

Supplementary Information

CO₂-derived functional polycarbonates as a sustainable platform for photosensitive polymeric materials

Andreia C. S. Gonzalez, Rafael T. Aroso, Carla Cunha, J. Sérgio Seixas de Melo, M. Ermelinda S. Eusébio, Teresa M. R. Maria, Gabriela J. da Silva, Pedro F. Cruz, Rui M. M. Brito, Rui M. B. Carrilho and Mariette M. Pereira**

Table of Contents

1. Nuclear Magnetic Resonance Spectroscopy (NMR)	3
Figure S1 – ¹ H NMR spectrum of 1-PS_A in CDCl ₃ at 25 °C.	3
Figure S2 – ¹³ C NMR spectrum of 1-PS_A in CDCl ₃ at 25 °C.	3
Figure S3 – ¹ H NMR spectrum of 2-PS_A in CDCl ₃ at 25 °C.	4
Figure S4 – ¹³ C NMR spectrum of 2-PS_A in CDCl ₃ at 25 °C.	4
Figure S5 – ¹ H NMR spectrum of 3-PS_A in CDCl ₃ at 25 °C.	5
Figure S6 – ¹³ C NMR spectrum of 3-PS_A in CDCl ₃ at 25 °C.	5
Figure S7 – ¹ H NMR spectrum of 1-PS_B in CDCl ₃ at 25 °C.	6
Figure S8 – ¹³ C NMR spectrum of 1-PS_B in CDCl ₃ at 25 °C.	6
Figure S9 – ¹ H NMR DOSY spectrum of 1-PS_A versus 1-PS_B in CDCl ₃ at 25 °C.	7
Figure S10 – ¹ H NMR DOSY spectrum of 1-PS_A + PS_A in CDCl ₃ at 25 °C.	7
2. Size Exclusion Chromatography (SEC/GPC)	8
Figure S11 – SEC chromatogram of 1-PS_A in THF, using a polystyrene standard.	8
Figure S12 – SEC chromatogram of 2-PS_A in THF, using a polystyrene standard.	8
Figure S13 – SEC chromatogram of 3-PS_A in THF, using a polystyrene standard.	8
Figure S14 – SEC chromatogram of 1-PS_B in THF, using a polystyrene standard.	9
Figure S15 – SEC chromatogram of 3-PS_B in THF, using a polystyrene standard.	9

3. Powder X-Ray Diffraction (XRD)	10
Figure S16 – XRD spectrum of 1-PS_A .	10
Figure S17 – XRD spectrum of 2-PS_A .	10
Figure S18 – XRD spectrum of 3-PS_A .	11
Figure S19 – XRD spectrum of 1-PS_B .	11
Figure S20 – XRD spectrum of 2-PS_B .	12
Figure S21 – XRD spectrum of 3-PS_B .	12
4. Fourier Transform Infrared Spectroscopy (FTIR)	13
Figure S22 – FTIR deconvolution of the carbonyl region of 2-PS_A .	13
5. MALDI-TOF Mass Spectrometry	13
Figure S23 – MALDI-TOF MS spectrum of 1-PS_A .	13
Figure S24 – MALDI-TOF MS spectrum of 1-PS_B .	14
6. Formation of cross-linked polycarbonate 2-PS_B	14
Scheme S1 – Proposed pathway for the formation of cross-linked polycarbonate 2-PS _B .	14
7. Preparation of ethyl cellulose-polycarbonate biocomposite film	15
Figure S25 – Preparation of ethyl cellulose-polycarbonate biocomposite 2-PS_A(15%)@EC .	15
8. Antimicrobial Photodynamic Inactivation (aPDI) studies	15
Figure S26 – Overlap between 660 nm LED emission and PS_A absorption in CH ₂ Cl ₂ solution.	15
Figure S27 – Photograph of a 96-well plate containing the samples 1-PS_A , 2-PS_A and 3-PS_A , upon exposure to <i>S. aureus</i> bacterial suspensions.	15
Figure S28 – Representative pictures of Petri dishes obtained for surviving CFU counting in <i>S. aureus</i> photoinactivation assays.	16

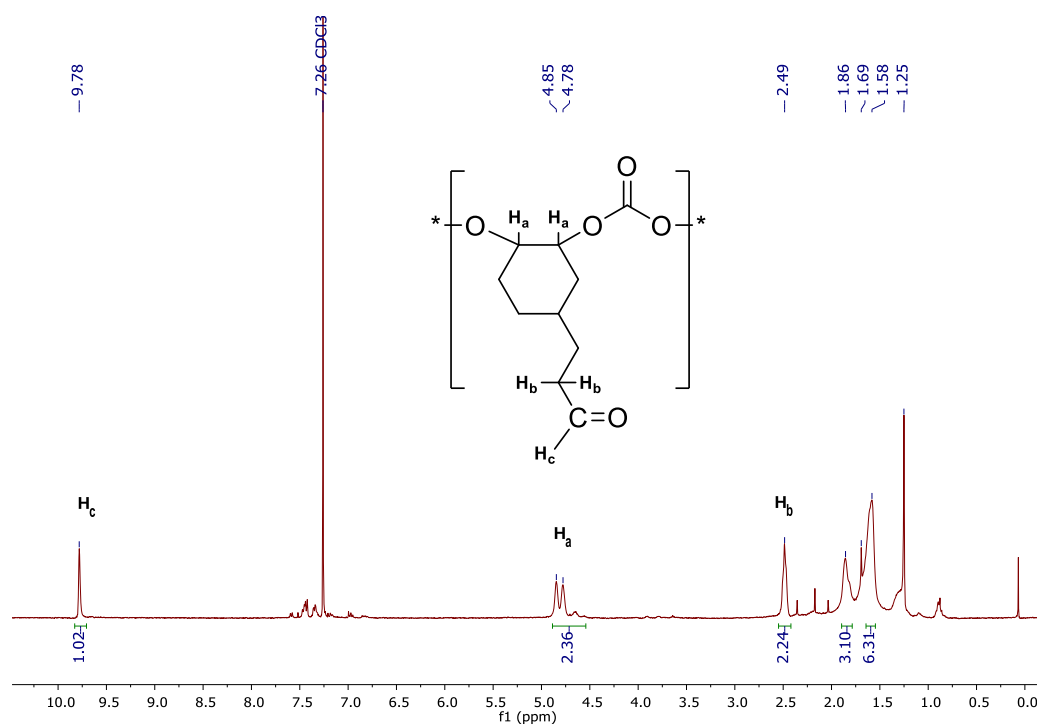


Figure S3 – ¹H NMR spectrum of 2-PS_A in CDCl₃ at 25 °C.

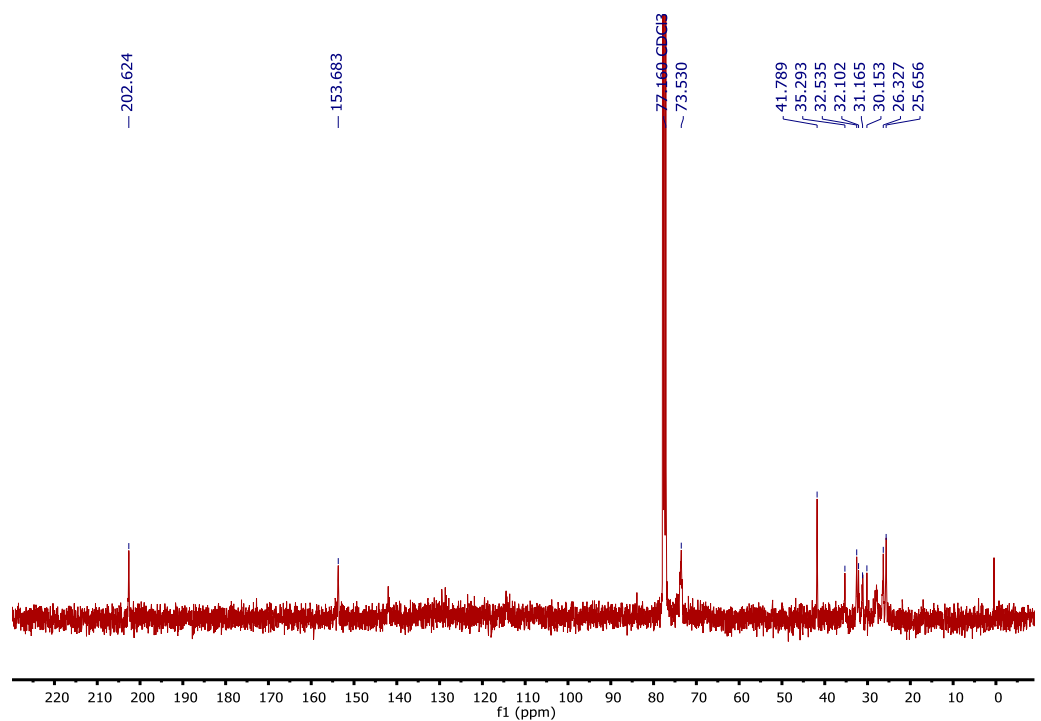


Figure S4 – ¹³C NMR spectrum of 2-PS_A in CDCl₃ at 25 °C.

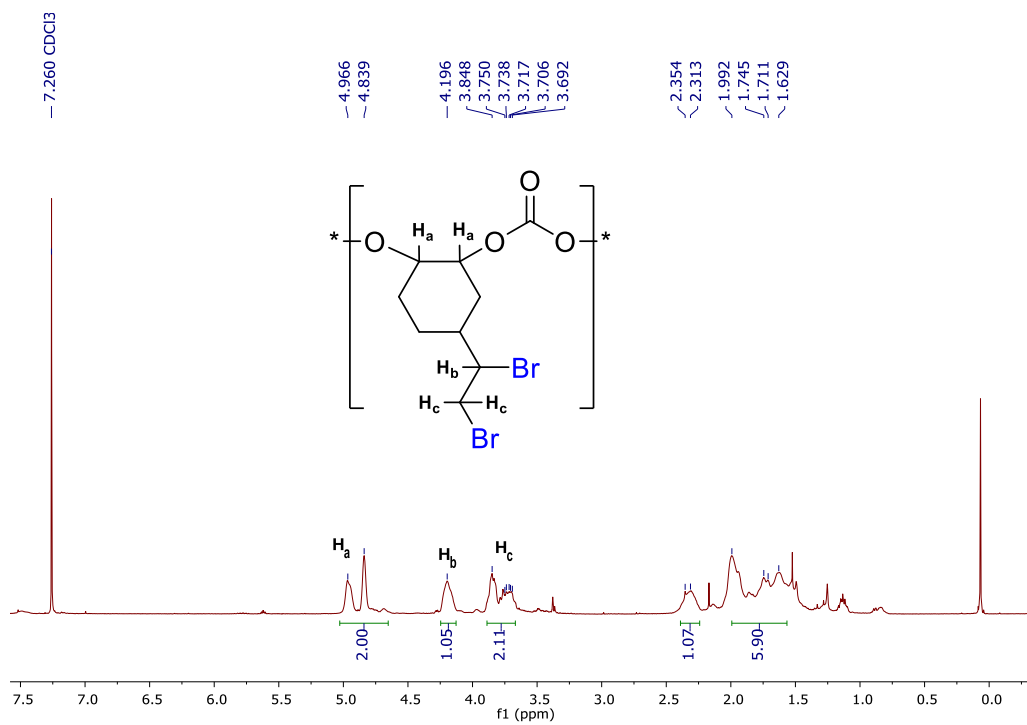


Figure S5 — ¹H NMR spectrum of **3-PS_A** in CDCl₃ at 25 °C.

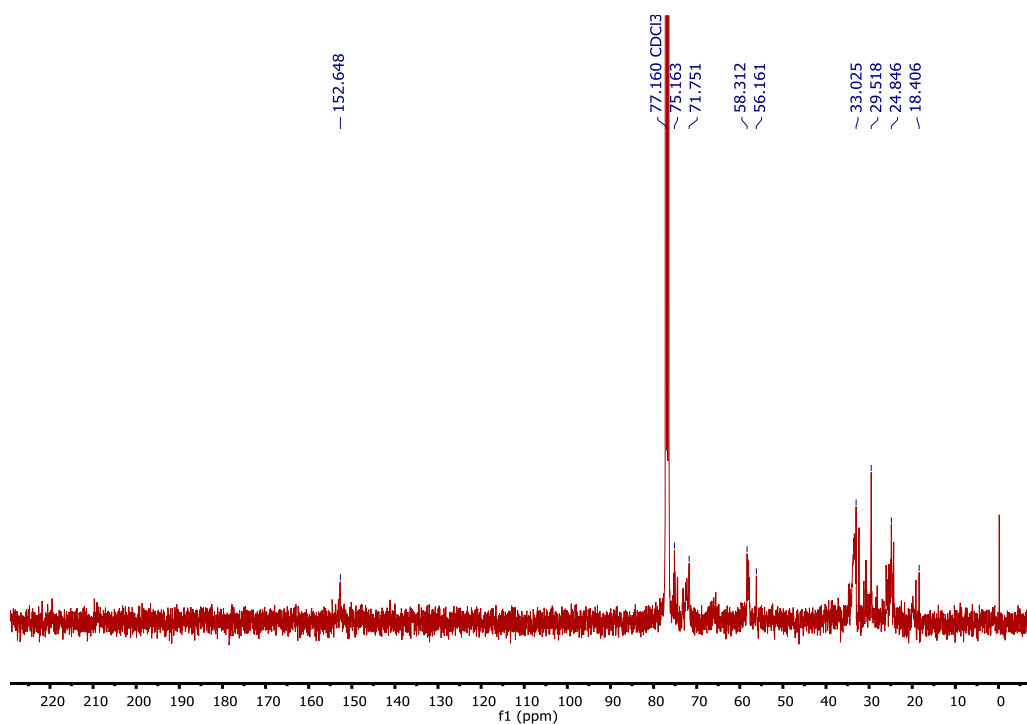
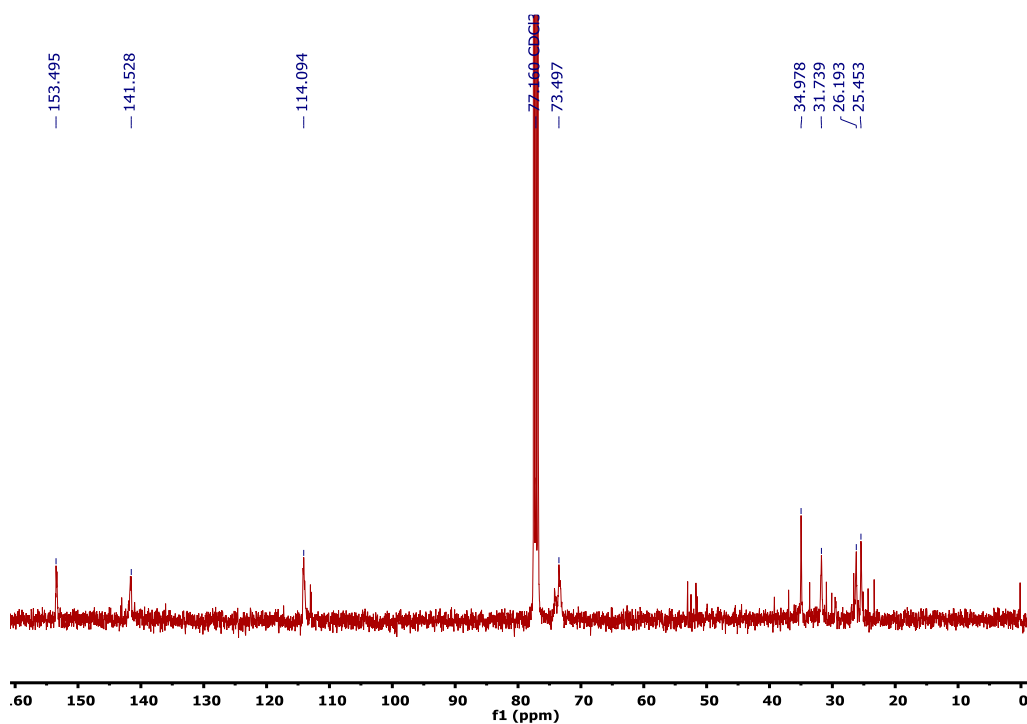
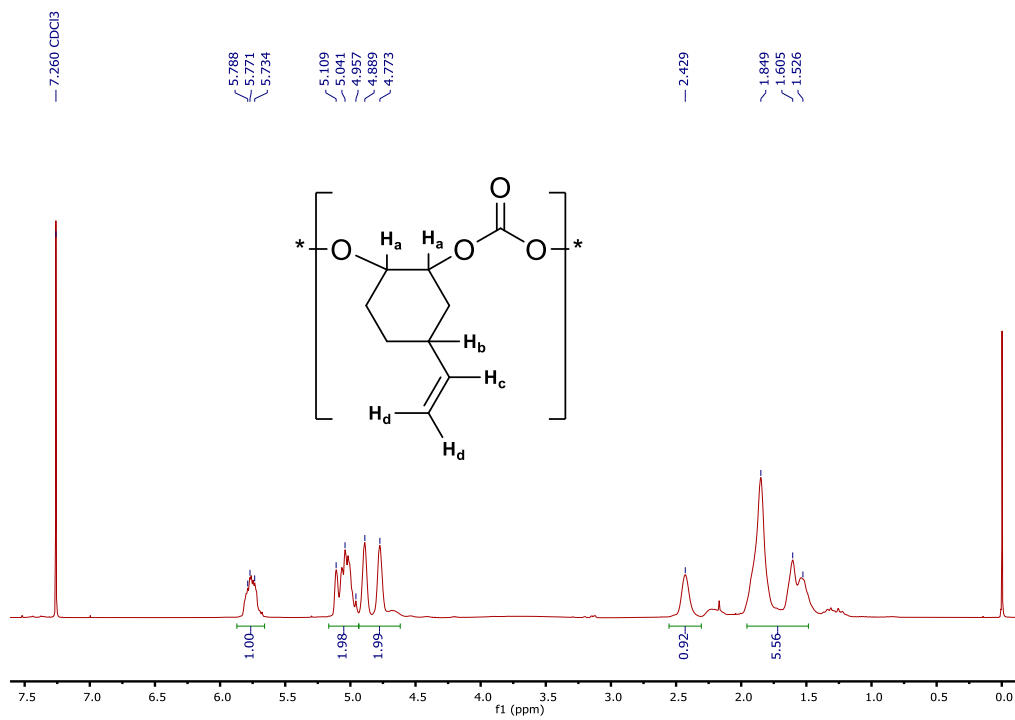


Figure S6 — ¹³C NMR spectrum of **3-PS_A** in CDCl₃ at 25 °C.



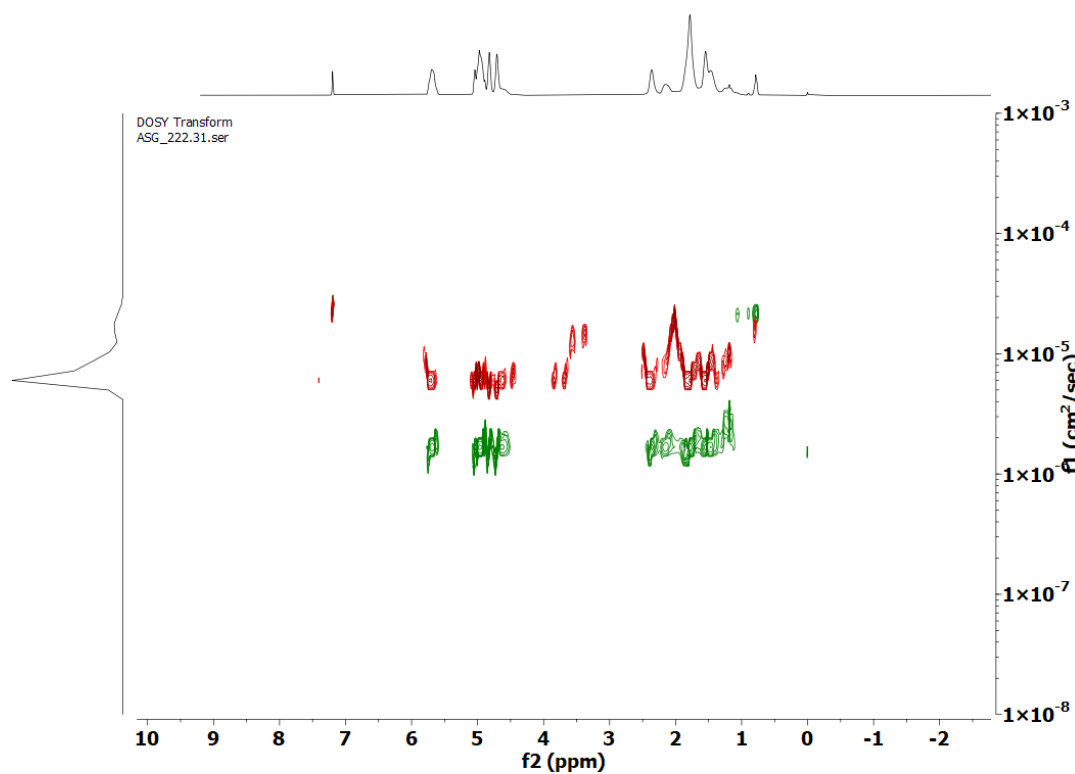


Figure S9 – ^1H NMR DOSY spectrum of **1-PS_A** (red) versus **1-PS_B** (green) in CDCl_3 at 25 °C.

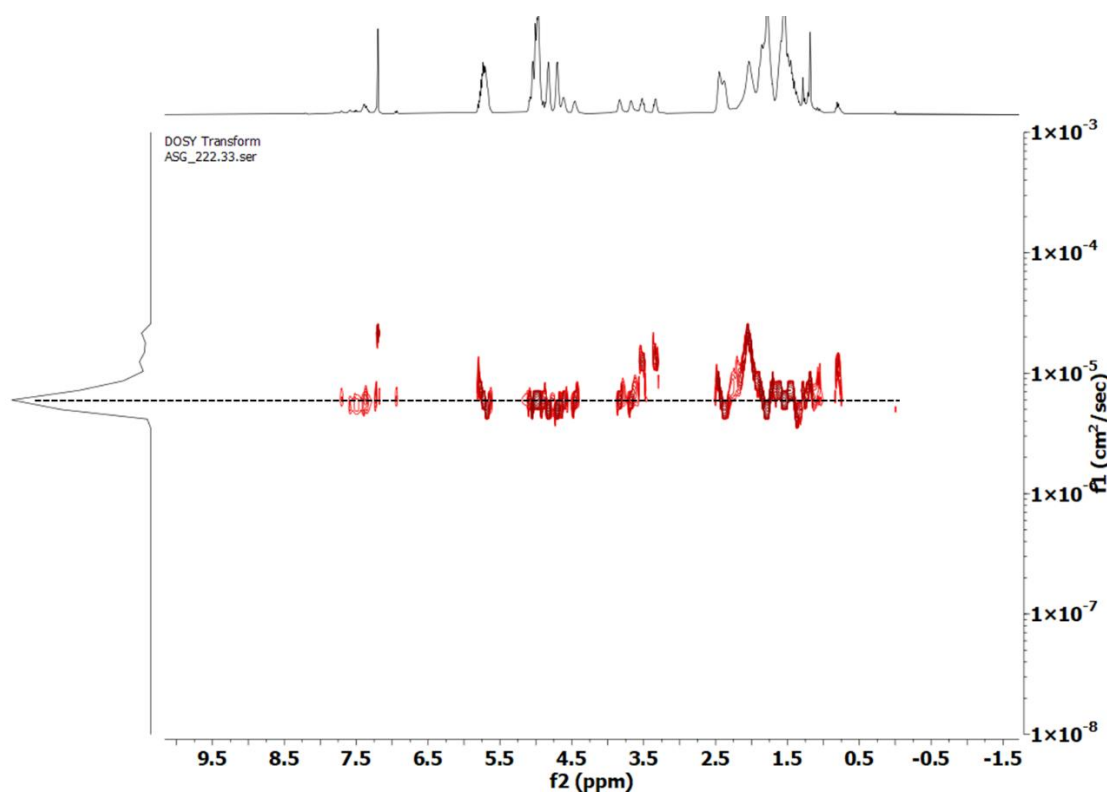


Figure S10 – ^1H NMR DOSY spectrum of **1-PS_A** + **PS_A** in CDCl_3 at 25 °C.

The signals assigned to the polycarbonate backbone ($\delta \approx 0.5\text{--}6.0$ ppm) and the aromatic protons assigned to PSA ($\delta \approx 6.5\text{--}8.5$ ppm) display the same diffusion coefficient ($D \approx 10^{-6}\text{--}10^{-5}$ $\text{cm}^2 \text{s}^{-1}$).

2. Size Exclusion Chromatography (SEC/GPC)

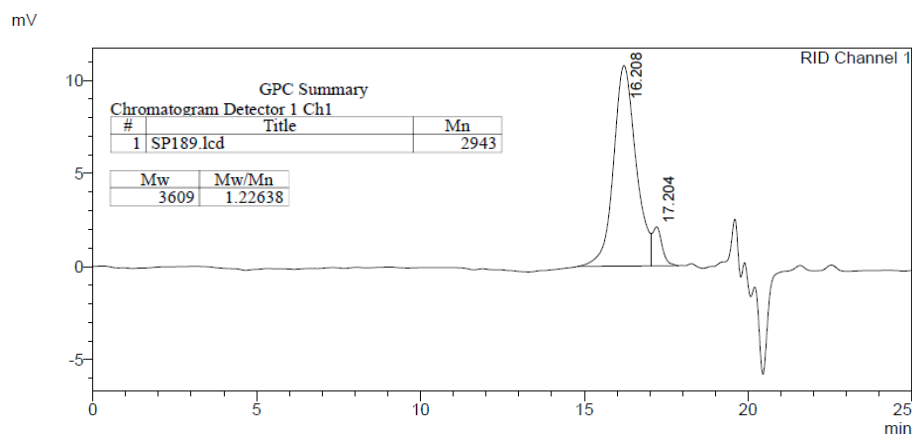


Figure S11 – SEC chromatogram of **1-PS_A** in THF, using a polystyrene standard.

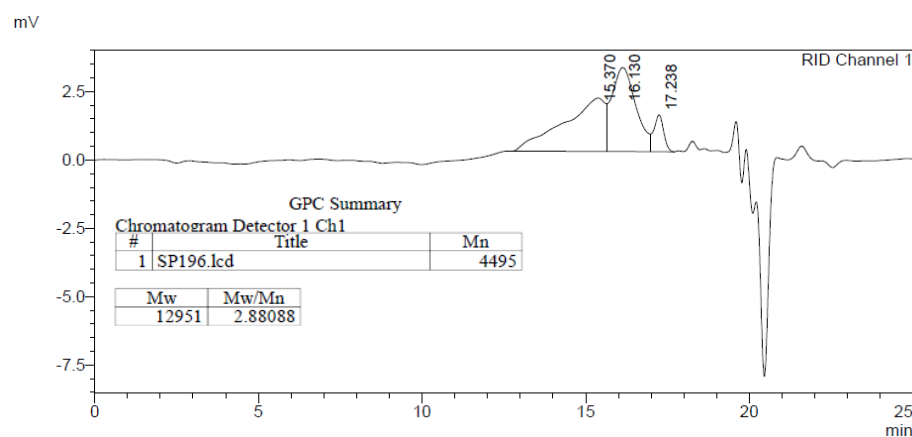


Figure S12 – SEC chromatogram of **2-PS_A** in THF, using a polystyrene standard.

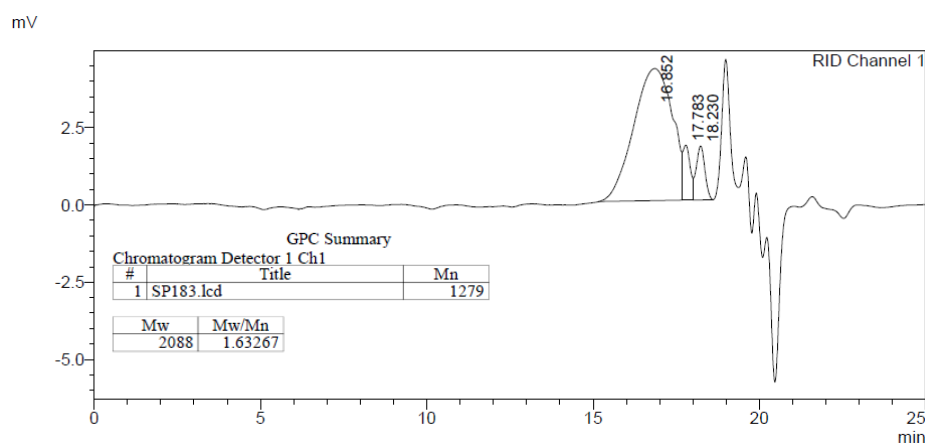


Figure S13 – SEC chromatogram of **3-PS_A** in THF, using a polystyrene standard.

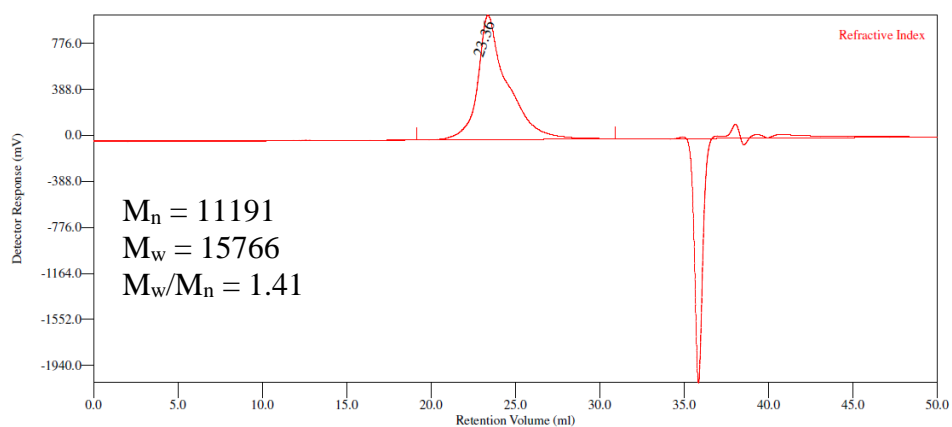


Figure S14 – SEC chromatogram of **1-PS_B** in THF, using a polystyrene standard.

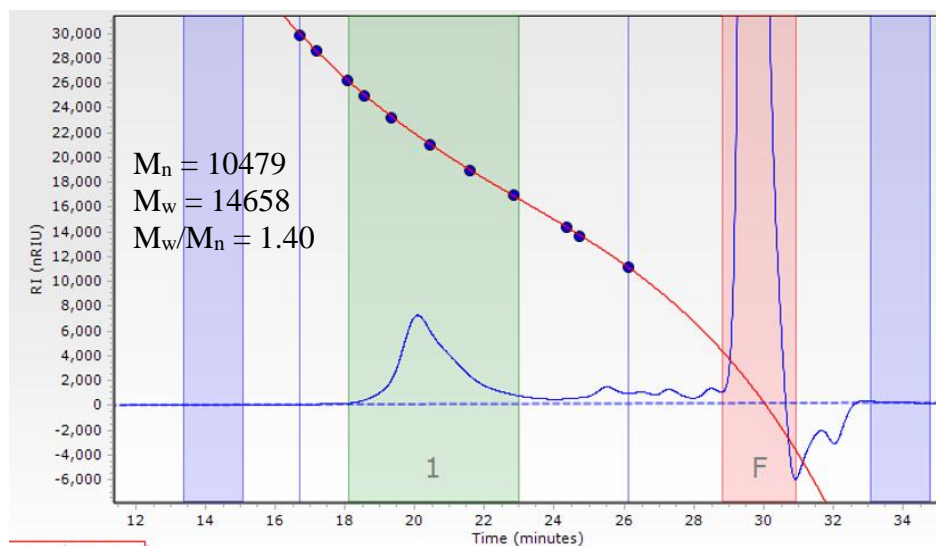


Figure S15 – SEC chromatogram of **3-PS_B** in THF, using a polystyrene standard.

3. Powder X-Ray Diffraction (XRD)

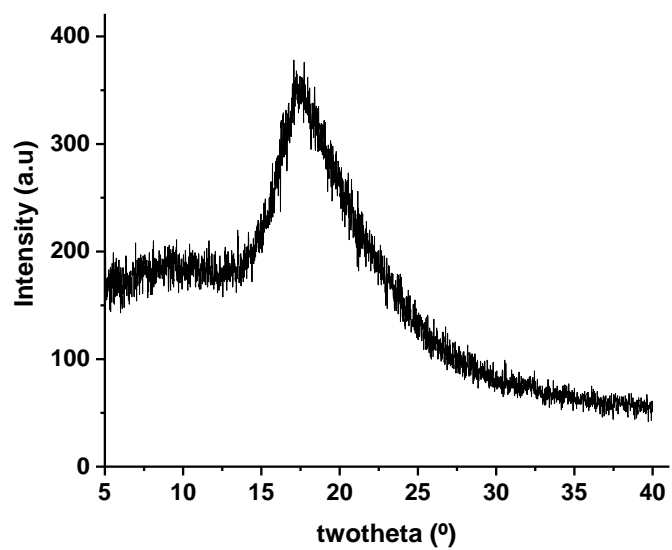


Figure S16 – XRD spectrum of 1-PS_A.

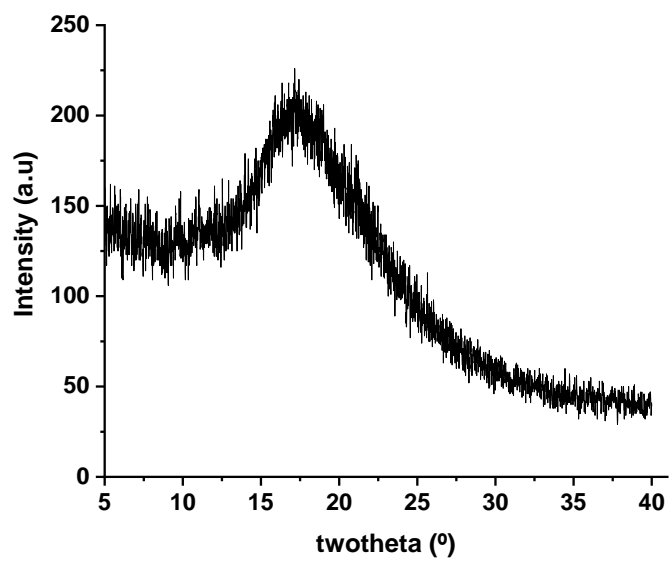


Figure S17 – XRD spectrum of 2-PS_A.

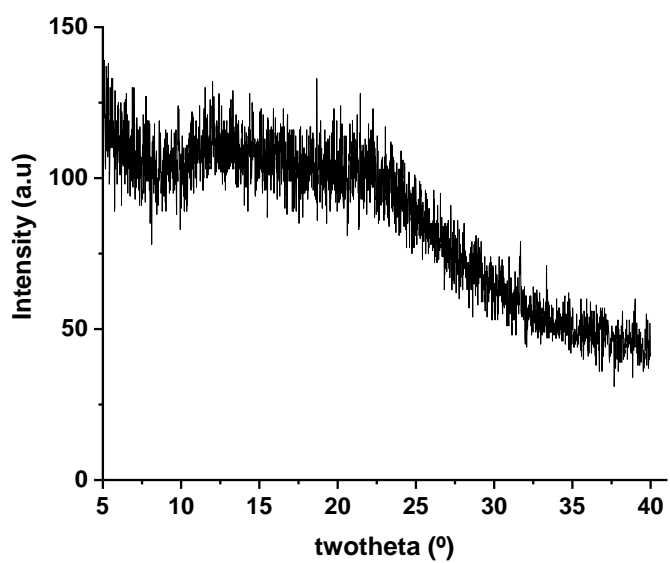


Figure S18 – XRD spectrum of **3-PS_A**.

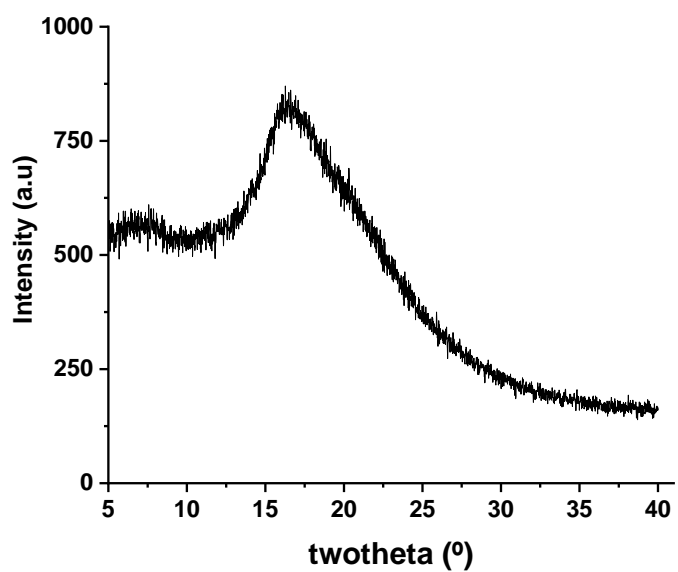


Figure S19 – XRD spectrum of **1-PS_B**.

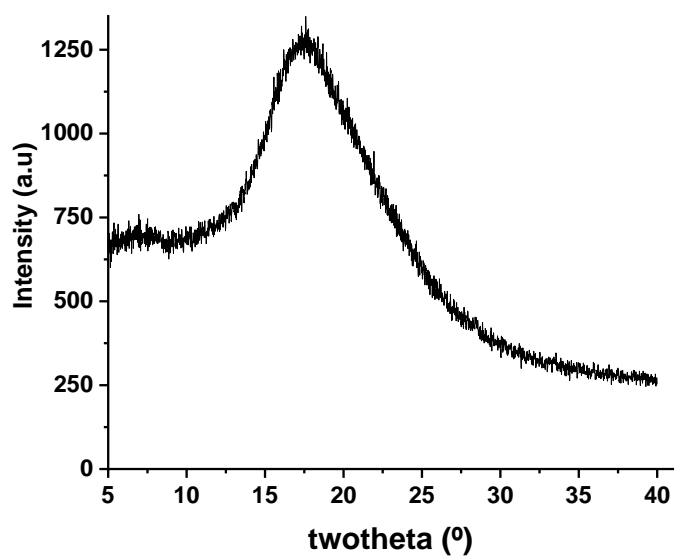


Figure S20 – XRD spectrum of 2-PS_B.

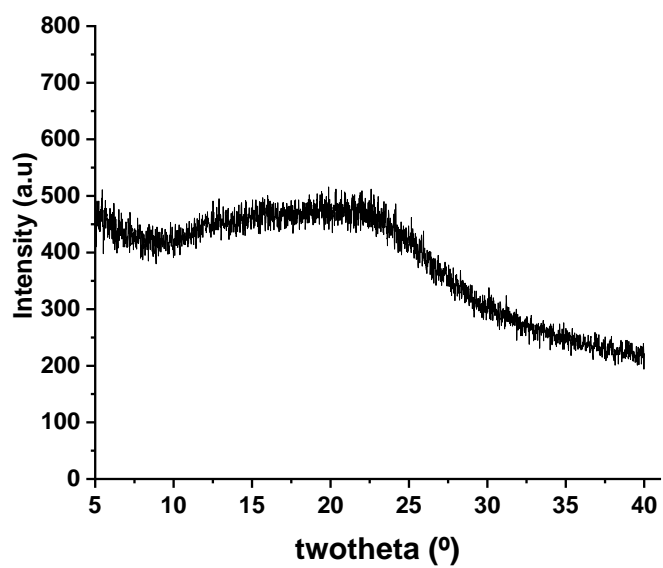


Figure S21 – XRD spectrum of 3-PS_B.

4. Fourier transform infrared spectroscopy (FTIR)

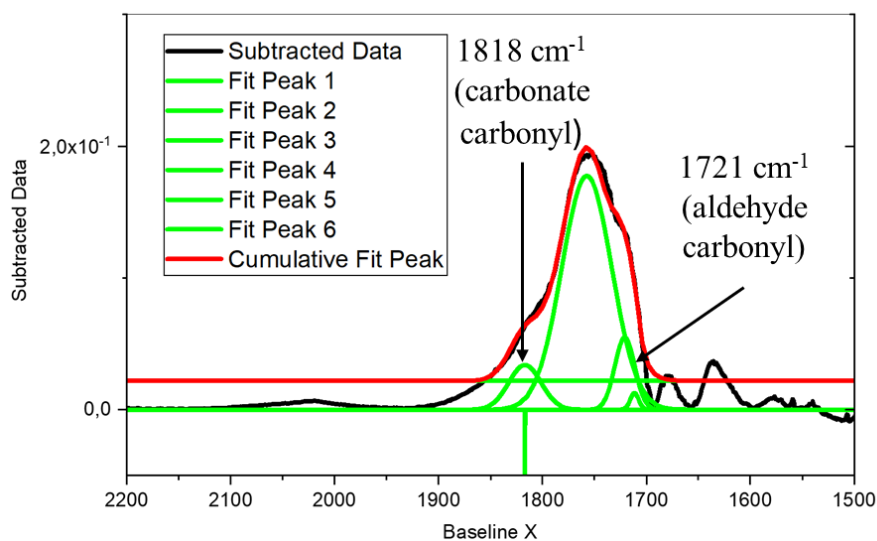


Figure S22 – FTIR spectrum deconvolution of the carbonyl region of **2-PS_A**.

5. MALDI-TOF Mass Spectrometry

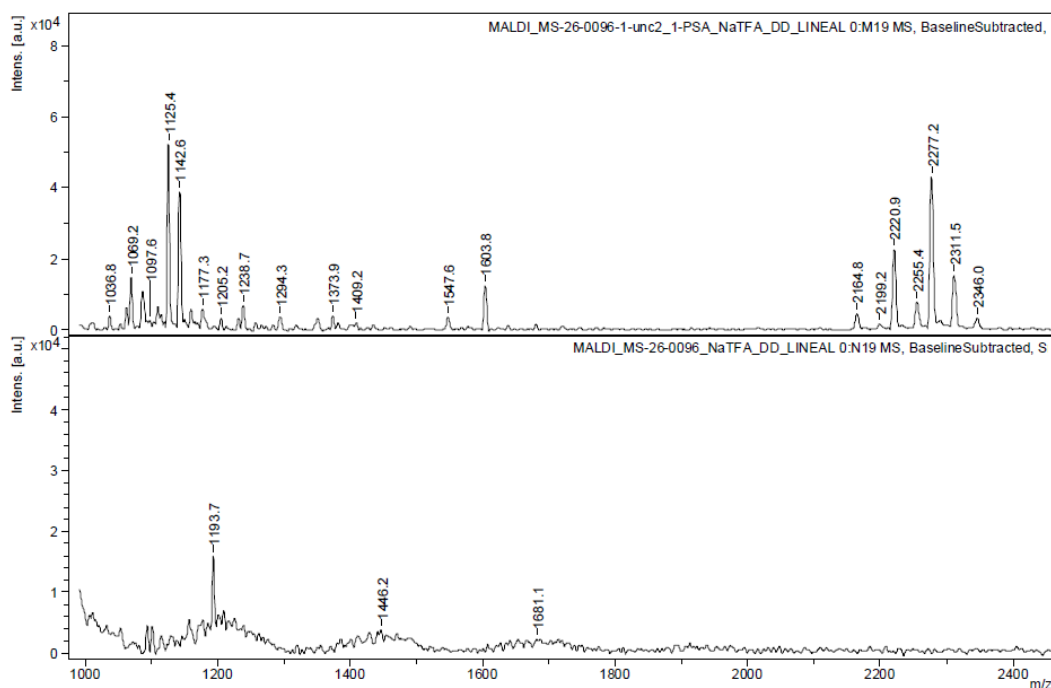


Figure S23 – MALDI-TOF MS spectrum of **1-PS_A**, recorded in positive ion mode using DIT (dithranol) as matrix and NaTFA (sodium trifluoroacetate) as cationization agent.

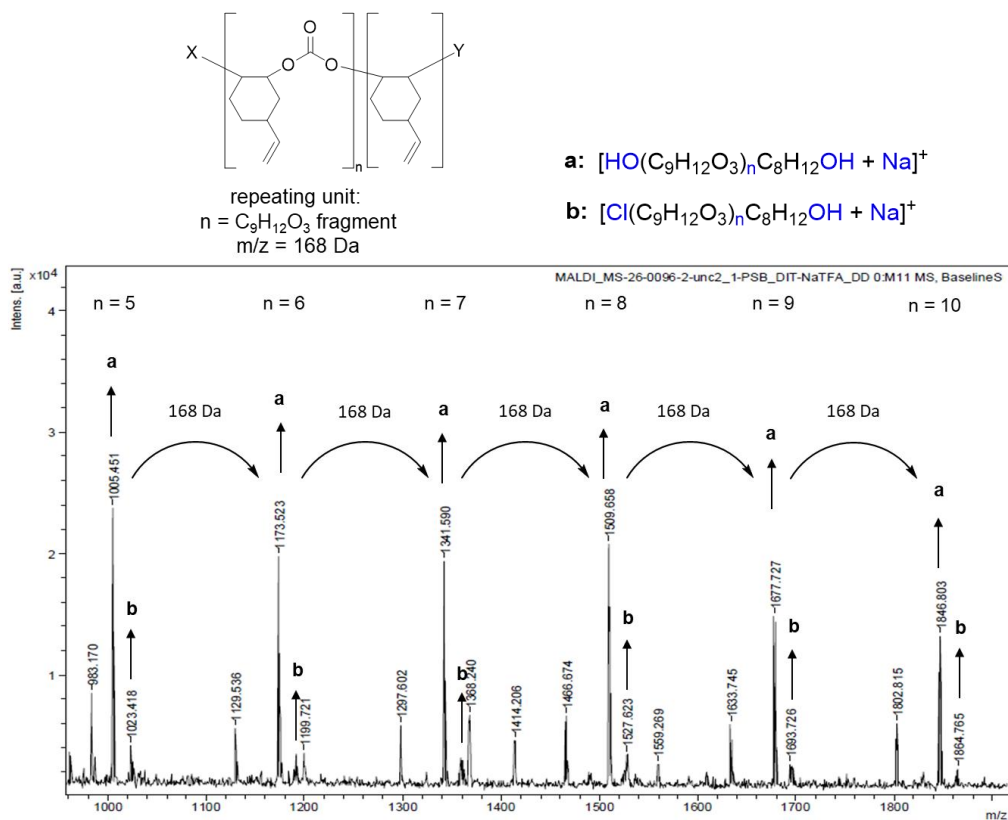
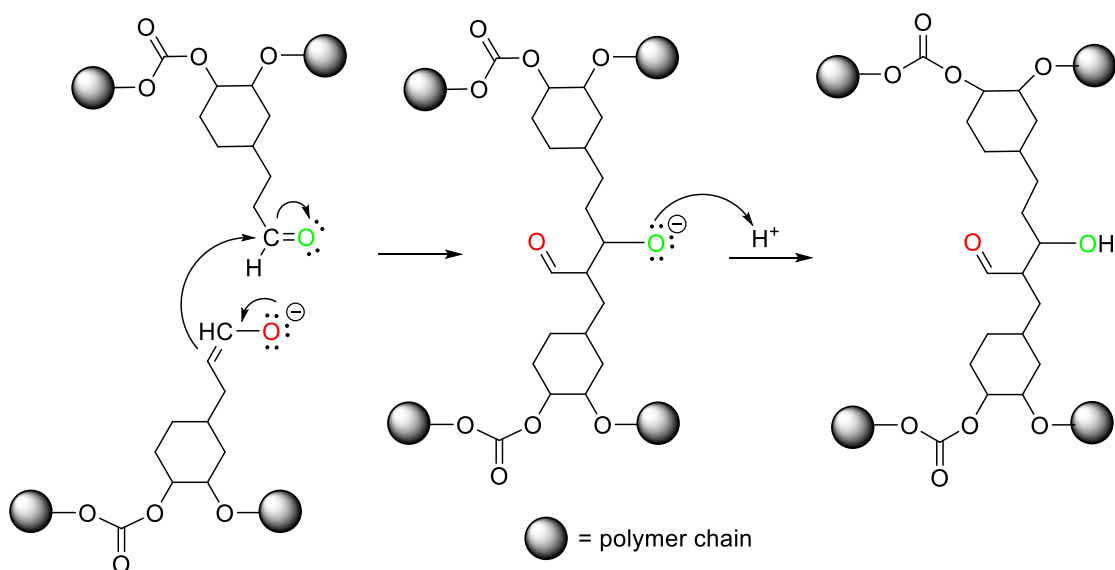


Figure S24 – MALDI-TOF MS spectrum of **1-PS_B**, recorded in positive ion mode using DIT dithranol) as matrix and NaTFA (sodium trifluoroacetate) as cationization agent.

6. Formation of cross-linked polycarbonate 2-PS_B



Scheme S1. Possible pathway for the formation of cross-linked aldehyde-functionalised polycarbonates.

7. Preparation of ethyl cellulose-polycarbonate biocomposite film

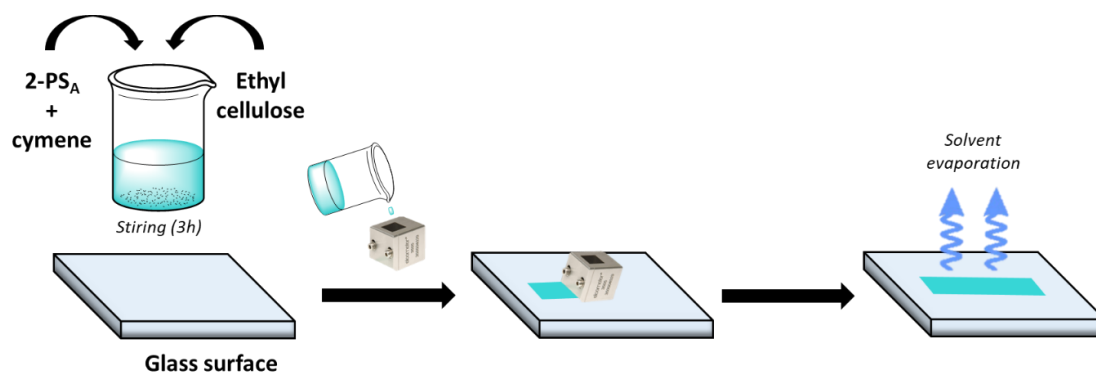


Figure S25. Preparation of ethyl cellulose-polycarbonate biocomposite 2-PS_A(15%)@EC.

8. Antimicrobial Photodynamic Inactivation (aPDI) studies

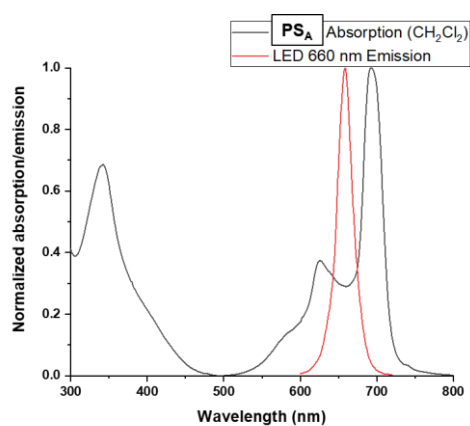
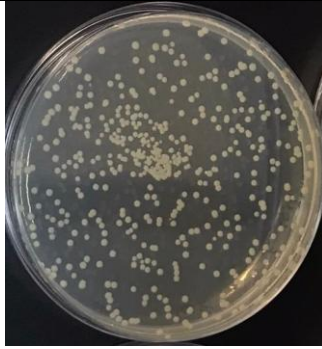


Figure S26. Overlap between 660 nm LED emission and PS_A absorption in CH₂Cl₂ solution.



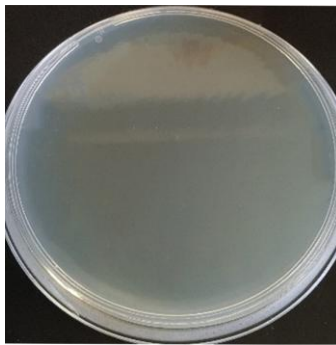
Figure S27. Photograph of a 96-well plate containing the samples 1-PS_A, 2-PS_A and 3-PS_A, upon exposure to *S. aureus* bacterial suspensions.



a) Ethyl cellulose (EC) without **2-PS_A**, after 120 min of irradiation, 49 J/cm² (with 100-fold dilution).



b) Biocomposite **2-PS_A(15%)@EC** after 120 minutes of dark incubation (With 100-fold dilution)



c) Biocomposite **2-PS_A(15%)@EC** after 120 minutes of irradiation – 49 J/cm² (Without inoculum dilution)

Figure S28. Representative pictures of Petri dishes obtained for surviving CFU counting in *S. aureus* photoinactivation assays.