the wavelength corresponding to the absorption maxima in the respective solvents. In case of ACN for both the excitation wavelengths (405 nm and 510 nm) the emission maxima is generated at 530 nm. For DMF, the emission peak is generated at 545 nm. Similarly, for DMSO, exciting at both 405 nm and 520 nm the emission peak is generated at 535 nm. No emission studies could be performed in case of THF. On gradual addition of GO for all the solvents, the intensity is quenched with no change in the emission maxima position. Due to the presence of various oxygen functional groups present in GO surface which interacts with NaFlu via hydrogen bonding and pi-pi stacking results in quenching of fluorescence signal drastically.

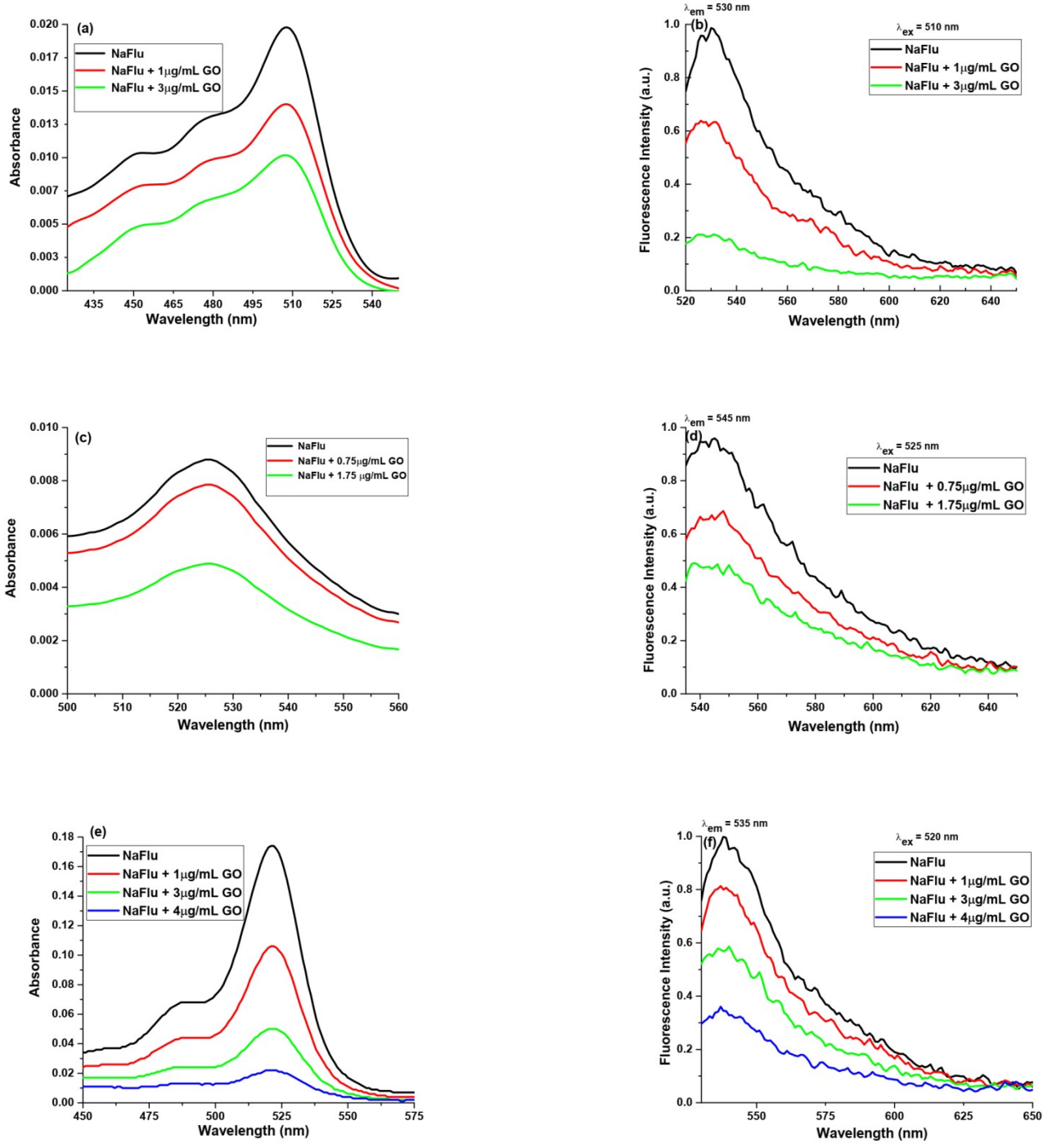

Figure S1 Absorption spectral profile of NaFlu with addition of GO in (a) ACN, (c) DMF and (e) DMSO. Fluorescence emission spectra of NaFlu with addition of GO in (b) ACN (λ_{ex} = 510 nm), (d) DMF (λ_{ex} = 525 nm) and (f) DMSO (λ_{ex} = 520 nm).

S2. Fluorescence Emission Studies on Interaction of NaFlu with GO in Water-Solvents Binary Mixtures.

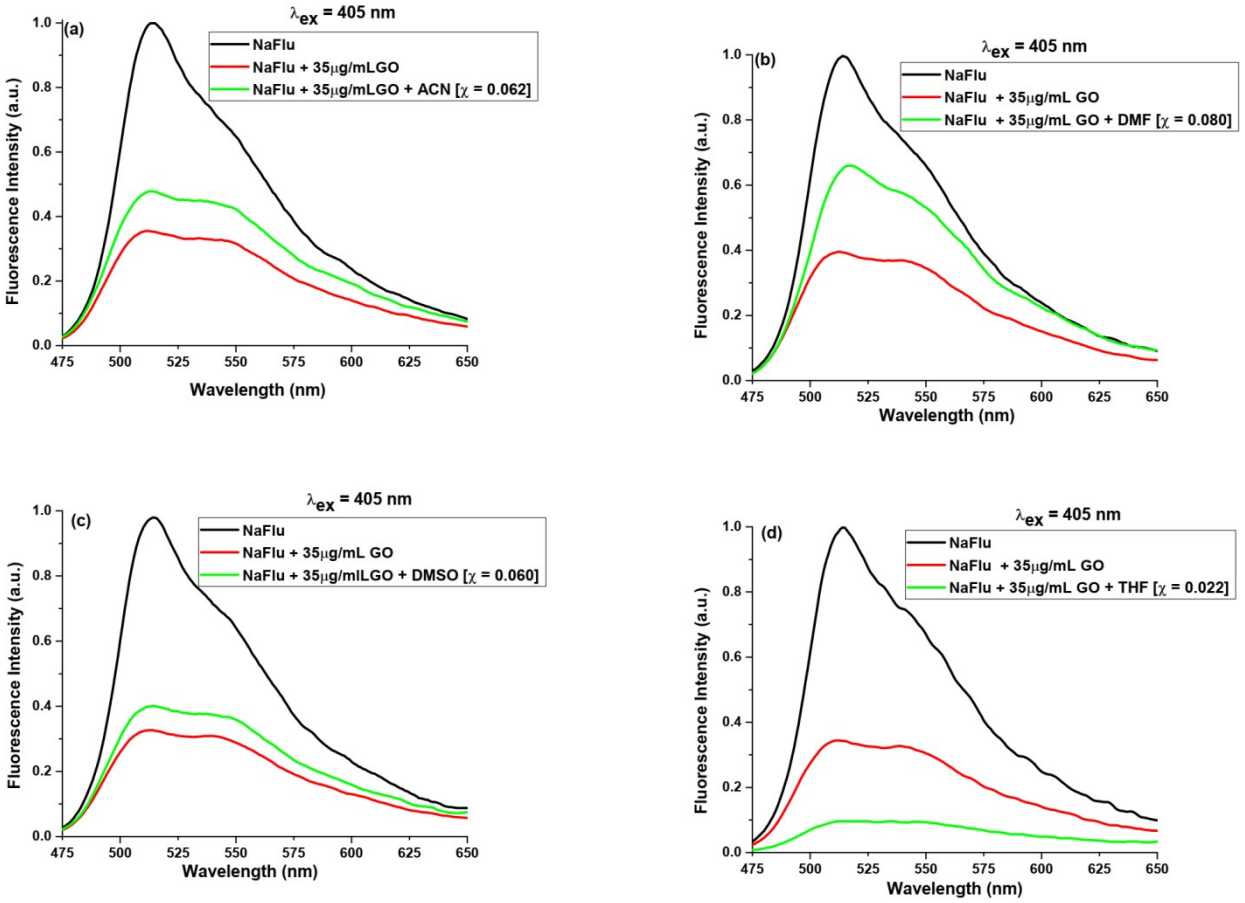

Figure S2 (a) Fluorescence emission spectra of NaFlu in presence of GO in (a) water-ACN binary mixture (λ_{ex} = 405 nm). (b) Fluorescence emission spectra of NaFlu in presence of GO in water-DMF binary mixture (λ_{ex} = 405 nm). (c) Fluorescence emission spectra of NaFlu in presence of GO in water-DMSO binary mixture (λ_{ex} = 405 nm). (d) Fluorescence emission spectra of NaFlu in presence of GO in water-THF binary mixture (λ_{ex} = 405 nm).

S3. Steady-State Absorption and Fluorescence Emission Studies on Interaction of NaFlu in Water-Binary Mixtures.

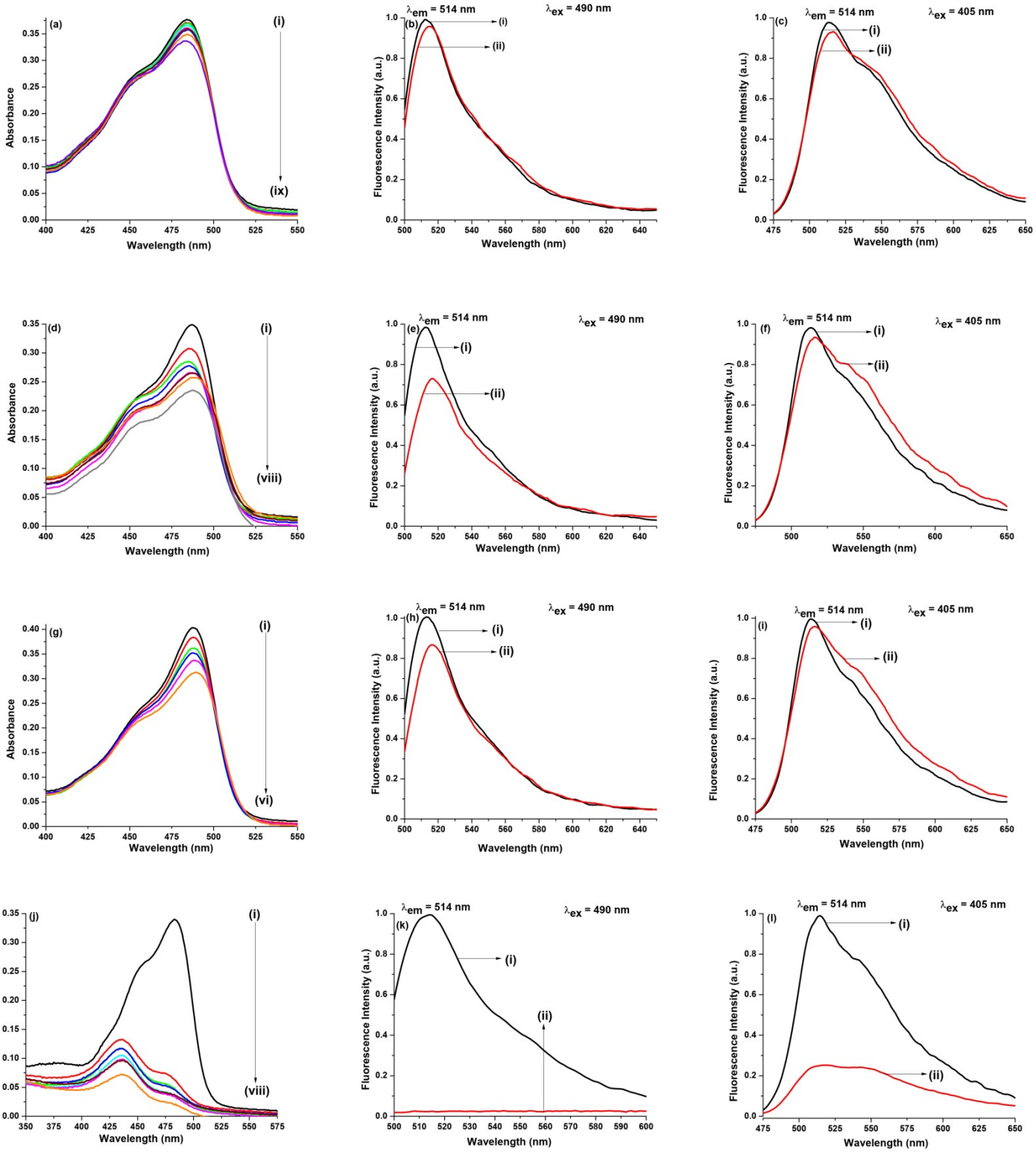

Figure S3 (a) Absorption spectral profile of NaFlu water-ACN mixture: (i) NaFlu, (ii) NaFlu + ACN [χ = 0.004], (iii) NaFlu + ACN [χ = 0.007], (iv) NaFlu + ACN [χ = 0.013], (v) NaFlu + ACN [χ = 0.018], (vi) NaFlu + ACN [χ = 0.024], (vii) NaFlu + ACN [χ = 0.034], (viii) NaFlu + ACN [χ = 0.046] and (ix) NaFlu + ACN [χ = 0.062], and fluorescence emission spectra (b) λ_{ex} = 490 nm and (c) λ_{ex} = 405 nm of NaFlu in water-ACN mixture: (i) NaFlu and (ii) NaFlu + ACN [χ = 0.062]. (d) Absorption spectral profile of NaFlu water-DMF mixture: (i) NaFlu (ii) NaFlu + DMF [χ = 0.003], (iii) NaFlu + DMF [χ = 0.009], (iv) NaFlu + DMF [χ = 0.015], (v) NaFlu + DMF [χ = 0.035], (vi) NaFlu + DMF [χ = 0.050], (vii) NaFlu + DMF [χ = 0.065], (viii) NaFlu + DMF [χ = 0.080] and fluorescence emission spectra (e) λ_{ex} = 490 nm and (f) λ_{ex} = 405 nm of NaFlu in water-DMF mixture: (i) NaFlu and (ii) NaFlu + DMF [χ = 0.080]. (g) Absorption spectral profile of NaFlu water-DMSO mixture: (i) NaFlu, (ii) NaFlu + DMSO [χ = 0.004], (iii) NaFlu + DMSO [χ = 0.010], (iv) NaFlu + DMSO [χ = 0.015], (v) NaFlu + DMSO [χ = 0.037] and (vi) NaFlu + DMSO [χ = 0.060] and fluorescence emission spectra (h) λex = 490 nm and (i) λex = 405 nm of NaFlu in water-DMSO mixture: (i) NaFlu and (ii) NaFlu + DMF [χ = 0.060]. (j) Absorption spectral profile of NaFlu water-THF mixture: (i) NaFlu, (ii) NaFlu + THF [χ = 0.002], (iii) NaFlu + THF [χ = 0.003], (iv) NaFlu + THF [χ = 0.005], (v) NaFlu + THF [χ = 0.008], (vi) NaFlu + THF [χ = 0.012], (vii) NaFlu + THF [χ = 0.016] and (viii) NaFlu + THF [χ = 0.022] and fluorescence emission spectra (h) λex = 490 nm and (i) λex = 405 nm of NaFlu in water-THF mixture: (i) NaFlu and (ii) NaFlu + THF [χ = 0.022]. where χ means mole fraction of co-solvents.

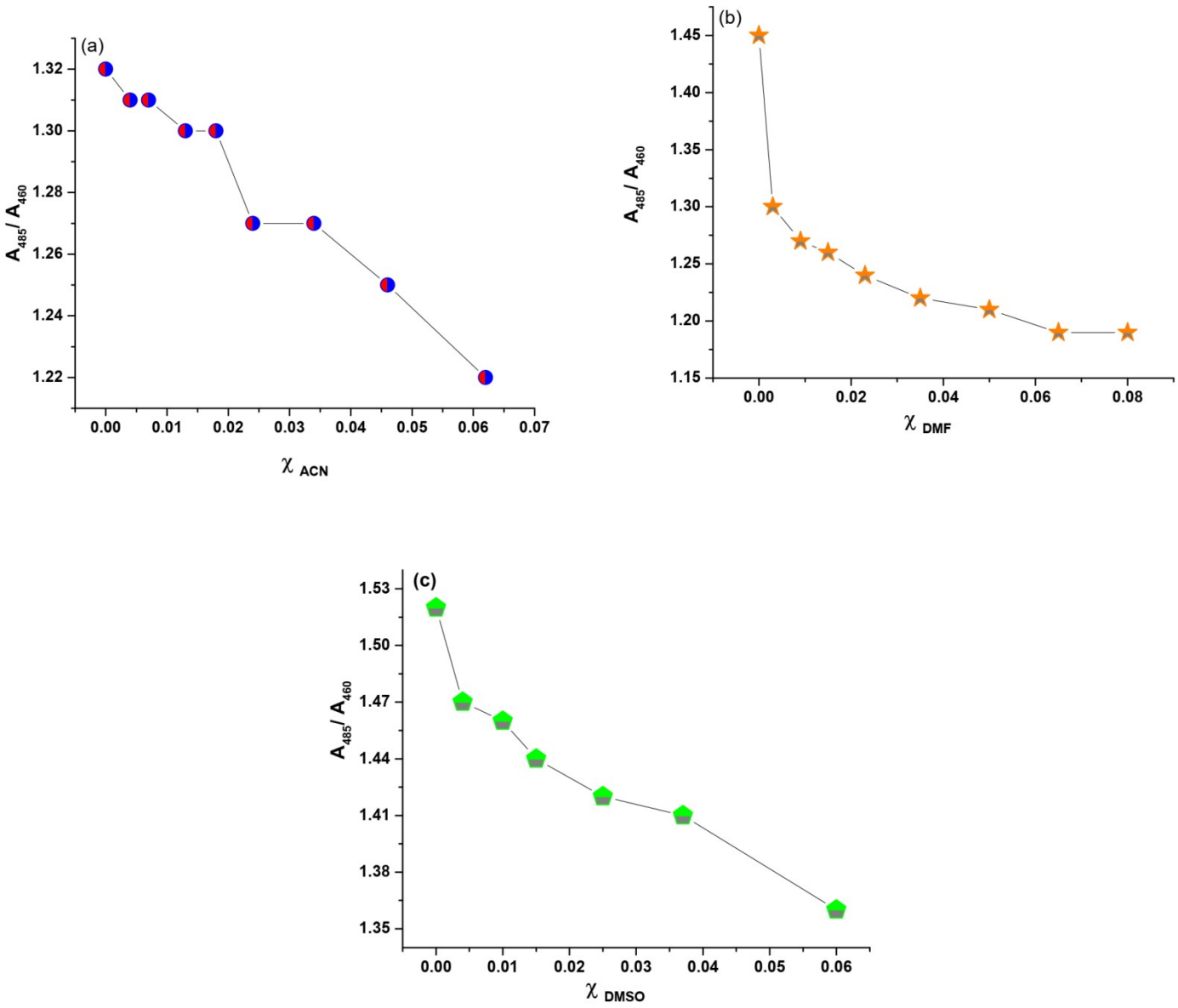

Figure S4 The plot of absorbance ratio $\frac{A_{485\,nm}}{A_{460\,nm}}$ vs mole fraction of polar aprotic solvents in absence of GO (a) ACN, (b) DMF and (c) DMSO.

Table S1 Absolute Quantum Yield **(ϕ_f)** of NaFlu in presence and absence of GO in water co-solvents binary mixtures.

S. No	Sample	ϕ_f
1.	NaFlu in water	0.92
2.	NaFlu in water + 35 µg/mL GO	0.34
3.	NaFlu in water + 35 µg/mL GO + ACN (χ_{ACN} = 0.062**)**	0.42
4.	NaFlu in water + ACN (χ_{ACN} = 0.062**)**	0.63
5.	NaFlu in water + 35 µg/mL GO + DMF (χ_{DMF} = 0.080**)**	0.70
6.	NaFlu in water + DMF (χ_{DMF} = 0.080**)**	0.60
7.	NaFlu in water + 35 µg/mL GO + DMSO (χ_{DMSO} = 0.060**)**	0.44
8.	NaFlu in water + DMSO (χ_{DMSO} = 0.060**)**	0.74
9.	NaFlu in water + 35 µg/mL GO + THF (χ_{THF} = 0.022**)**	0.08
10.	NaFlu in water + THF (χ_{THF} = 0.022**)**	0.05

S4. Excitation Spectra of NaFlu in Neat Solvents.

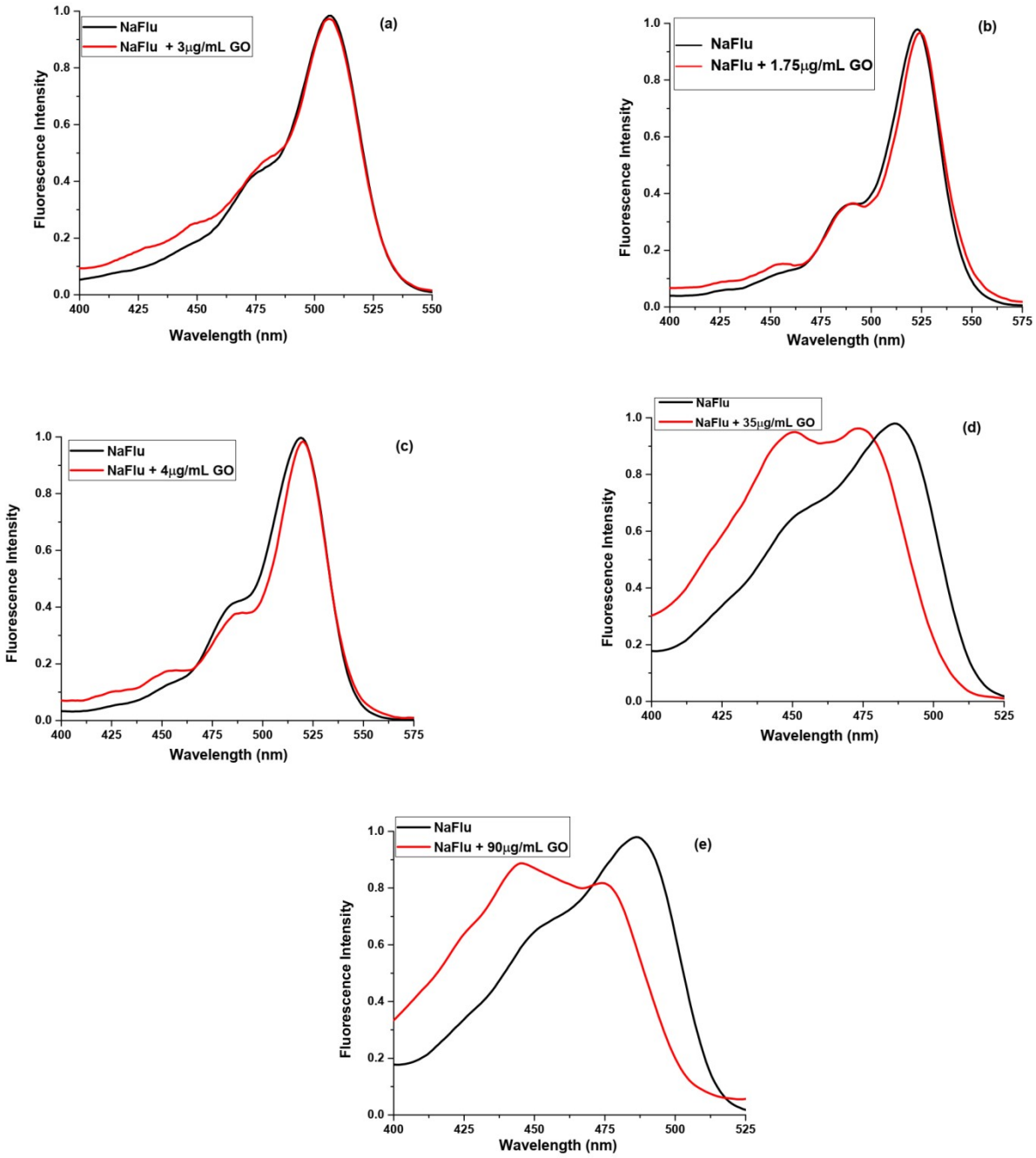

Figure S5 Normalized fluorescence excitation spectral profiles of NaFlu in the presence of GO in (a) ACN (b) DMF, (c) DMSO and (d) and (e) water.

S5. Excitation Spectral Studies of NaFlu in Presence and Absence of GO in Water co Solvents Binary Mixtures.

Existence of multiple emissive species of NaFlu in neat solvents, and binary mixtures involving water and polar aprotic solvents, in presence as well as in absence of GO was monitored by analysing the excitation spectra (Figure S6). We report the excitation spectra at the emission wavelength of λ_{em} = 600 nm. Normalized fluorescence excitation spectra of NaFlu in different systems were reported. The result obtained resonates with the result that was obtained in steady-state absorption measurements. In short, excitation spectral study justifies the formation of various emissive sates as well as conversion of various forms of NaF in water depending upon the choice of solvents as discussed previously in steady state section. The excitation spectra of NaFlu in water-binary mixtures both in the presence and absence of GO are represented below. The excitation spectra of NaFlu in neat water and polar aprotic solvents in presence of GO are provided in S4.

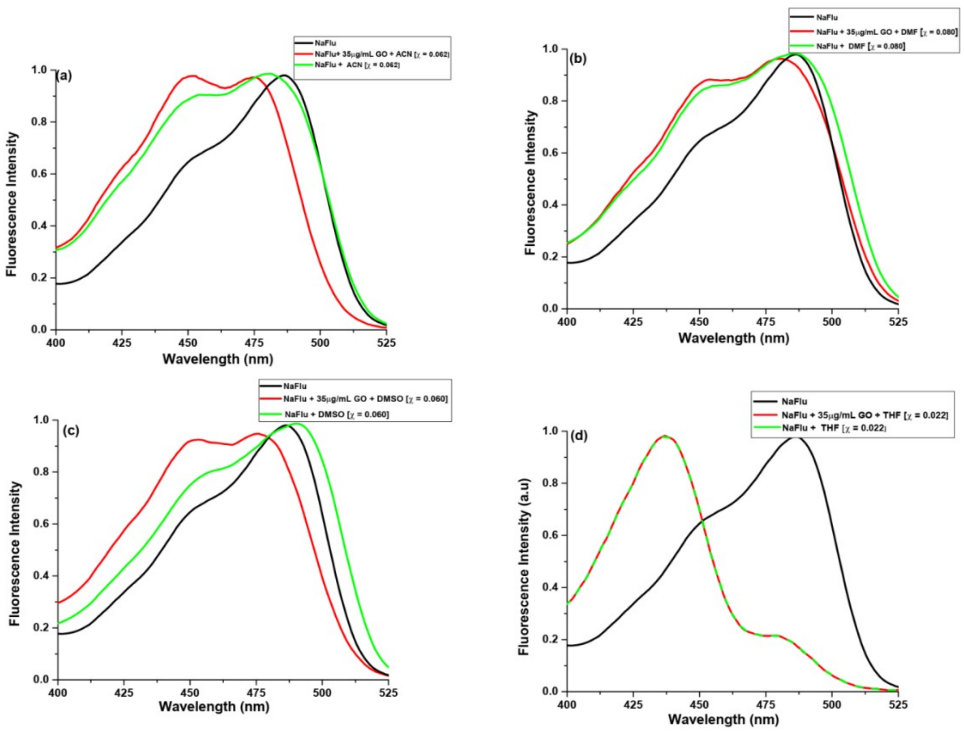

Figure S6 Normalized fluorescence excitation spectral profiles of NaFlu in presence and absence of GO in (a) water-ACN mixture, (b) water-DMF mixture, (c) water-DMSO mixture and (d) water-THF mixture.

S6. Time-Resolved Fluorescence Emission (TRFE) data of NaFlu in Polar Aprotic Solvents.

The time resolved emission decays of NaFlu was obtained by using an excitation source of 405 nm. The polar aprotic solvents used are ACN, DMF and DMSO. For solvents except DMF, the decays exhibit biexponential character i.e. there is both a short and long component. The lifetime values of NaFlu in neat ACN are 1.76 ns (49%) and 3.84 ns (51%) and for DMSO are 1.66 ns (12%) and 4.04 ns (88%). The average lifetime value of NaFlu in ACN and DMSO are 2.82 ns and 3.75 ns respectively. In presence of GO, the decay exhibits biexponential nature and the components for ACN are 1.87 ns (66%) and 3.70 ns (34%) and for DMSO are 1.93 ns (28%) and 3.86 (72%). The average lifetime values are 2.50 ns and 3.32 ns for ACN and DMSO respectively. In case of DMF, the decay showcases triexponential character both in the presence and absence of GO. In neat DMF, the components are 0.26 ns (22%), 2.08 ns (43%) and 4.28 ns (35%) with the average lifetime value being 2.45 ns, and in presence of GO the components are 0.37ns (31%), 2.46 ns (50%) and 5.13 ns (19%) with the average lifetime value being 2.32 ns. This decrease in the lifetime value and their corresponding changes in the relative contribution signify the interaction of NaFlu with the oxygen functional groups in the respective solvents. The data are represented in table S1.

Table S2 Fluorescence lifetime of NaFlu in absence/presence of GO in neat solvents.

S. No	Sample	τ_1 (ns)	a_1	τ_2 (ns)	a_2	τ_3 (ns)	a_3	$\langle\tau\rangle^{\#}$ (ns)	χ^2
1.	NaFlu in water	3.70	100%	-	-	-	-	3.70	1.134
2.	NaFlu in water +3 µg/mL GO	3.72	100%	-	-	-	-	3.72	1.179
3.	NaFlu in water + 15 µg/mL GO	3.54	100%	-	-	-	-	3.54	1.155
4.	NaFlu in water + 35 µg/mL GO	3.37	100%	-	-	-	-	3.37	1.174
5.	NaFlu in water + 60 µg/mL GO	3.34	100%	-	-	-	-	3.34	1.139
6.	NaFlu in water + 90 µg/mL GO	3.27	100%	-	-	-	-	3.27	1.166
7.	NaFlu in ACN	1.76	49%	3.84	51%	-	-	2.82	1.007
8.	NaFlu in ACN + 3 µg/mL GO	1.87	66%	3.70	34%	-	-	2.50	1.150
9.	NaFlu in DMF	0.26	22%	2.08	43%	4.28	35%	2.45	1.096
10.	NaFlu in DMF + 1.75 µg/mL GO	0.37	31%	2.46	50%	5.13	19%	2.32	1.144
11.	NaFlu in DMSO	1.66	12%	4.04	88%	-	-	3.75	1.102
12.	NaFlu in DMSO + 4 µg/mL GO	1.93	28%	3.86	72%	-	-	3.32	1.091

$^{\#}\langle\tau\rangle = a_1*\tau_1 + a_2*\tau_2 + a_3*\tau_3$

Table S3 Fluorescence lifetime of NaFlu in absence/presence of GO in water-cosolvents binary mixtures.

S. No	Sample	τ_1 (ns)	a_1	$\langle\tau\rangle^{\#}$ (ns)	χ^2
1.	NaFlu in water + 35 µg/mL GO + ACN (χ_{ACN} = 0.004)	3.42	100%	3.42	1.180
2.	NaFlu in water + 35 µg/mL GO + ACN (χ_{ACN} = 0.013)	3.48	100%	3.48	1.153
3.	NaFlu in water + 35 µg/mL GO + ACN (χ_{ACN} = 0.018)	3.51	100%	3.51	1.122
4.	NaFlu in water + 35 µg/mL GO + ACN (χ_{ACN} = 0.034)	3.60	100%	3.60	1.163
5.	NaFlu in water + 35 µg/mL GO + ACN (χ_{ACN} = 0.062)	3.75	100%	3.75	1.124
6.	NaFlu in water + ACN (χ_{ACN} = 0.062)	3.89	100%	3.89	1.111
7.	NaFlu in water + 35 µg/mL GO + DMF (χ_{DMF} = 0.009)	3.51	100%	3.51	1.181
8.	NaFlu in water + 35 µg/mL GO + DMF (χ_{DMF} = 0.015)	3.60	100%	3.60	1.164
9.	NaFlu in water + 35 µg/mL GO + DMF (χ_{DMF} = 0.023)	3.70	100%	3.70	1.117
10.	NaFlu in water + 35 µg/mL GO + DMF (χ_{DMF} = 0.050)	3.87	100%	3.87	1.120
11.	NaFlu in water + 35 µg/mL GO + DMF (χ_{DMF} = 0.080)	4.02	100%	4.02	1.178
12.	NaFlu in water + DMF (χ_{DMF} = 0.080)	4.03	100%	4.03	1.184
13.	NaFlu in water + 35 µg/mL GO + DMSO (χ_{DMSO} = 0.004)	3.37	100%	3.37	1.174
14.	NaFlu in water + 35 µg/mL GO + DMSO (χ_{DMSO} = 0.015)	3.46	100%	3.46	1.180
15.	NaFlu in water + 35 µg/mL GO + DMSO (χ_{DMSO} = 0.025)	3.51	100%	3.51	1.125
16.	NaFlu in water + 35 µg/mL GO + DMSO (χ_{DMSO} = 0.060)	3.66	100%	3.66	1.146
17.	NaFlu in water + DMSO (χ_{DMSO} = 0.060)	3.85	100%	3.85	1.186
18.	NaFlu in water + 35 µg/mL GO + THF (χ_{THF} = 0.002)	3.14	100%	3.14	1.180
19.	NaFlu in water + 35 µg/mL GO + THF (χ_{THF} = 0.005)	3.12	100%	3.12	1.198
20.	NaFlu in water + 35 µg/mL GO + THF (χ_{THF} = 0.012)	3.18	100%	3.18	1.200
21.	NaFlu in water + 35 µg/mL GO + THF (χ_{THF} = 0.022)	3.31	100%	3.31	1.190
22.	NaFlu in water + THF (χ_{THF} = 0.022)	3.56	100%	3.56	1.199

S7. Raman Spectral Study in Binary Mixtures in Absence of NaFlu.

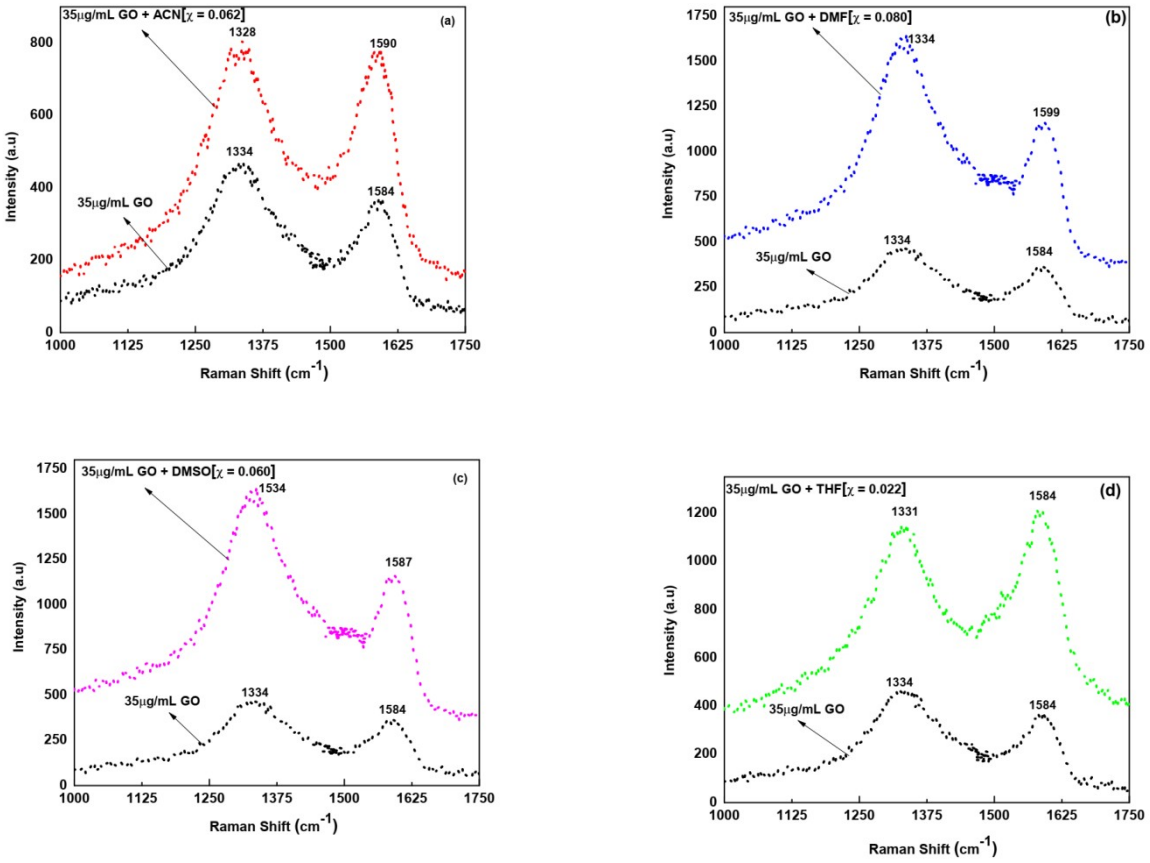

Figure S7 Raman spectra of GO in (a) water-ACN binary mixture, (c) water-DMF binary mixture, (d) water-DMSO binary mixture and (e) water-THF binary mixture.

S8. Field Emission Scanning Electron Microscopy Images (FE-SEM) of GO in Different Solvent Mixtures in Absence of NaFlu.

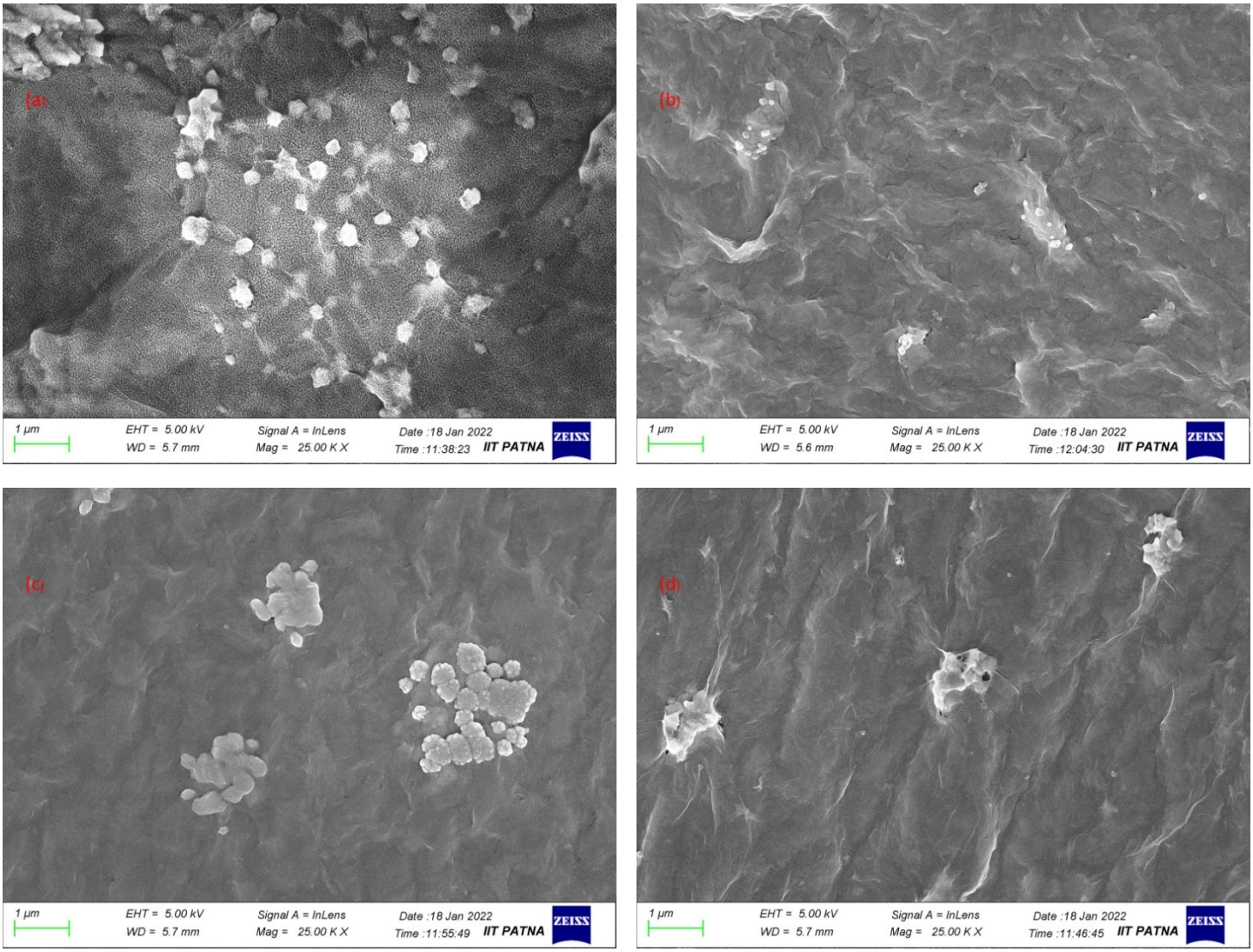

Figure S8. FE-SEM images of GO in absence of NaFlu (a) water-ACN ($\chi_{ACN} = 0.062$) binary mixture, (d) water-DMF ($\chi_{DMF} = 0.080$) binary mixture, (c) water-DMSO ($\chi_{DMSO} = 0.060$) binary mixture and (d) water-THF ($\chi_{THF} = 0.022$) binary mixture.

S9. Fluorescence Lifetime Imaging Microscopy (FLIM).

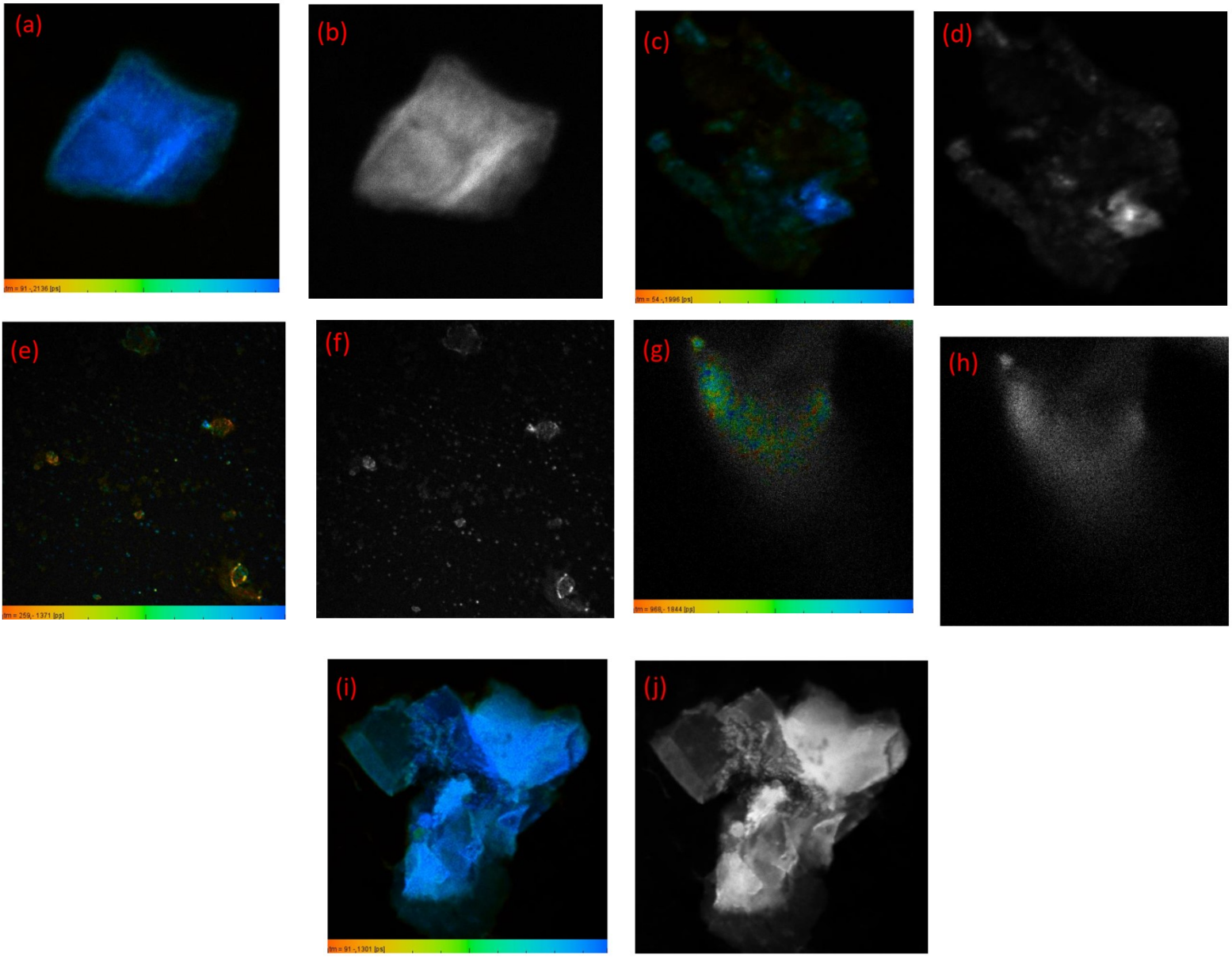

Figure S9 FLIM images of GO in the presence of NaFlu in (a) water, (c) water-ACN (χ_{ACN} = 0.062) binary mixture, (e) water-DMF (χ_{DMF} = 0.080) binary mixture, (g) water-DMSO (χ_{DMSO} = 0.060) binary mixture and (i) water-THF (χ_{THF} = 0.022) binary mixture. The corresponding intensity images of GO in the presence of NaFlu in (b) water, (d) water-ACN (χ_{ACN} = 0.062) binary mixture, (f) water-DMF (χ_{DMF} = 0.080) binary mixture, (h) water-DMSO (χ_{DMSO} = 0.060) binary mixture and (j) water-THF (χ_{THF} = 0.022) binary mixture.

Table S4: Fluorescence lifetime of NaFlu in the presence of GO in binary solvent mixtures obtained from FLIM.

Sample	τ (ns)	χ2
NaFlu in water + 35 µg/mL GO	2.31	1.18
NaFlu in water + 35 µg/mL GO + ACN (χ_{ACN} = 0.062)	2.13	1.04
NaFlu in water + 35 µg/mL GO + DMF (χ_{DMF} = 0.080)	1.20	1.20
NaFlu in water + 35 µg/mL GO + DMSO (χ_{DMSO} = 0.060)	2.24	0.90
NaFlu in water + 35 µg/mL GO + THF (χ_{THF} = 0.022)	1.42	1.12