

**Irradiation-responsive polysulfone film as a colorimetric  
UVA/UVB differentiator**

## General information

Reagent grade chemicals were obtained from Aldrich (Hfod and [C<sub>2</sub>mim]Cl) and Iolitec ([C<sub>2</sub>mim]BF<sub>4</sub>) and used without further purification.

Microanalyses for C and H were carried using a Thermo Finnigan-CE Instruments Flash EA 1112 CHNS series. FT-IR spectra (range 4000– 400 cm<sup>-1</sup>) were collected as KBr pellets (Sigma-Aldrich, FT-IR grade) using a Thermo Scientific Nicolet iS50 FT-IR spectrometer, by averaging 64 scans at a maximum resolution of 4 cm<sup>-1</sup>. Analysis of the heated sample was performed by heating previously 1 in an oven and then prepare the KBr pellet, assuring that the pallet had a purple color during acquisition of the FT-IR spectra. TGA curves were obtained using a Thermal Analysis Ta Q500-2207, with a scanning rate of 10 °Cmin for 1, with samples weighing around 8 mg in Aluminum crucibles. The calibration of the TGA equipment was made following the recommendation described in the manufacturer's manual.

Luminescence spectra were measured using a SPEX Fluorolog-3 Model FL3-22 spectrofluorimeter, with variable slits and measurement step of 0.1 nm.

Luminescence quantum efficiencies were measured by the absolute method with an Integrated Sphere. All spectra are corrected with correction functions provided by the supplier following standard procedures.

The mass spectra were acquired on a LCQ Fleet ion trap mass spectrometer equipped with an ESI ion source (Thermo Scientific TM) operated in the ESI positive and negative ion modes, using the with the following optimized parameters: ion spray voltage, 4.5 kV; capillary voltage, 16/@18 V; tube lens offset, @70/58 V; sheath gas (N<sub>2</sub>), 40 arbitrary units; auxiliary gas (N<sub>2</sub>), 20 arbitrary units; capillary temperature, 300 °C. Spectra typically correspond to the average of 20–35 scans and were recorded in the

range between 70–1500 Da. Data acquisition and data processing were done with Thermo Xcalibur 2.3 software.

## Synthetic Details

**Synthesis of [C<sub>2</sub>mim][fod]:** 1 equivalent of NaOH (0.135 g, 1.689 mmol, 50 % W/W aqueous solution) was added to a solution of Hfod (0,500 g, 1.689 mmol) previously dissolved in ethanol. The reaction mixture was left stirring for 2 hours at room temperature. Then 1 equivalent of C<sub>4</sub>mimCl (0,247 g, 1.689 mmol) previously dissolved in a minimum of ethanol/water (1:1) was added dropwise to the solution with constant stirring. After 1h in the transparent solution the solvent was removed under low pressure and the resulting reaction mixture was dissolved in CH<sub>2</sub>Cl<sub>2</sub>. NaCl was removed by filtration and the pure compound was recovered as a purple liquid, that solidified slowly at room temperature to give a white solid, after solvent evaporation at 40 °C, with a yield of ca. 80 %. If necessary, wash the material with water to remove any excess of reagents. Anal. Calcd. for [C<sub>6</sub>H<sub>11</sub>N<sub>2</sub>][C<sub>10</sub>H<sub>10</sub>O<sub>2</sub>F<sub>7</sub>]: C, 47.29; H, 10.10%; N, 5.21. Experimental; C, 47.25; H, 10.25; N, 5.18.

**[C<sub>2</sub>mim][fod]@PSU (7% w/w):** Polysulfone (0.226 g) and [C<sub>2</sub>mim][fod] (0.0158 g) were left stirring in a closed vial with 8 mL CH<sub>2</sub>Cl<sub>2</sub> until complete dissolution of the polysulfone. The resulting transparent solution was then transferred into a loosely closed petri dish, and left evaporating overnight in a room with a controlled temperature of 21 °C. The dopped membrane was then collected from the petri dish and used without any further treatment.

**Nafod@PSU (7% w/w):** Nafod@PSU was prepared equally to 1@PSU but using 0.232 g of polysulfone and and 0.0162 of Nafod.

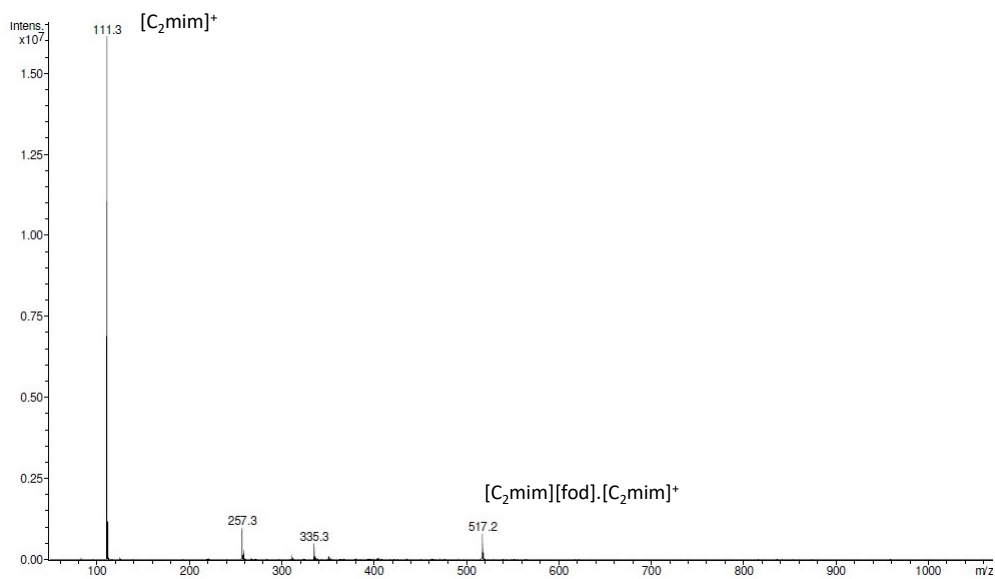
**C<sub>2</sub>mimCl@PSU (7% w/w):** C<sub>2</sub>mimCl@PSU was prepared equally to 1@PSU but using 0.218 g of polysulfone and and 0.0153 of C<sub>2</sub>mimCl.

**C<sub>2</sub>mimBF<sub>4</sub>@PSU (7% w/w)** C<sub>2</sub>mimBF<sub>4</sub>@PSU was prepared equally to 1@PSU but using 0.241 g of polysulfone and 0.0169g of C<sub>2</sub>mimCl.

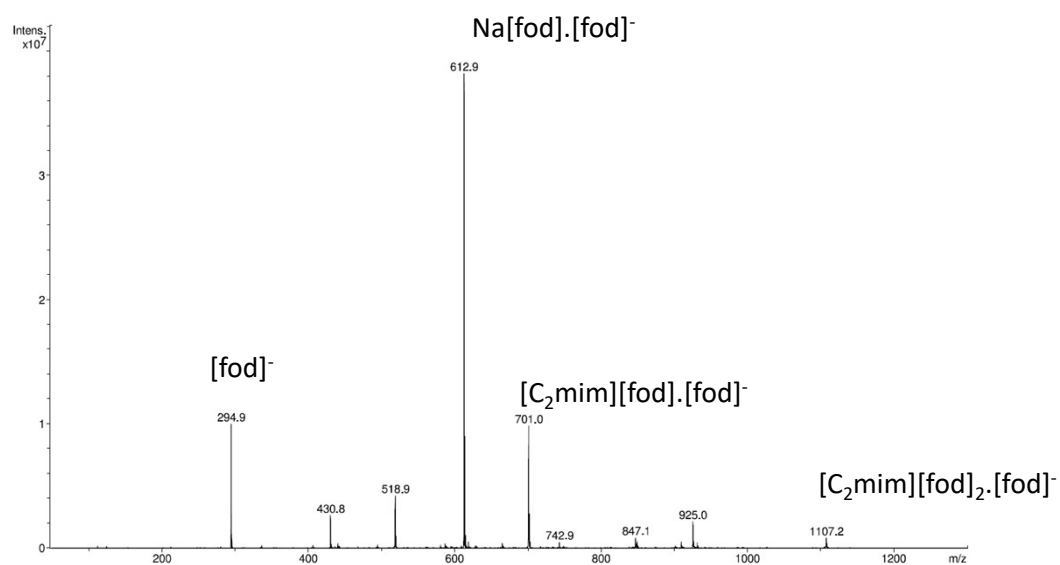
## Mass spectrometry characterization (ESI-MS)

ESI/MS uses a soft ionization technique which allows direct analysis of the species in solution, reducing collision induced dissociation at higher energies. [C<sub>2</sub>mim][fod] was analysed to evaluate the degree of aggregation and the cation-anion interaction strength. In the positive mode spectra the most intense peak was attributed to the free cation [C<sub>2</sub>mim]<sup>+</sup>, followed by [C<sub>2</sub>mim][fod].[C<sub>2</sub>mim]<sup>+</sup> (m/z 517.2), Fig. S1. When studied in the negative mode, Fig. S2, the most abundant species corresponds to [Na][fod].[fod]<sup>-</sup> anion while lower intensities, correspondent to other negatively charged species, were observed for [fod]<sup>-</sup>, [C<sub>2</sub>mim][fod].[fod]<sup>-</sup> and with the lowest intensity {[C<sub>2</sub>mim][fod]}<sub>2</sub>[fod]<sup>-</sup> (m/z 1107.2).

The presence of supramolecular aggregates was previously described for several imidazolium based ionic liquids<sup>1</sup>, including those that are highly fluorinated.<sup>2,3</sup> In one of this studies it was also observed that the 'CF<sub>2</sub>' group leads to a small but significant increase of the cohesive interactions resulting in a higher cohesive energy of the ionic pairs. The negative mode of ESI/MS detects the presence of the uncharged [C<sub>2</sub>mim][fod] species, associated with a fod unit.

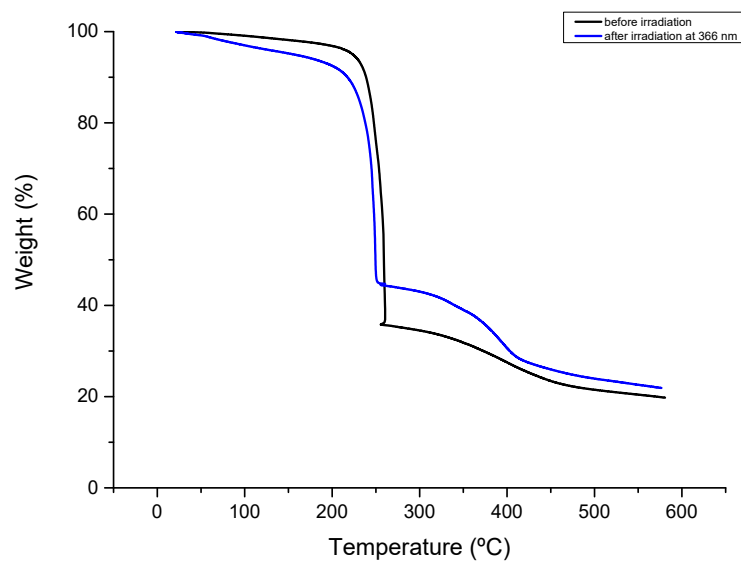


**Fig. S1** ESI-MS spectra in the positive mode in acetonitrile

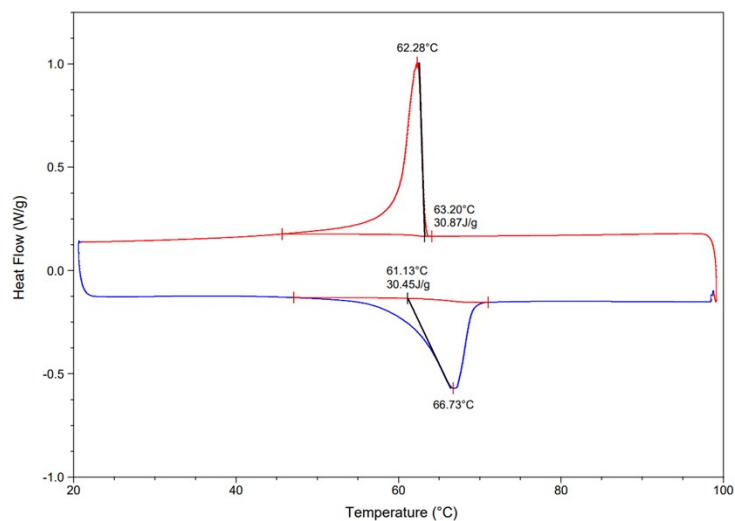


**Fig. S2** ESI-MS spectra in the positive mode in acetonitrile

## Thermal characterization

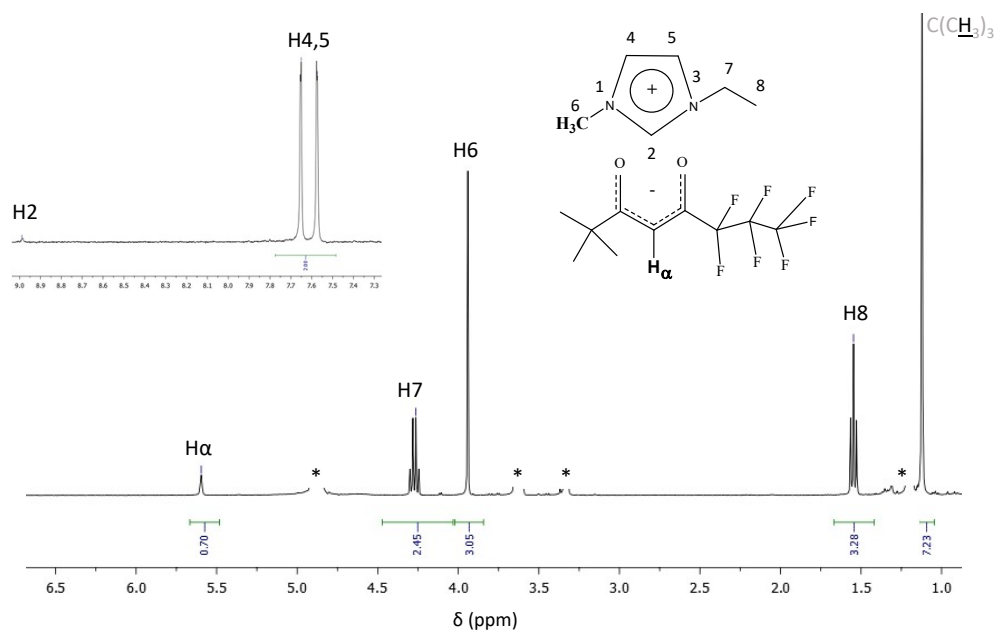


**Fig. S3** TGA curves for [C<sub>2</sub>mim][fod] before and after irradiation at 366 nm.



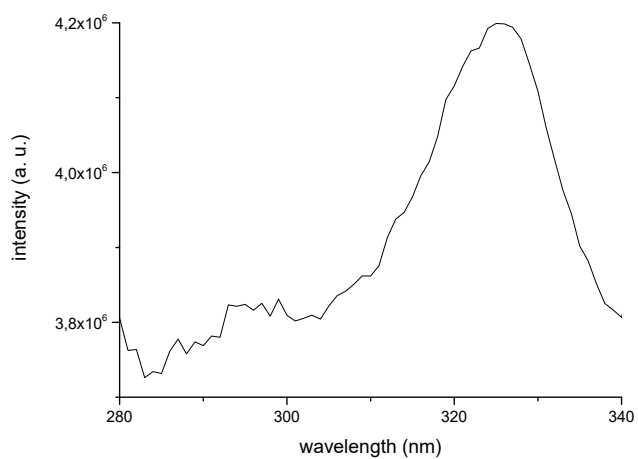
**Fig. S4** DSC curves for [C<sub>2</sub>mim][fod] (white solid), up-exothermic; down-endothermic

## NMR characterization

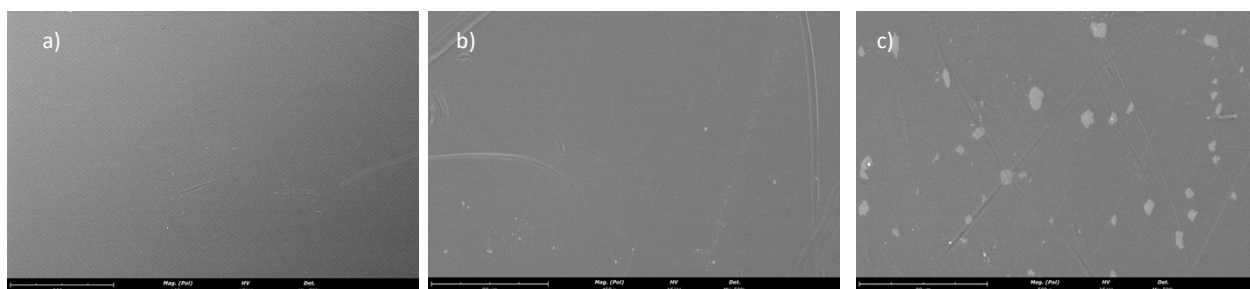


**Fig. S5**  $^1\text{H-NMR}$  spectra of  $[\text{C}_2\text{mim}][\text{fod}]$  before irradiation in methanol-d. \* Solvent peaks traces were omitted for clarity. The numbering of spectral lines corresponds to the numbering of atoms in the inset figure.

## Spectroscopic characterization

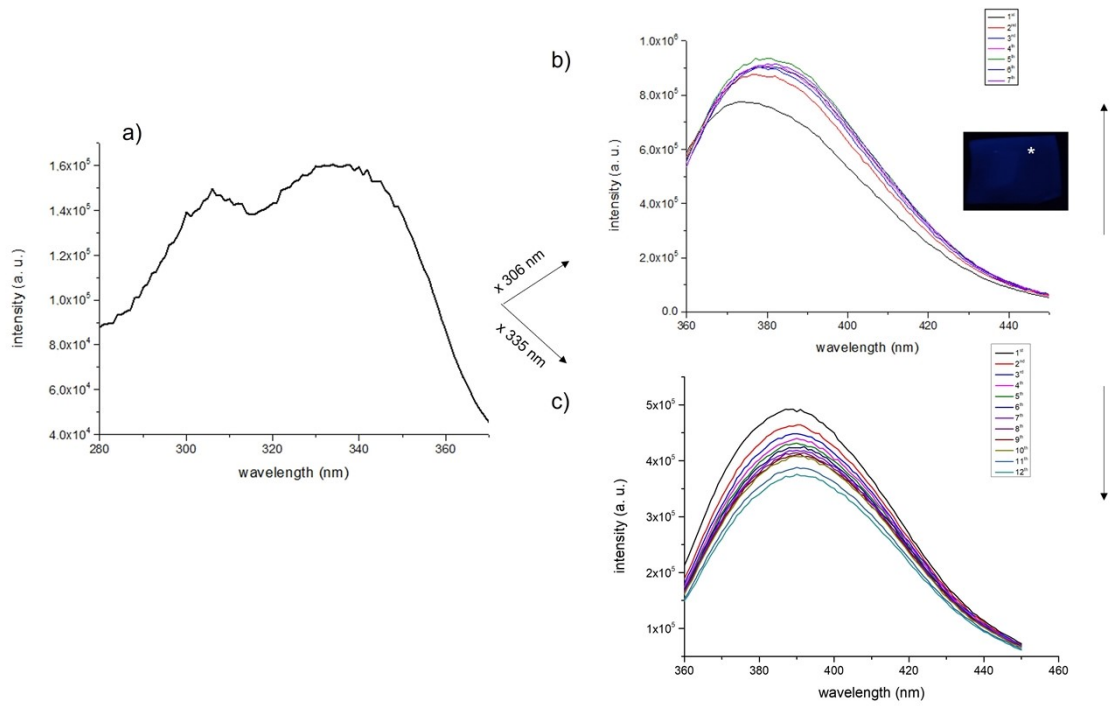


**Fig. S6** Excitation spectra of pristine PSU for the maximum emission band at 380 nm.

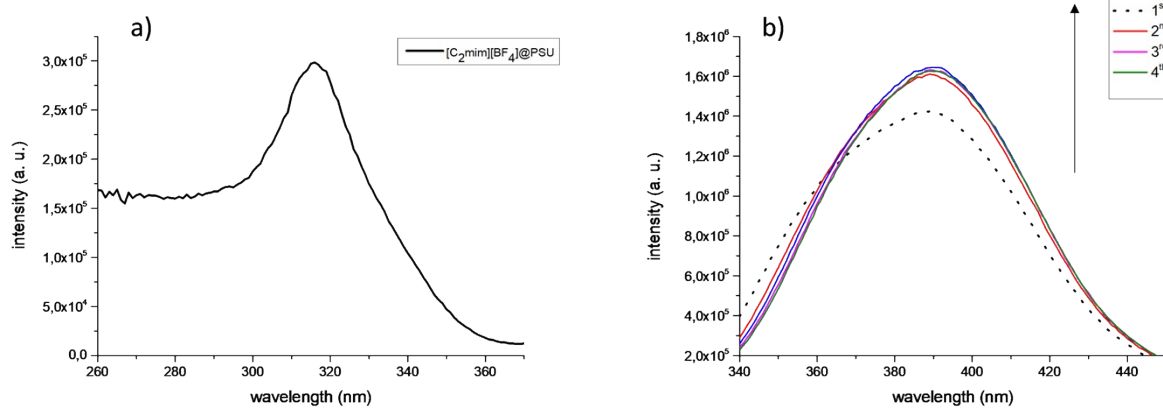


**Fig. S7** a) SEM image of PSU film, b) SEM image of irradiated PSU film at 295 nm, c) SEM image of irradiated PSU film at 325 nm

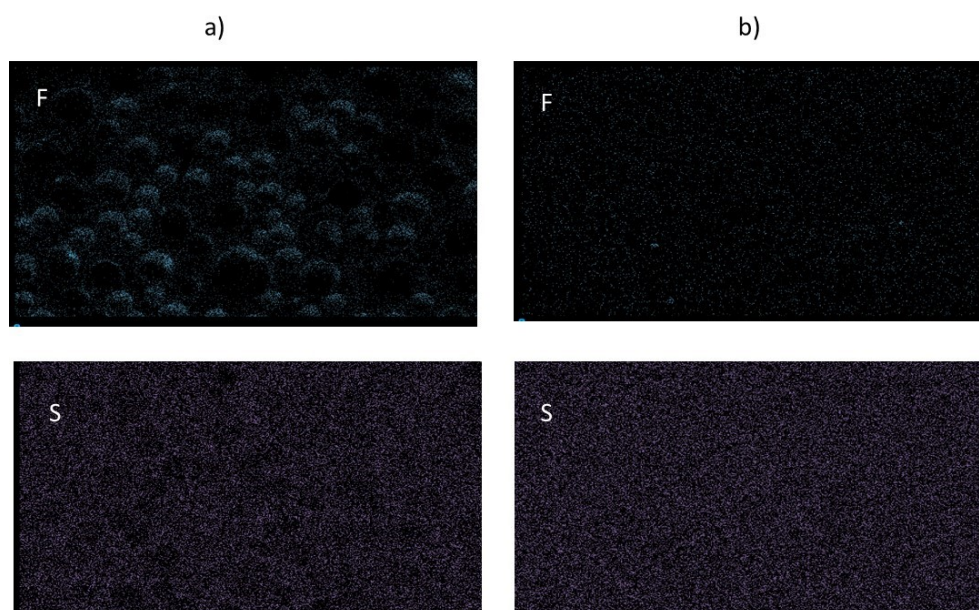




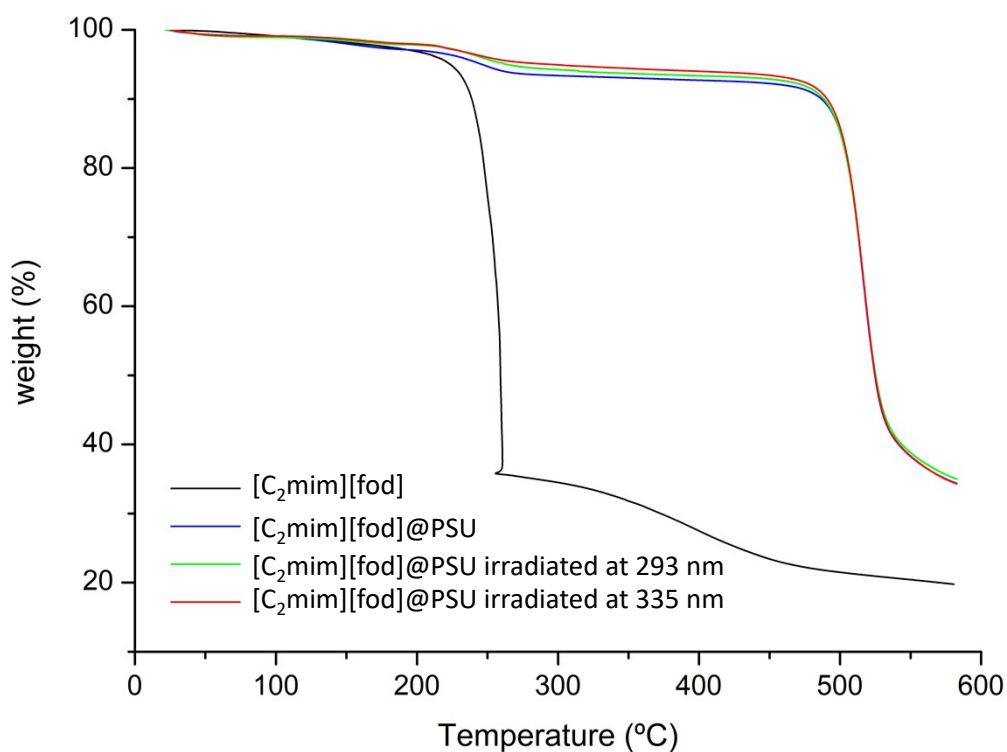
**Fig. S8** a) excitation spectra of Nafod@PSU for the most intense emission band at 390 nm b) emission spectra upon 306 nm excitation, c) emission spectra upon 335 nm excitation. \* irradiated area of the film under 366 nm UV lamp.



**Fig. S9** a) excitation spectra of  $[C_2mim][BF_4]@PSU$  for the most intense emission band at 390 nm, emission spectra upon 317 nm excitation.

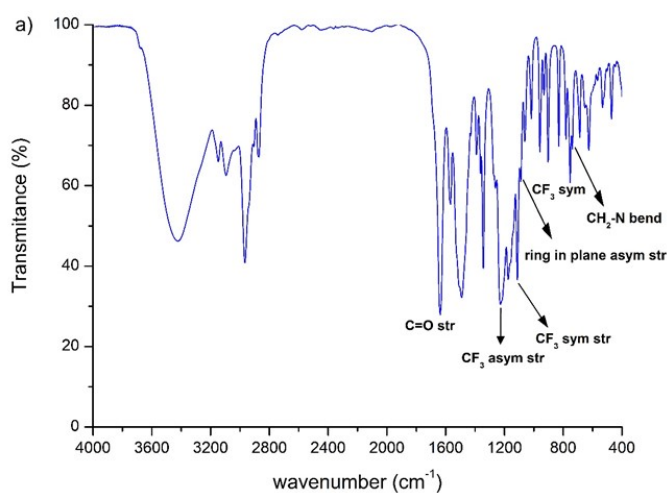


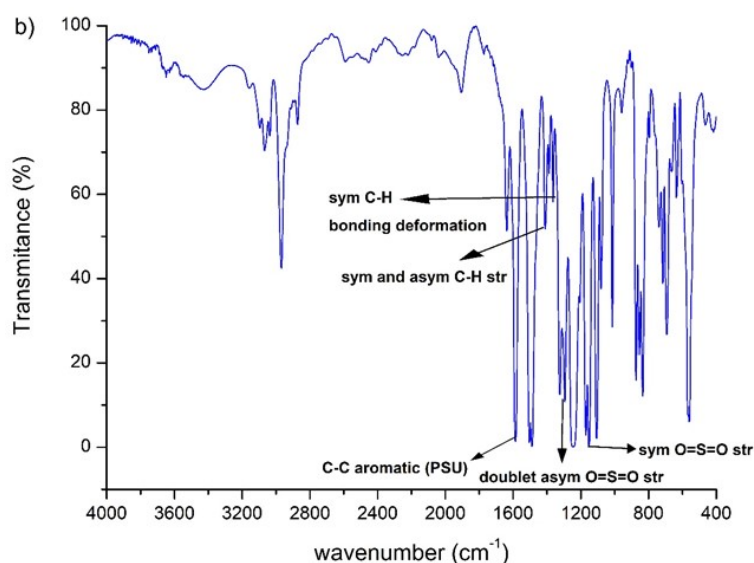
**Fig. S10** Energy dispersive spectroscopy mapping of F and S of a)  $[C_2mim][fod]@PSU$  and b)  $[C_2mim][fod]@PSU$  irradiated at 335nm.



**Fig. S11** TGA curves for the prepared [C<sub>2</sub>mim][fod]@PSU films before and after irradiation at different wavelengths.

## FT-IR

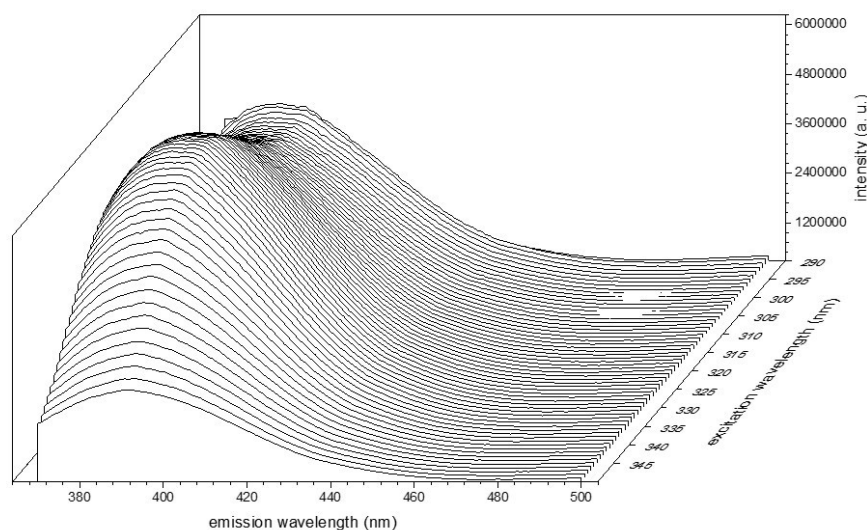




**Fig. S12** FTIR spectrum of a)  $[C_2mim][fod]$  and b)  $[C_2mim][fod]@PSU$ .

The FT-IR spectra of the  $[C_2mim][fod]$  (Fig. S12a) and  $[C_2mim][fod]@PSU$  (Fig. S12b) present the vibration of the expected functional groups. The  $[C_2mim][fod]$  spectra presents around 3425  $cm^{-1}$  a broad band due to the  $\nu(O-H)$  stretching modes from adsorbed water in the sample. The symmetric and asymmetric C–H stretching vibrational modes of the alkyl groups from the fod and  $C_2mim$  moieties are responsible for the medium intensity bands in the ranges 2860–3000  $cm^{-1}$  and 3000–3200  $cm^{-1}$ , respectively. The very strong band around 1636  $cm^{-1}$  is ascribed to the –C–O stretching mode of the fod ligands while the the  $\delta_{as}(O-H)$  bending vibrations appears at ca. 1570  $cm^{-1}$ . The band at ca. 1514  $cm^{-1}$  is ascribed to the alkene C=C bond. The bands in the range 600–1200  $cm^{-1}$  are ascribed to the stretching modes of the C–C bond and between 800–970  $cm^{-1}$  are due to the stretching of the C–F bonds. The  $[C_2mim][fod]@PSU$  spectra presents a much lower intensity broad band, in comparison to the free  $[C_2mim][fod]$ , due to the  $\nu(O-H)$  stretching modes from adsorbed water around 3420  $cm^{-1}$ , which is expected from the increased hydrophobicity of the membrane. Although the spectra is dominated by the PSU vibrations some characteristic bands of the  $[C_2mim][fod]$  are isolated from the PSU and clearly visible like the bands ascribed to the symmetric and asymmetric C–H stretching vibrational modes of the alkyl groups from the fod anion in the range 2860–3000  $cm^{-1}$  and between 3000–3200  $cm^{-1}$  from the

C<sub>2</sub>mim cation. Ascribed to the PSU, the band at ca. 1586 cm<sup>-1</sup> corresponds to the vibrations of the aromatic C-C bonds, the band around 1411 cm<sup>-1</sup> is due to the asymmetric and symmetric C-H stretching vibrations and the symmetric C-H bending deformation of CH<sub>3</sub> is responsible for the band at ca. 1387 cm<sup>-1</sup>. The doublet at ca. 1324 and 1295 cm<sup>-1</sup> and the band around 1151 cm<sup>-1</sup> can be ascribed to the asymmetric and symmetric stretchings of the structural O=S=O. The bands at ca. 874, 835 and 693 cm<sup>-1</sup> are ascribed to C-H bending vibrations.



**Fig. S13** 3D-spectra of excitation vs emission wavelength of [C<sub>2</sub>mim][fod]@PSU.

<sup>1</sup> H. K. Stassen, R. Ludwig, A. Wulf and Dupont, *Chem. Eur. J.*, 2015, **21**, 8324-8335.

<sup>2</sup> A. S. M. C. Rodrigues, A. M. Fernandes, J. Dévemy, M. Costa Gomes, L. M. N. B. F. Santos. *J. Mol. Liq.*, 2019, **282**, 385-391.

<sup>3</sup> S. Muhammad, M. N. Javed, F. I. Ali, A. Bari and I. A. Hashmi, *J. Mol. Liq.*, 2020, **300**, 112372.