Energy transfer in FRET pairs in a supramolecular hydrogel template

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Fig. Sl1 Excitation spectra of 2AA (12 μ M) in NaCh (15 mM) and YCh₃ with different concentrations of Y(III). The redshift in excitation spectra of 2AA on increasing Y(III) concentration shows that 2AA is bound to the metal. Excitation spectra were used instead of absorption spectra, because of the scattering by the gel samples.



SI2. Fluorescence Lifetime of Naphthalene (12 μ M) and 2-Anthroic acid (12 μ M) in NaCh (15 mM) solution (λ_{ex} =286 nm). The lifetime did not change significantly (SI3), suggesting none or a very weak energy transfer.

SI3 Lifetimes of Naphthalene (Donor) and 2-Anthroic Acid (Acceptor) in NaCh solution*									
Samples	τ ₁ (ns)	τ ₂ (ns)	τ ₃ (ns)	Amplitude Average, τ_{ave}	R-square				
Donor	59.5 (68%)	7.7 (22%)	0.5 (10%)	42.1	1.3				
Donor in presence of Acceptor	60.2 (67%)	6.8 (20%)	0.3 (12%)	41.7	1.3				
Acceptor	19.4 (62%)	9.6 (35%)	0.4 (3%)	15.4	1.1				
Acceptor in presence of Donor	19.1(61%)	9.5 (34%)	0.4 (4%)	14.9	1.1				

*Donor lifetime is measured at 325 nm and acceptor lifetime at 425 nm; Excitation wavelength is 286 nm. Cholate aggregates are usually polydisperse and have different binding sites.¹ This leads to a multi-component lifetime of the chromophores.



SI4. Fluorescence Lifetime of 2-Anthroic acid (12 μ M) in YCh₃ gel (λ_{ex} =286 nm).

SI5 Lifetimes of Naphthalene (Donor) and 2-Anthroic Acid (Acceptor)in YCh ₃ hydrogel*									
Samples	τ ₁ (ns)	τ ₂ (ns)	τ ₃ (ns)	Amplitude Average, τ _{ave}	R-square				
Donor	88.3 (51%)	10.9 (17%)	0.2 (31%)	46.9	1.2				
Donor in presence of Acceptor	83.1 (20%)	13.2 (15%)	0.2 (65%)	18.7	1.2				
Acceptor	28.6 (35%)	14.4 (59%)	2.2 (6%)	19.9	1.3				
Acceptor in presence of Donor	41.2 (19%)	14.4 (63%)	3.1 (18%)	17.4	1.2				

*Donor lifetime is measured at 325 nm and acceptor lifetime at 425 nm; Excitation wavelength is 286 nm. Cholate gels are usually polydisperse and have different binding sites.¹ This leads to a multi-component lifetime of the chromophores.

The reported fluorescence lifetime of donor (naphthalene) in water is 36-40 ns. We have not observed this component in the gel. This suggests that there is no significant fraction of molecules unassociated with the gel network. Moreover, the increase in fluorescence anisotropy from 0.01 to 0.1 also suggests that a majority of the chromophores are not present in the bulk solution but are rather associated within the gel network.

Experimental Section

Preparation of the gel

Aqueous NaCh (30 mM) and $Y(NO_3)_3$ (10 mM) were prepared in MiliQ water. Metal-cholate hydrogels were prepared by mixing the solutions and sonication (~1 min).

Spectroscopy and Photography

The fluorescence emission, excitation spectra, and anisotropy were measured on an Edinburgh Instruments FLS980 fluorescence spectrometer.

All photographic images were taken using a Sony DSC–H70 digital camera.

Fluorescence lifetimes were recorded on a Horiba Delta Flex Time-Correlated Single Photon Counting (TCSPC) instrument with 286 nm LED.

Rheology of the gel

Dynamic rheology was performed on a TA instrument AR1000 rheometer. A solvent trap was used to minimize solvent evaporation. After sonicating the gel (~1 min), ~ 1 ml of the gel was transferred to the rheometer with a 20 mm parallel plate using a pipette (Accupipet by Tarson). Frequency sweep (Fig. 2d) was done with a stress of 1 Pa and stress sweep (Fig. 2e) was done with a frequency of 1 Hz at 25 °C with a 600 μ m gap.

Microscopy

SEM and AFM imaging were done in FEI Sirion XL30 FEG SEM (10 kV) and JPK Nano wizard II (Non–contact mode) respectively.

References

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