Supporting information

Long Stokes shifts and vibronic couplings in perfluorinated polyanilines

Panagiotis Dallas,[a]* Ilija Rašović,[a] Tim Puchtler,[b] Robert A.Taylor,[b] and Kyriakos Porfyrakis [a]

Department of Materials, University of Oxford, OX1 3PH, UK.

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*panagiotis.dallas@materials.ox.ac.uk; Tel: +44(0)1865283342; Fax: +44(0)1865273789;

Section S1. Experimental section

We employed various organic solvents and performed the interfacial polymerization in the presence of different amount of Triton X-100 and triethylene glycole ethylether as a surfactant added in the aqueous phase. Experimental details for the two main systems can be found below:

1.1. **Hydrofluoroether-water with Triton X-100**: Three different samples were synthesized.

   A) 240 mg (0.47 mmol) of the monomer were dissolved in 10 ml toluene. The aqueous phase consisted from 8 ml of water and 0.1 ml HCl, 240 mg S_2O_8 (1 mmol) and 14 mg Triton X-100.

   B) 240 mg of the monomer were dissolved in 10 ml toluene. The aqueous phase consisted from 8 ml of water and 0.3 ml HCl, 720 mg S_2O_8 (3 mmol) and 14 mg Triton.

   C) 240 mg of the monomer were dissolved in 10 ml toluene. The aqueous phase consisted from 8 ml of water and 0.1 ml HCl, 0.72 mg S_2O_8 and 68 mg Triton.

1.2. **Hydrofluoroether-Water-Triton Conc.A** was the sample employed for the separation of three different oligomers through silica column chromatography.

1.3. **Hydrofluoroether-water-triethylene glycol:**

   A) The aqueous solution consisted from 8 ml of H_2O, 240 mg of Na_2SO_8, 0.1 ml H_2O and 30 mg of the glycol while the organic phase from 10 ml of HFE and 300 mg (0.59 mmol) monomer.

   B) The aqueous solution consisted from 8 ml of H_2O, 720 mg of Na_2SO_8, 0.3 ml H_2O and 30 mg of the glycol while the organic phase from 10 ml of HFE and 300 mg monomer.

1.4. **Toluene-water without surfactant:** 300 mg of the monomer were dissolved in 10 ml toluene. The aqueous phase consisted from 8 ml of water and 0.3 ml HCl, 0.72 mg S_2O_8.

1.5. **Toluene-water with surfactant**: 300 mg of the monomer were dissolved in 10 ml toluene. The aqueous phase consisted from 8 ml of water and 0.3 ml HCl in all cases, 0.72 mg S_2O_8 for 0 and 10 mg Triton and 0.24 mg S_2O_8 for 1 and 100 mg Triton.

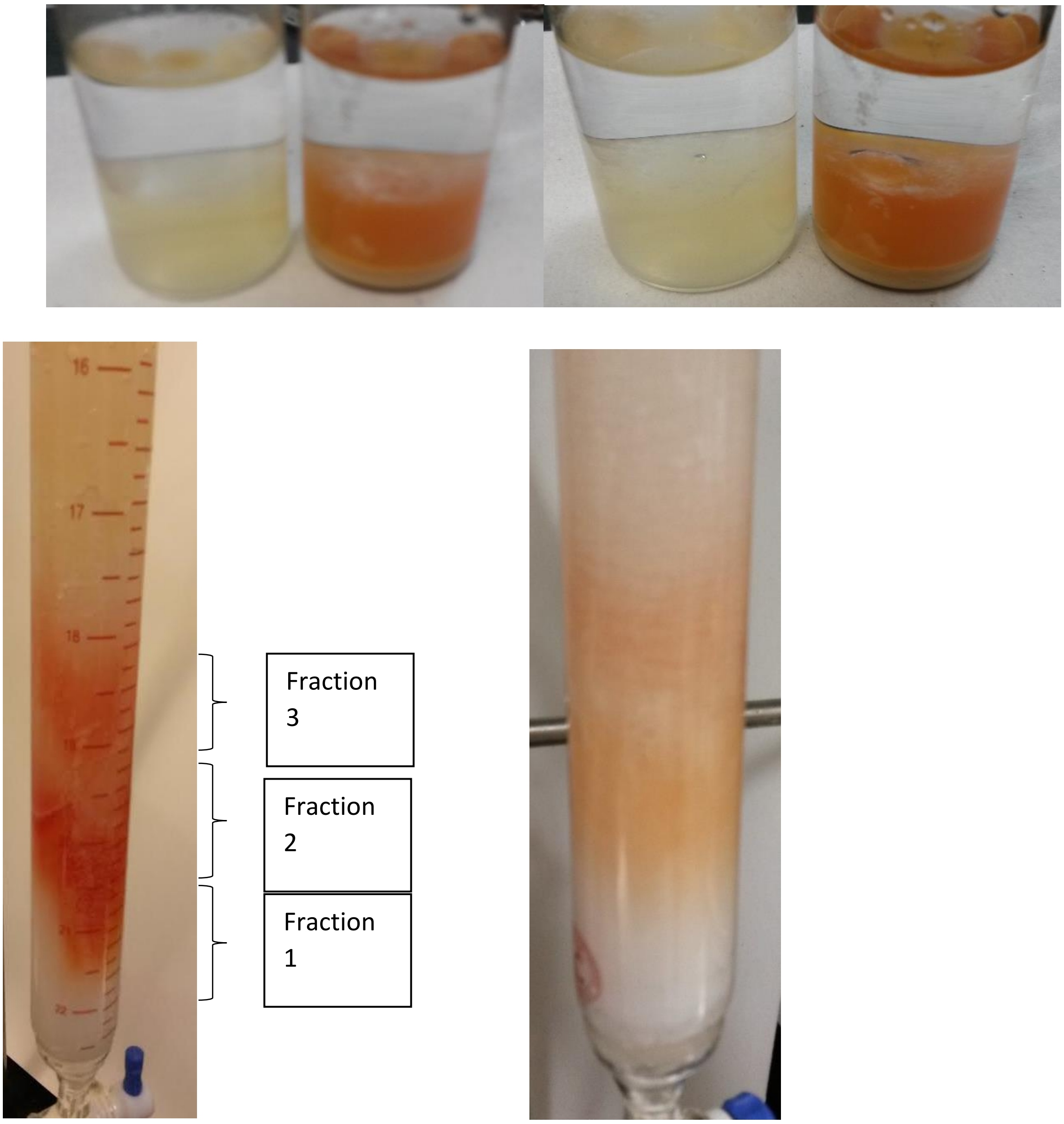


Figure S1. The hydrofluoroether-water-triethylene glycol reaction mixture for concentrations (I) and (II) in different time intervals. The separation with silica column chromatography for a toluene-water sample with (left) and without (right) surfactant.

Section S2. Characterization techniques

The UV-Visible absorbance spectra were recorded on a Jasco V-570 spectrometer and the excitation dependent photoluminescence maps on a Jasco 7200 model. The FTIR spectra were recorded on a Varian Excalibur FTS 3500 FT-IR, while the Raman spectra were recorded on a JY Horiba LabRAM ARAMIS imaging confocal Raman microscope (532 nm laser). Matrix-assisted laser-desorption ionization time-of-flight mass spectra (MALDI-TOF MS) were obtained from a Bruker MALDI-TOF spectrometer using Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) and dithranol as a matrix. ^{1}H and ^{19}F NMR spectra were recorded in toluene-d8 solutions on a Bruker 400 MHz. For the fluorescence lifetime measurements, a Ti:sapphire excitation source frequency doubled to 400nm with a pulse repetition frequency of 81.7MHz was used. The pulse duration was 250 fs and the time resolution of the time-correlated photon counting system used for detection was 50ps.

Section S3: UV-Visible spectra

UV-Visible spectra were recorded during the course of the polymerization reaction in three different systems: water-dicholoromethane; water-o dichlorobenzene and water-HFE were the organic phase is heavier than water and in two systems were the organic phase is lighter than water; water-hexane and water-toluene. The evolution of the optical absorption spectra can be seen in Fig.S2.

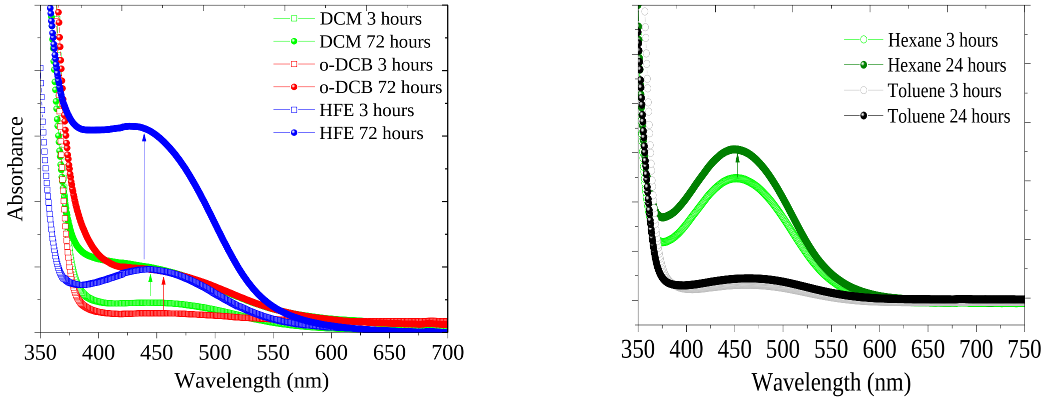


Figure S2. The UV-Vis spectra during the course of the reaction for five different solvents. No surfactant is added.

Section S4: Excitation dependent photoluminescence maps

The insoluble in the reaction mixture precipitate may be solubilized in an acetone-toluene mixture. The spectra for three different systems (dichlorobenzene, dichloromethane and HFE) are identical signalling the same emeraldine salt form oxidation state (Figure S3). The three different soluble fraction for water-toluene without surfactant do not show any differences in the PL spectra. The soluble fractions from HFE-water and DCM-water without surfactants, present the opposite picture from the materials in the presence of Triton X-100 in toluene: the fractions at higher retention time have a red shifted spectrum compared to those from lower retention times (Figure S5).

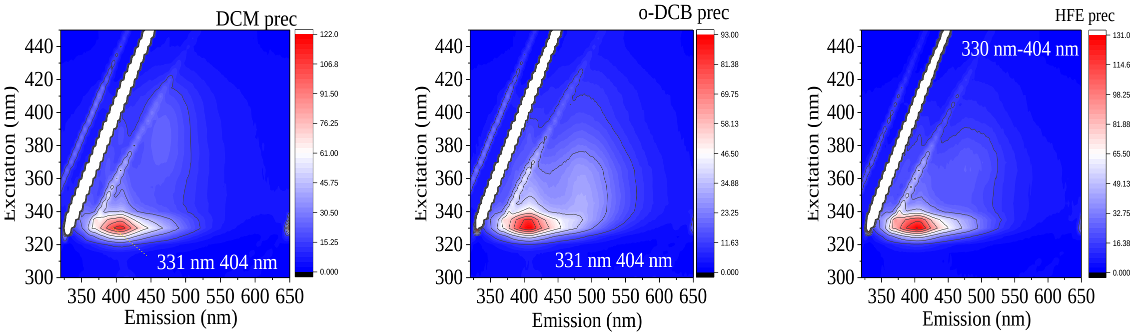


Figure S3. The photoluminescence excitation dependent maps of the precipitates derived from dichloromethane, dichlorobenzene and hydrofluoroether without the addition of any surfactants. The polymers are all in the same oxidation state.

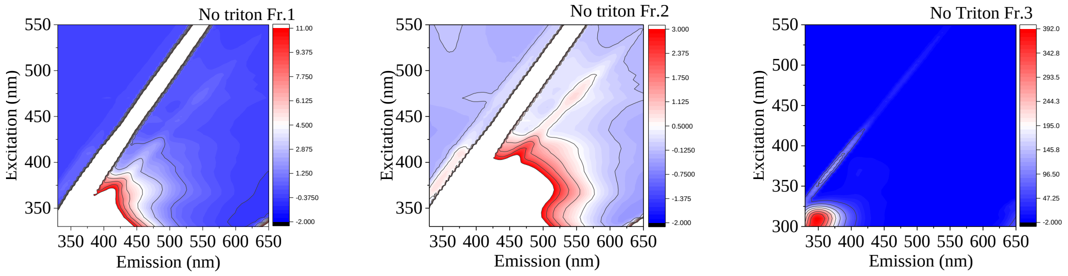


Figure S4. The three fractions from a toluene-water without any surfactant addition.

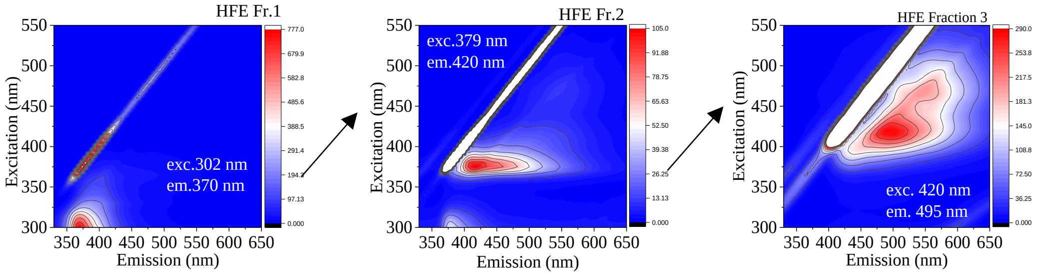


Figure S5. The photoluminescence excitation dependent maps of the soluble part derived from hydrofluoroether without the addition of any surfactants.

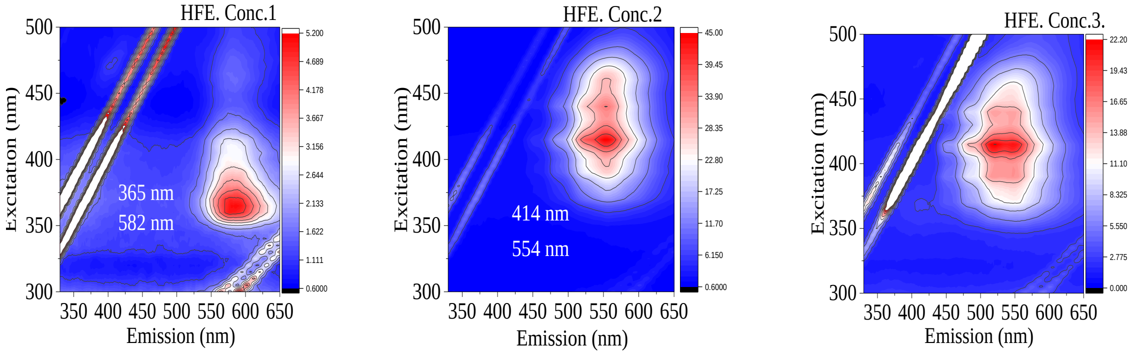


Figure S6. Excitation dependent photoluminescence maps for the hydrofluoroether derived mixtures when synthesized with Triton X-100. The molar ratio is given in the experimental section and the spectra were recorded prior to silica column separation.

λ_{exc} nm (cm^{-1})	λ_{em} nm (cm^{-1})	Shift (cm^{-1})	λ_{exc} nm (cm^{-1})	λ_{em} nm (cm^{-1})	shift (cm^{-1})
373 (26810)	453 (22075)	4735	394 (25380)	516 (19380)	6000
373 (26810)	516 (19380)	7430	394 (25380)	453 (22075)	3305
373 (26810)	484 (20661)	6149	394 (25380)	484 (20661)	4719
419 (23866)	523 (19120)	4746	419 (23866)	487 (20534)	3332
419 (23866)	487 (20534)	3332	444 (22522)	484 (20661)	1861

Table 1. The emission and excitation maxima and the vibronic couplings for the toluene-water-Triton systems.

Section S5. MALDI-TOF analysis

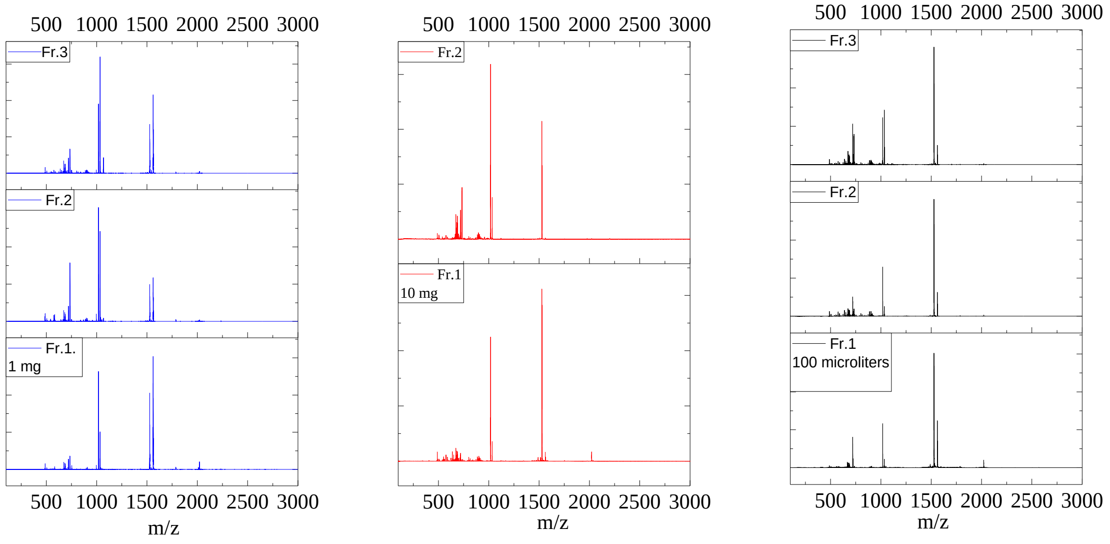


Figure S7. The MALDI-TOF of the toluene-water-Triton systems a) 1 mg b) 10 mg c) 100 mg

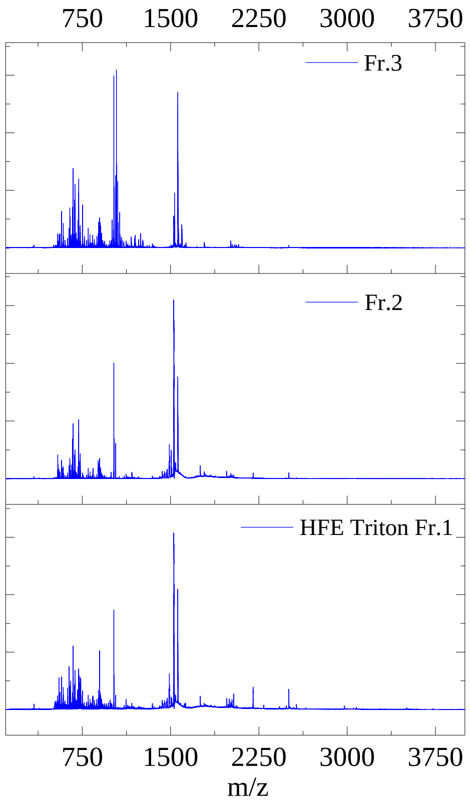


Figure S8. The MALDI-TOF of the three fractions derived from the HFE-water-Triton systems with 14 mg Triton

Section S6. Vibrational spectroscopy (FTIR and Raman)

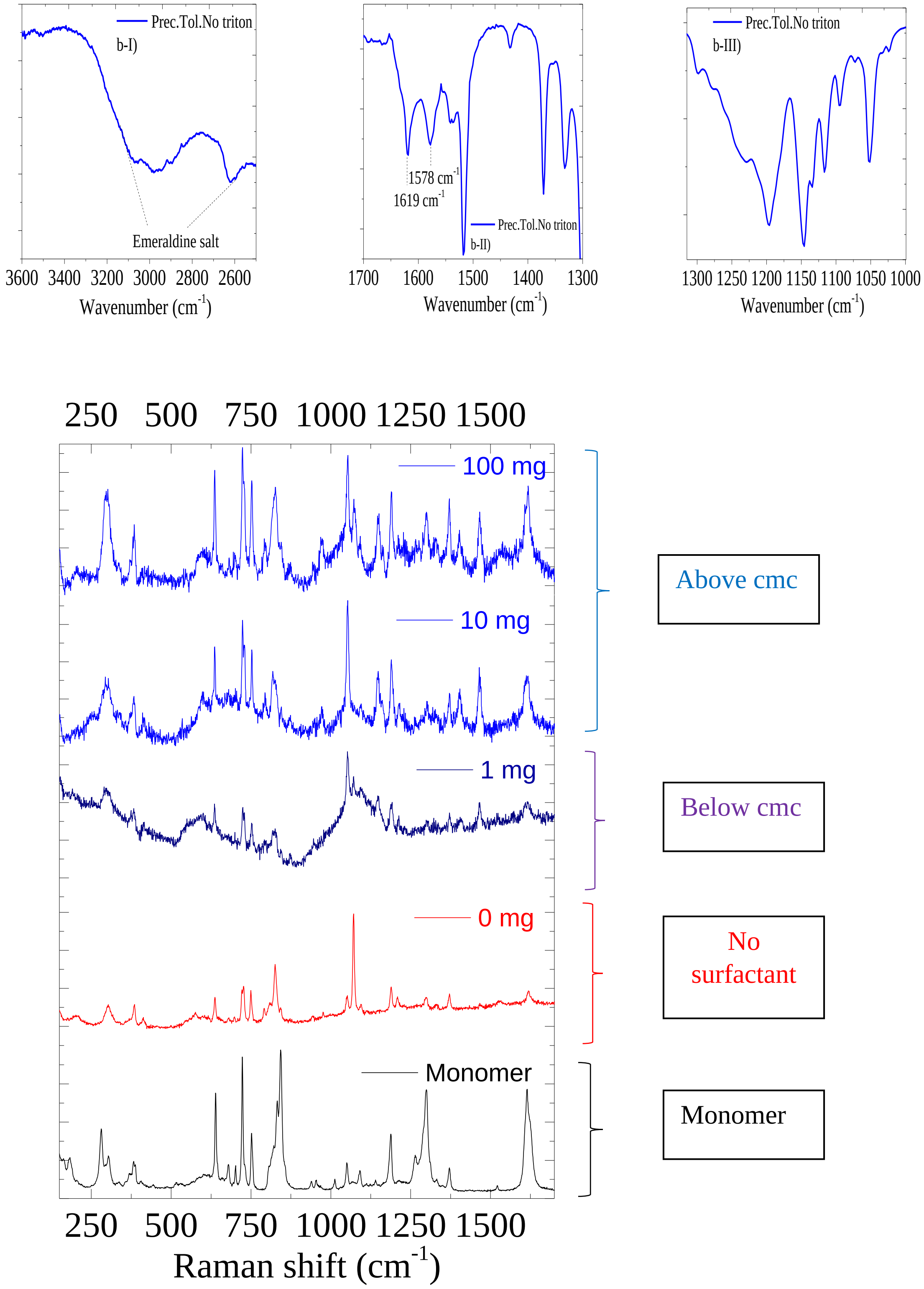
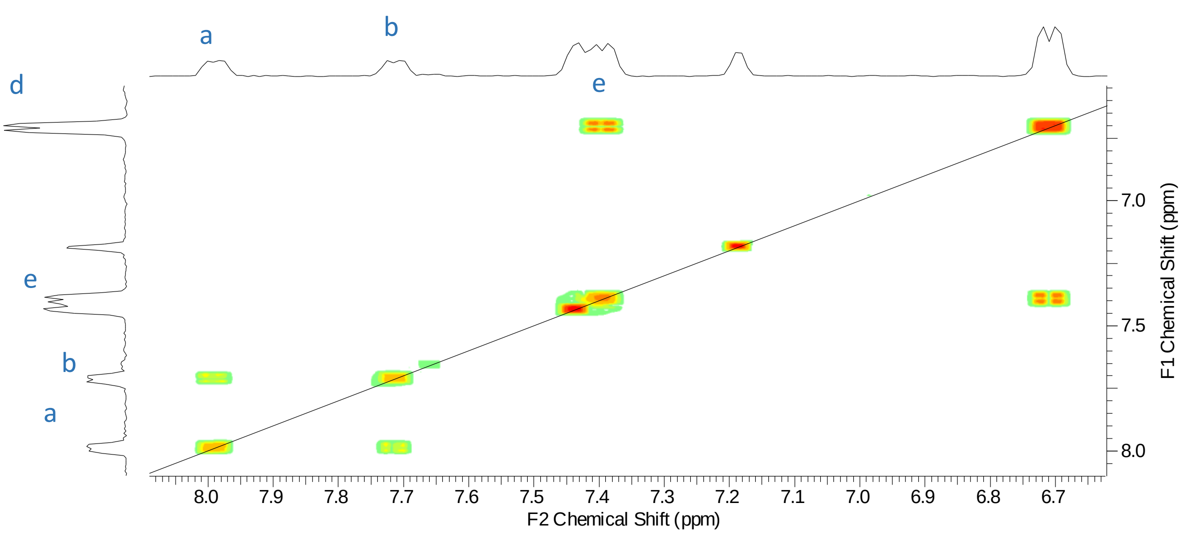
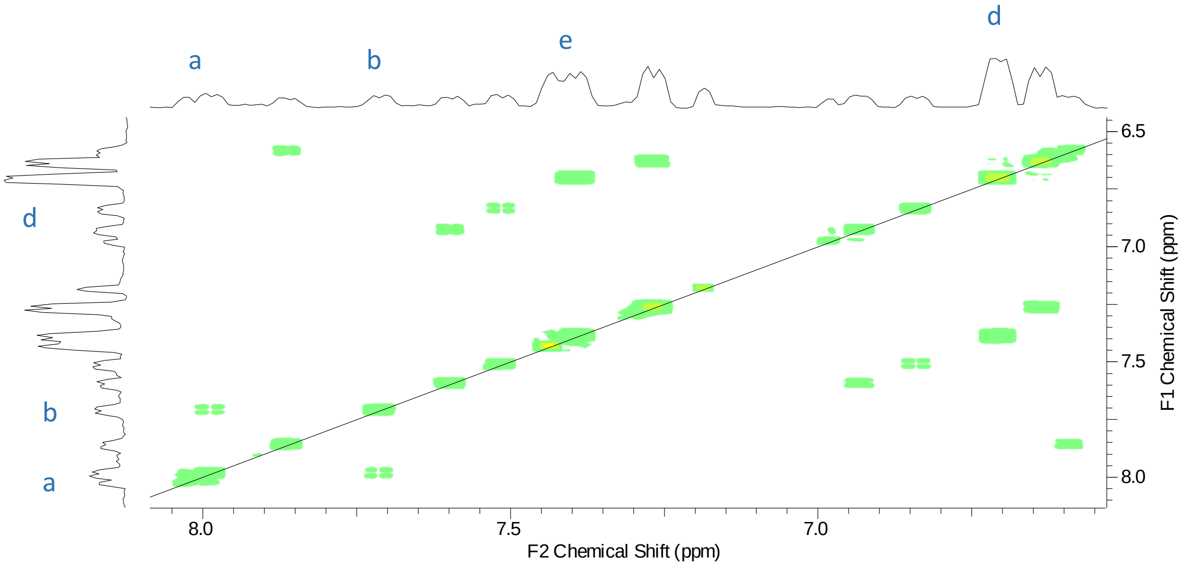


Figure S9. FTIR of the insoluble thin film and the Raman spectra of the insoluble films derived from a water-toluene system with the following amounts of Triton: 0; 1;10;100 mg.

Section S7. ^{1}H and ^{19}F NMR and 2D COSY NMR



The COSY NMR spectrum for the soluble fraction synthesized without Triton X-100 in toluene-aqueous system



The COSY NMR spectrum of the soluble fraction (Fr.2) synthesized in the presence of 14 mg Triton in HFE-aqueous system.

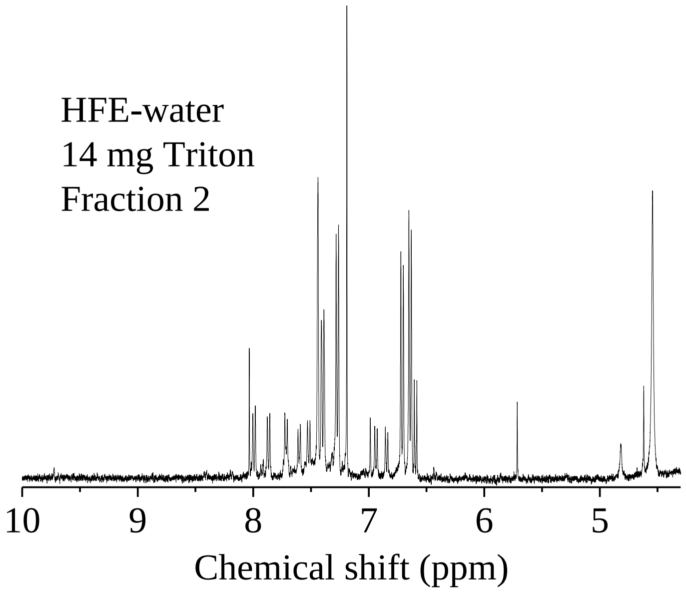


Figure 11. 2D COSY NMR and the 1H NMR of an HFE derived sample (Fraction 2).

Section S8: Quantum yield and absorption coefficient calculation. PL maps in different solvents

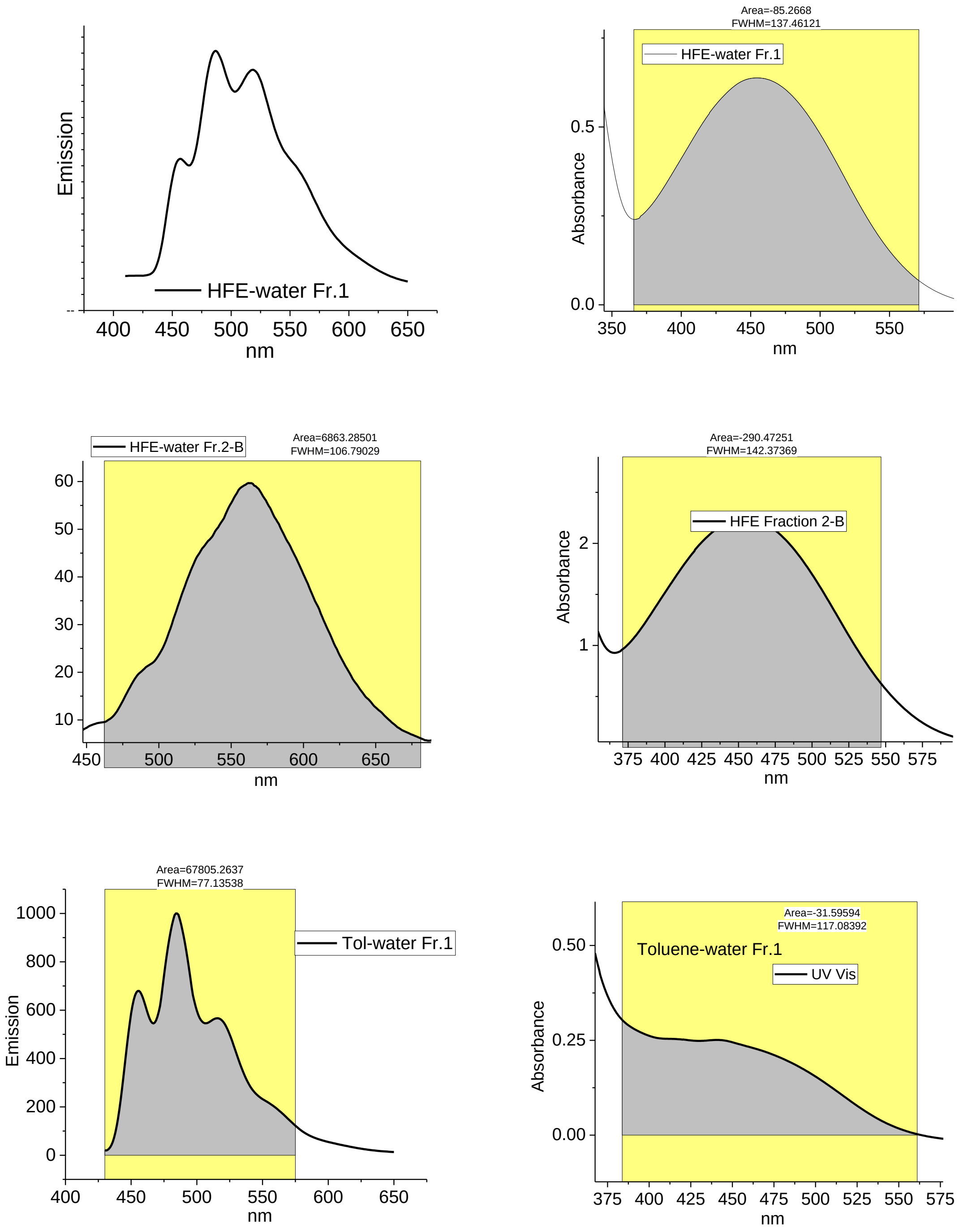


Figure S11. The PL and the UV-vis curves employed for the calculation of the quantum yield.

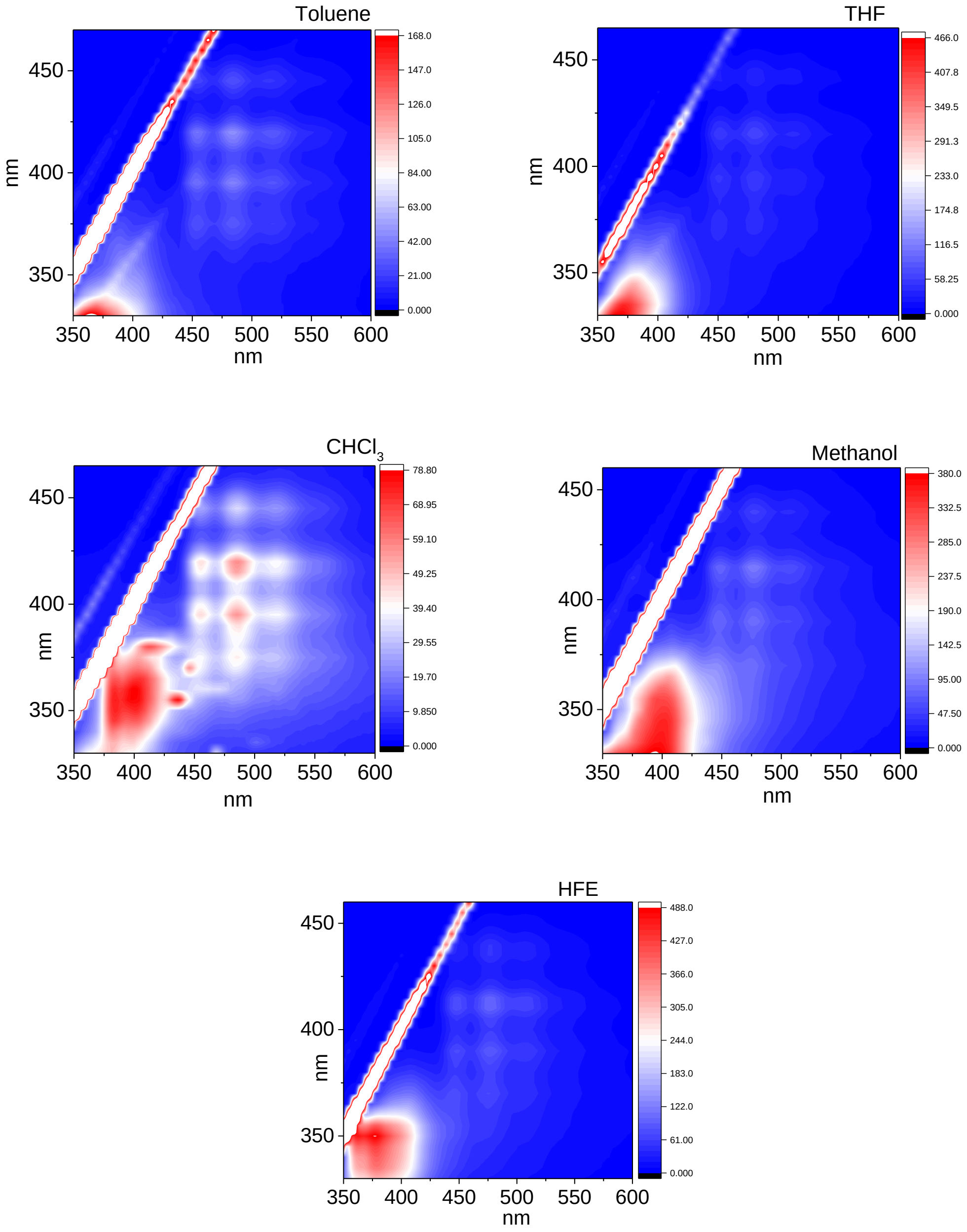
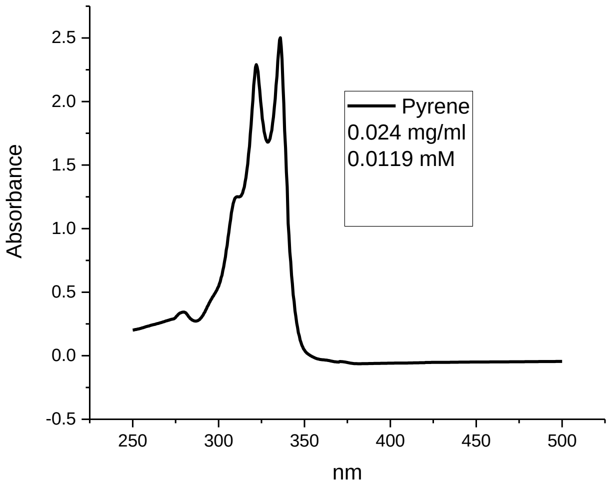


Figure S12. Photoluminescence excitation dependent maps in three different solvents a) Toluene b) Tetrahydrofuran c) Chloroform d) Methanol e) HFE



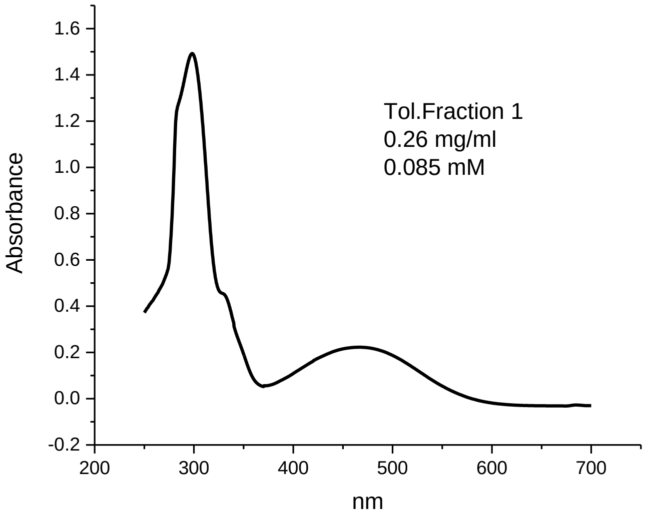


Figure S13. The UV-Visible absorbance curves for pyrene and the Fraction 1 from toluene-water-Triton used for the absorption coefficient calculation.