

Supplementary materials

“Sunlight bleaching of subporphyrazine dye films”

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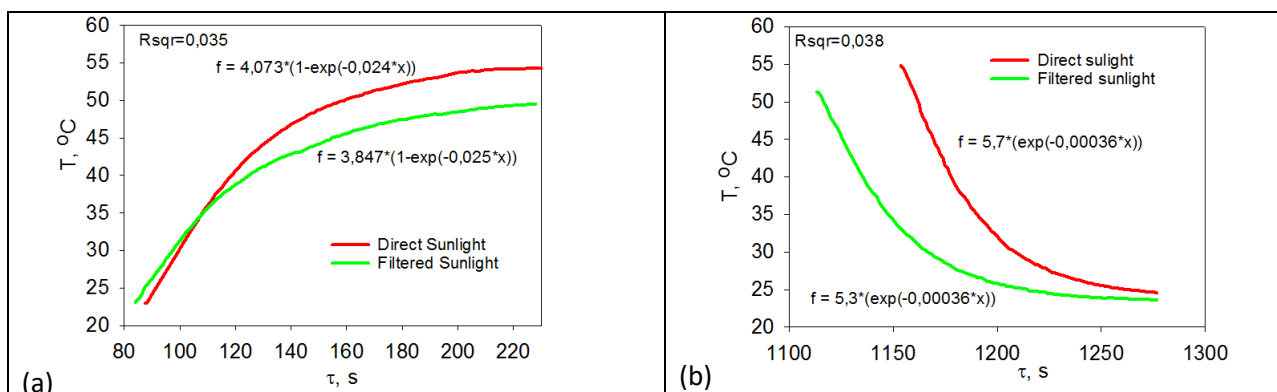


Figure S1. Initial sections of the ‘temperature vs time’ dependence: (a) light-On and (b) light-Off (direct sunlight). R_{sqr} – correlation coefficient.

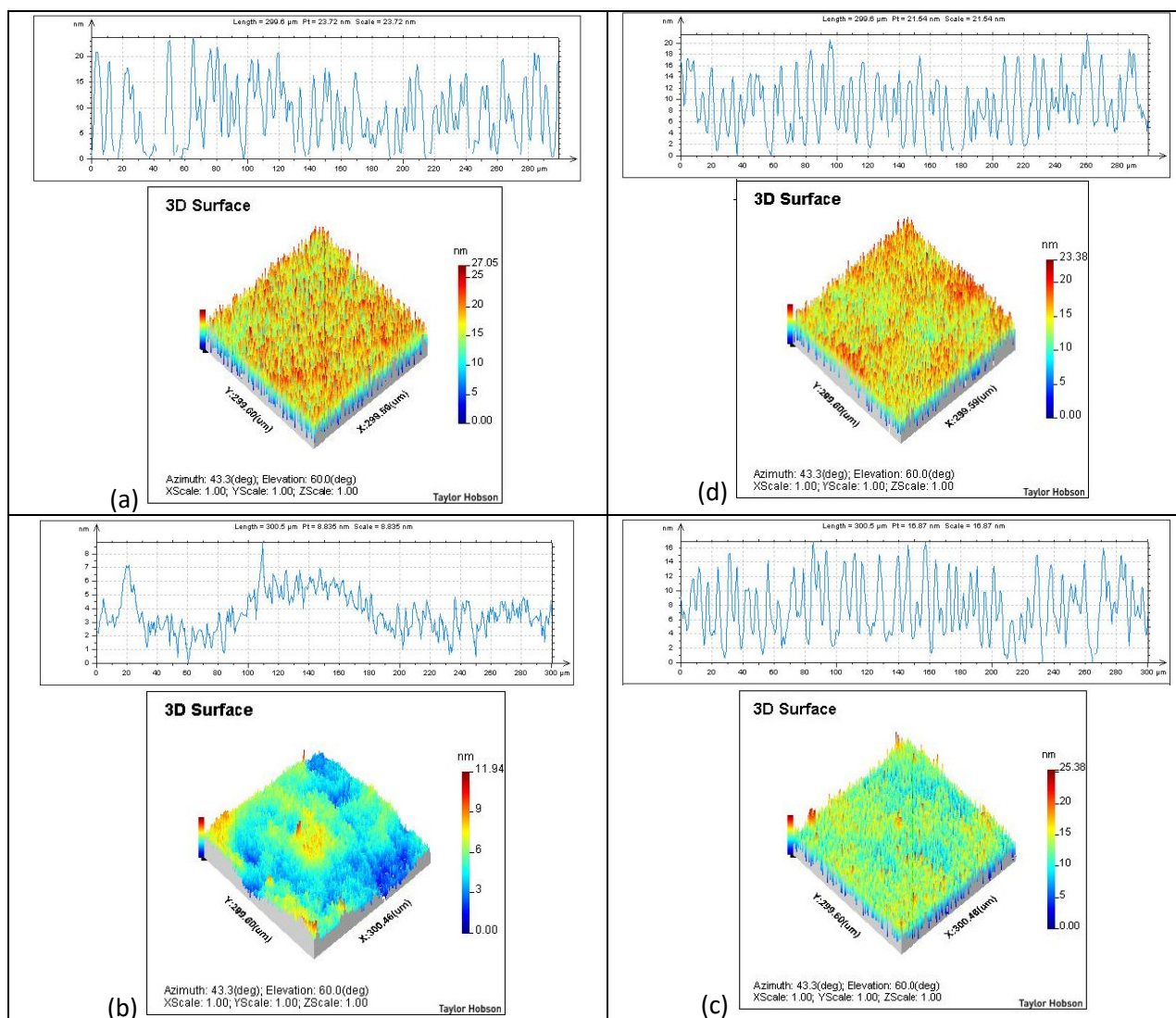


Figure S2. Cross-sectional profiles and 3D surface maps of V-metallized SubPzS₃H₆ films on glass, scanning area 0.3×0.3 mm²: pristine film (a) and films irradiated by the direct sunlight in Ar (b), filtered sunlight in Ar (c), and filtered sunlight in air (d).

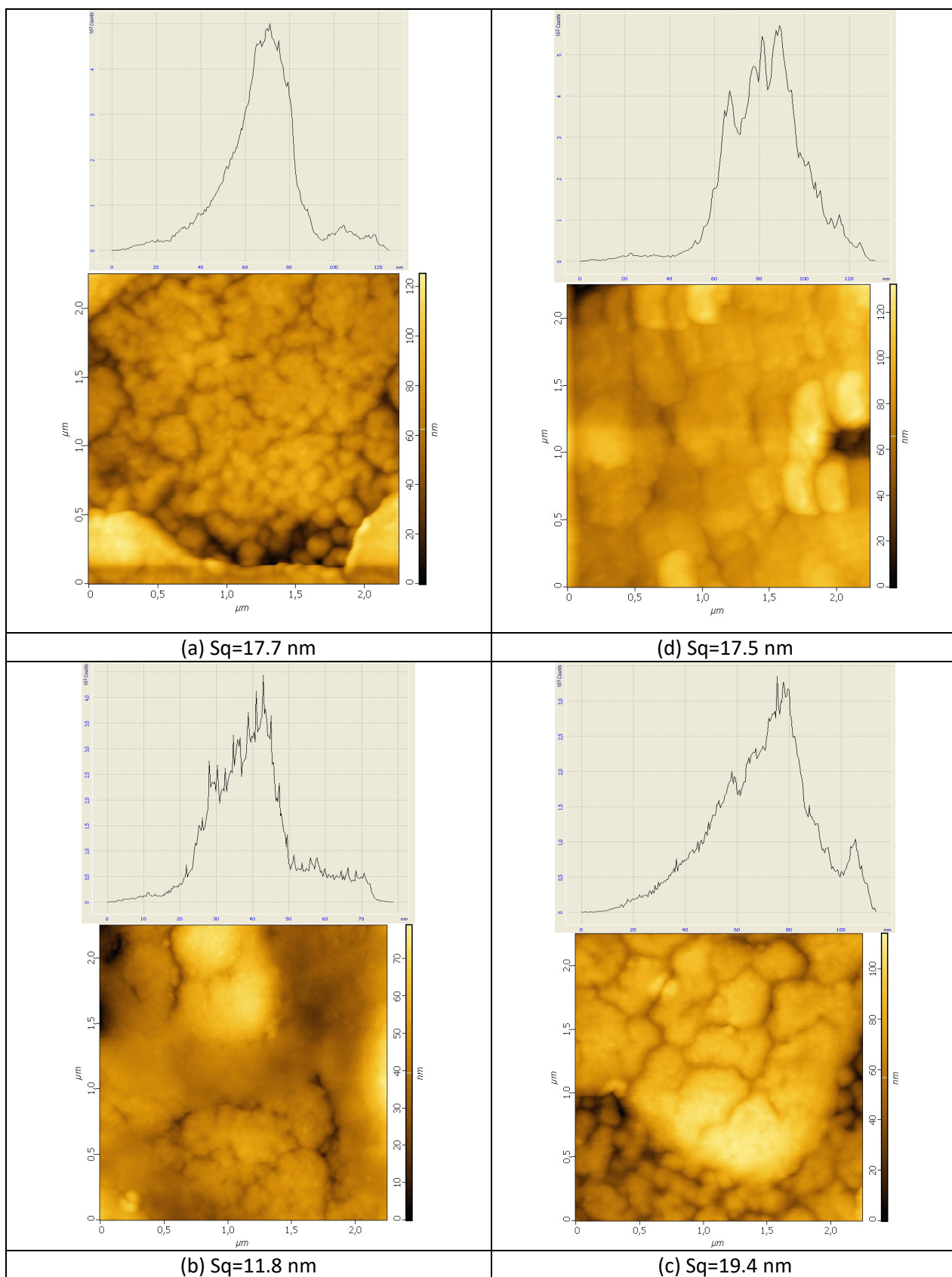


Figure S3. Height distribution (top panels) and 2D-images (bottom panels) of V-metallized SubPzS₃H₀ films **on glass**: pristine film (a) and films irradiated by the direct sunlight in Ar (b), filtered sunlight in Ar (c), and filtered sunlight in air (d).

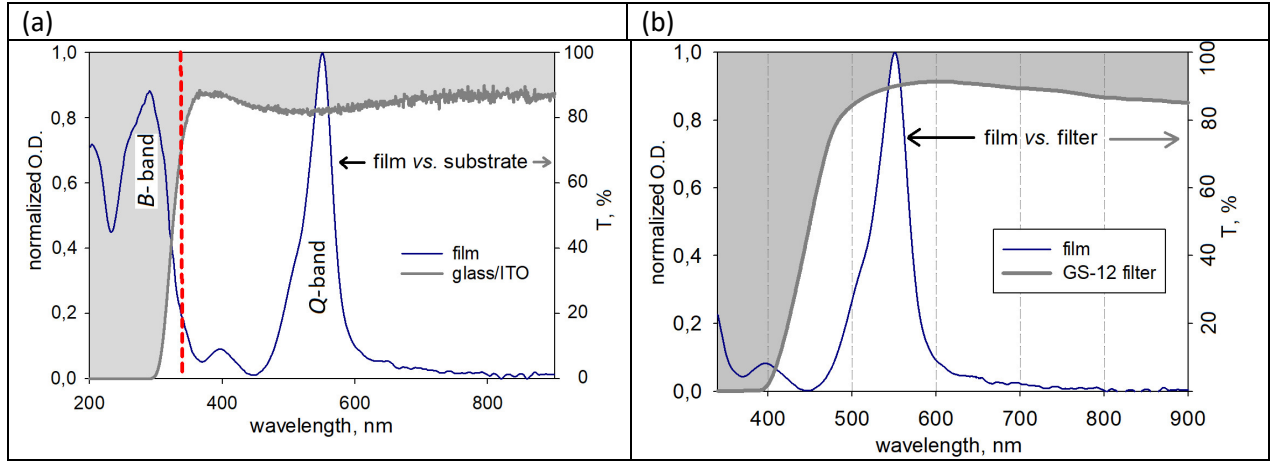
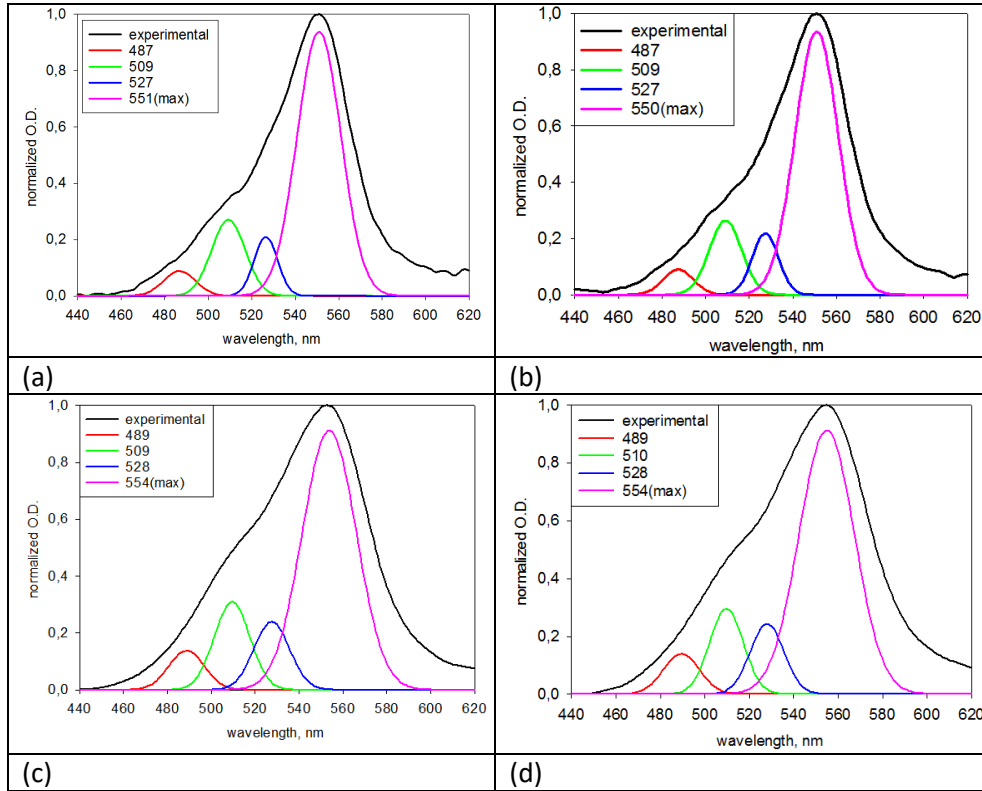


Figure S4. (a) Absorption spectrum of the SubPzS₃H₀ film in the UV/Vis/NIR range and transmission of the glass/ITO substrate (red dashed line).

(b) Absorption spectrum of the SubPzS₃H₀ film from Figure 4(a) and transmission of the GS-12 optical filter in the visible/NIR range. Filter cuts off the wavelengths <400 nm, while in the area of Q-band its transparency is better than 90%. The AM1.5G simulated sunlight has a shortwave limit at ~300 nm.



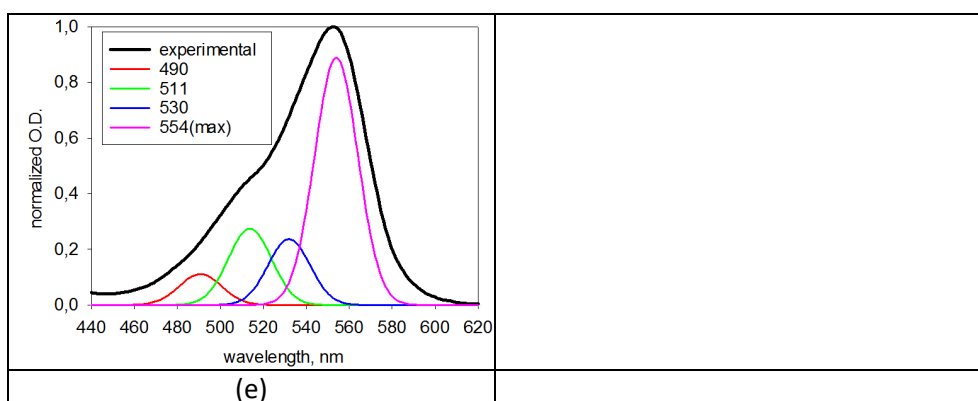


Figure S5. Deconvolution of the Q-band in the spectrum of the SubPzS₃H₀ film **on glass** exposed to direct (a) and filtered (b) sunlight in air; direct (c) and filtered sunlight in argon (d); direct sunlight in synthetic air (e).

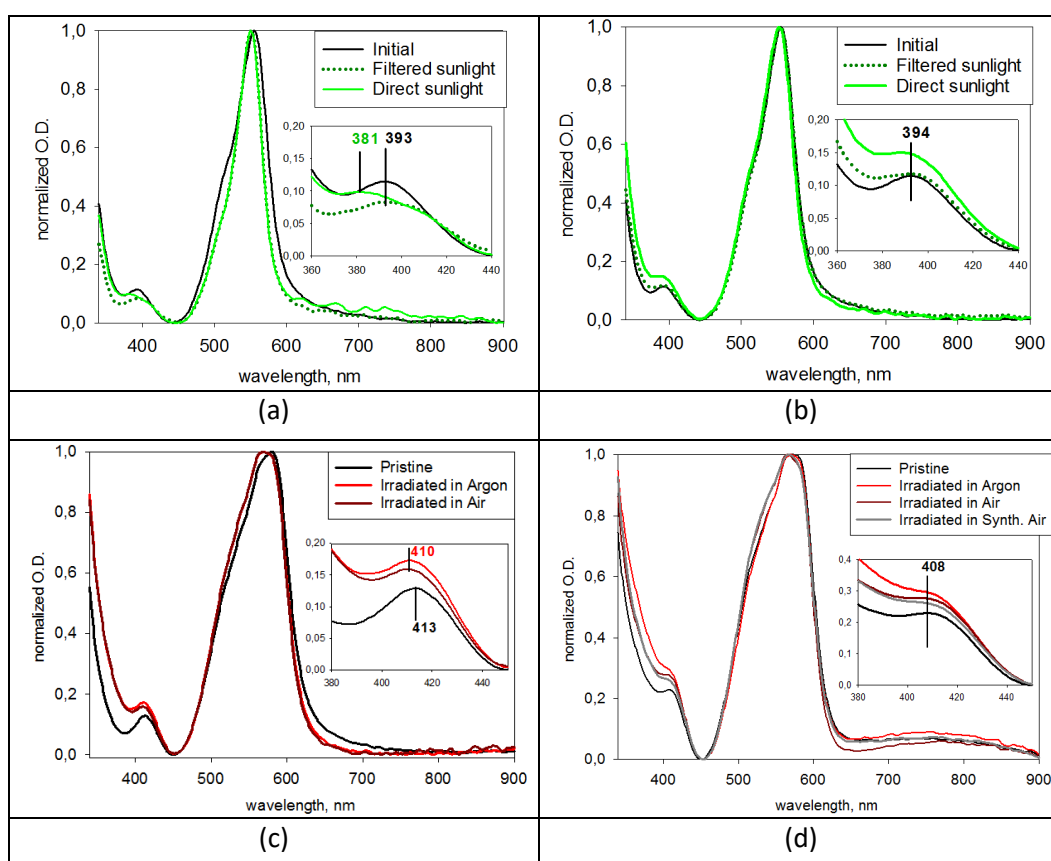
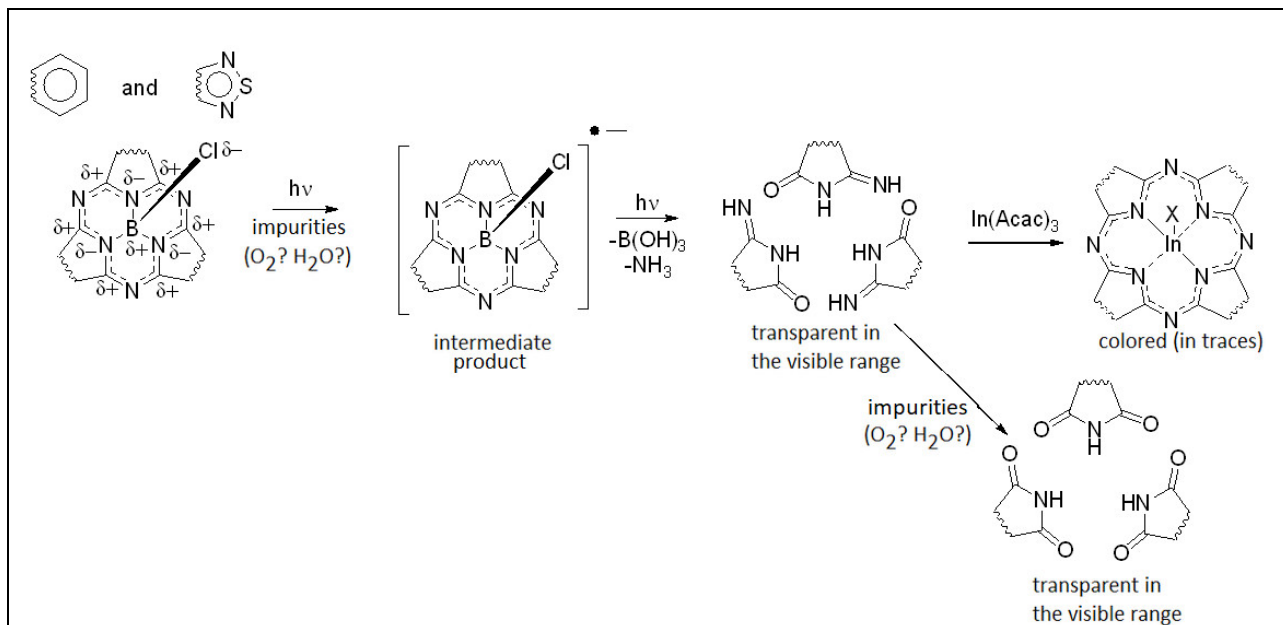
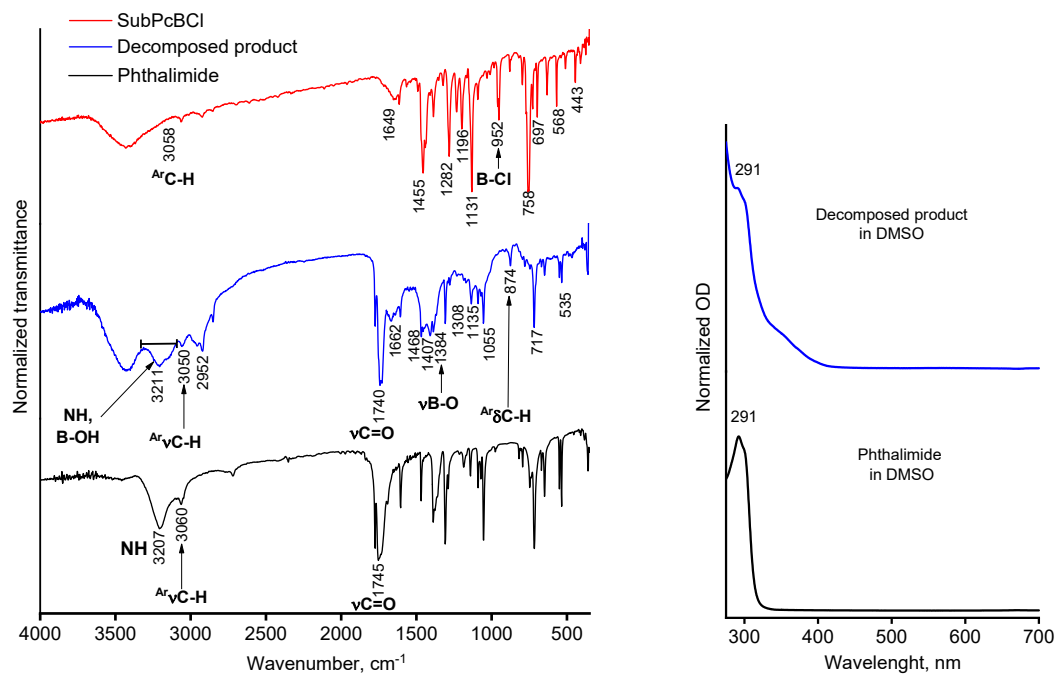


Figure S6. Normalized absorption spectra of SubPzS₃H₀ (a,b) and SubPzS₂H₄ (c,d) films: Before (black curves) and after exposure to the filtered (solid green curves) or direct (dotted green curves) sunlight in air (a) and argon (b) – all **on glass** substrate; Before (black curves) and after exposure to the direct sunlight in air (red curves) and argon (dark red curves) – **on glass** (c) and **on ITO** (d) substrate.



(a)



(b)

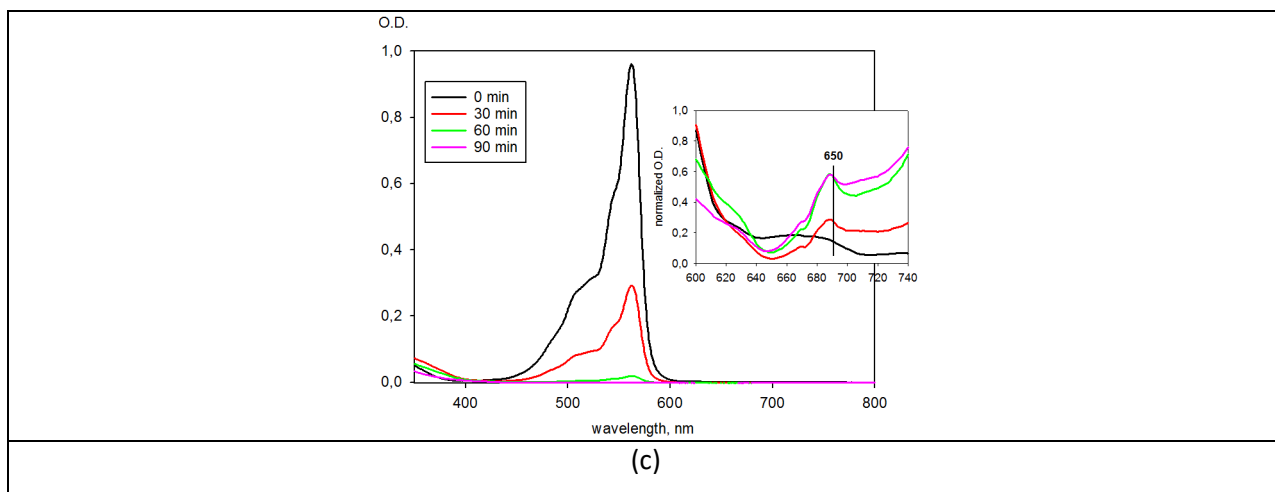


Figure S7. (a) Scheme of photodestruction of SubPc/SubPz induced by UV-light (tentative) and possible tetramerization.

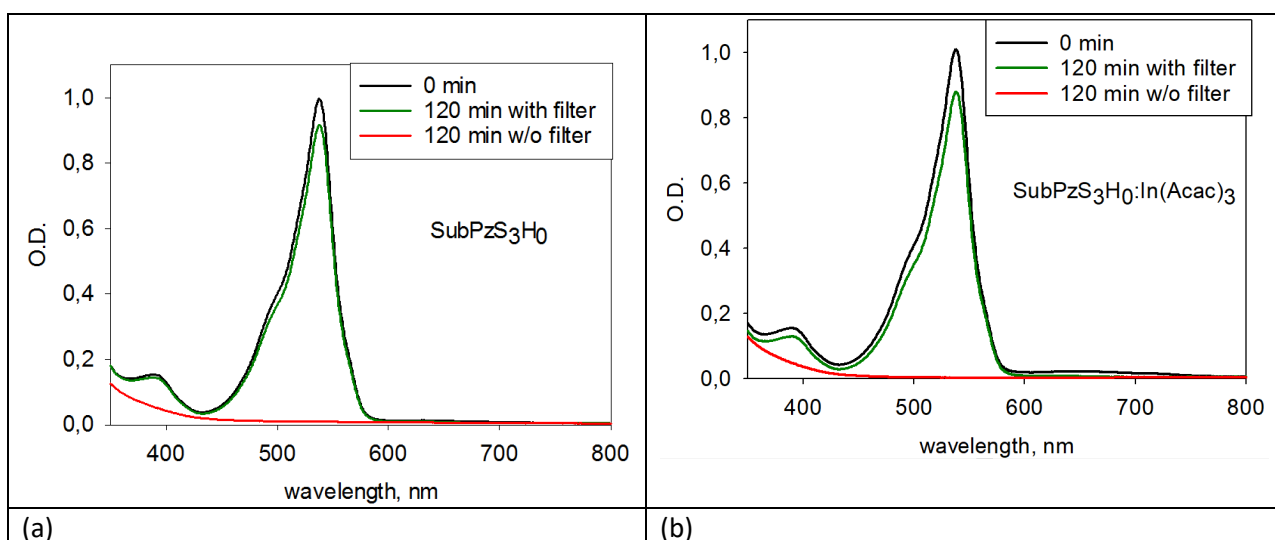
(b) FT-IR spectra of SubPcS₀H₁₂, decomposition product and phthalimide in the KBr pellets (left); and UV/Vis spectra of decomposition product and phthalimide in the DMSO solution (right).

(c) Time-resolved UV/Vis spectra of SubPzS₀H₁₂ solution in acetone in the presence of In(Acac)₃ before (black) and after (red, green, pink) direct illumination in argon (inset - 600-760 nm region, normalized).

Comment:

Presumably, the photobleaching proceeds in several stages: nucleophile attack of boron and/or α -carbon atoms in the photoexcited molecule by impurities; ring opening and subsequent decomposition with the formation of the products which are transparent in the visible range, such as boronic acid and phthalimide and/or 4H-pyrrolo[3,4-c][1,2,5]thiadiazole-4,6(5H)-dione.

Spectra of irradiated acetone solutions of SubPcS₃H₀ (Figure 6(b)) or SubPzS₀H₁₂ (Figure S7(c)) containing pre-added indium ions show appearance of new, very weak band(s) in the region of 600-800 nm. Formation of the colored products can be explained, with a great caution, by coordination of end-products to the metal ion (templating), a well-known process that usually yields four-leaf, brightly colored tetrapyrrolic heterocycles.



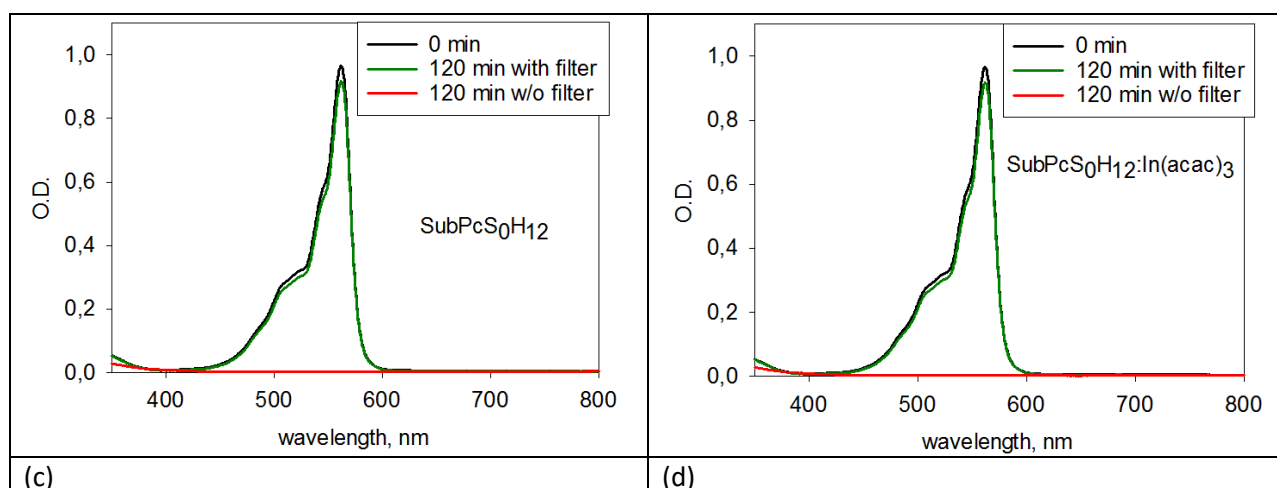


Figure S8. Spectra of SubPzS₃H₀ (a,b) and SubPcS₀H₁₂ (c,d) solutions in acetone before and after irradiation during 2h without and with the UV-filter and without (a,c) or with (b,d) In(Acac)₃.

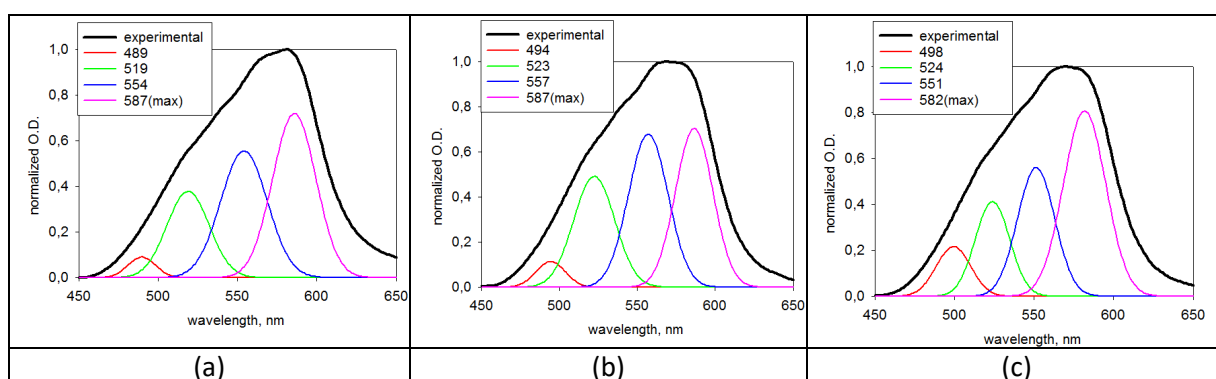


Figure S9.I. Deconvolution of Q-band in the spectrum of SubPzS₂H₄ film on glass: initial (a) and exposed to direct sunlight in air (b) and in argon (c).

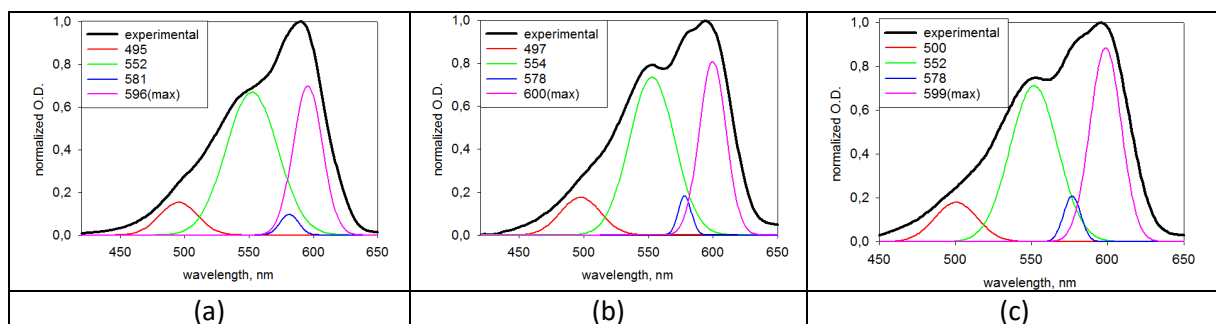


Figure S9.II. Deconvolution of Q-band in the spectrum of SubPcS₀H₁₂ film on glass: initial (a) and exposed to direct sunlight in air (b) and in argon (c).

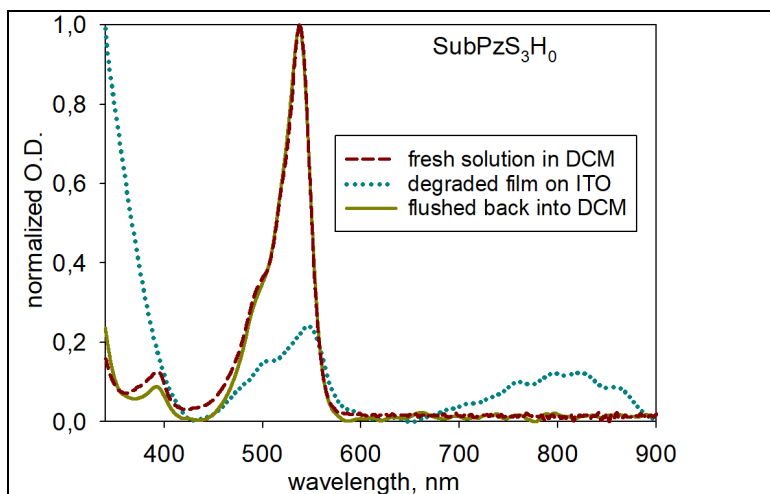


Figure S10. Comparison of spectra of freshly made SubPzS₃H₀ solution in DCM (dashed), film after irradiation treatment in air (dotted) and the solution made by flashing this film back into DCM.

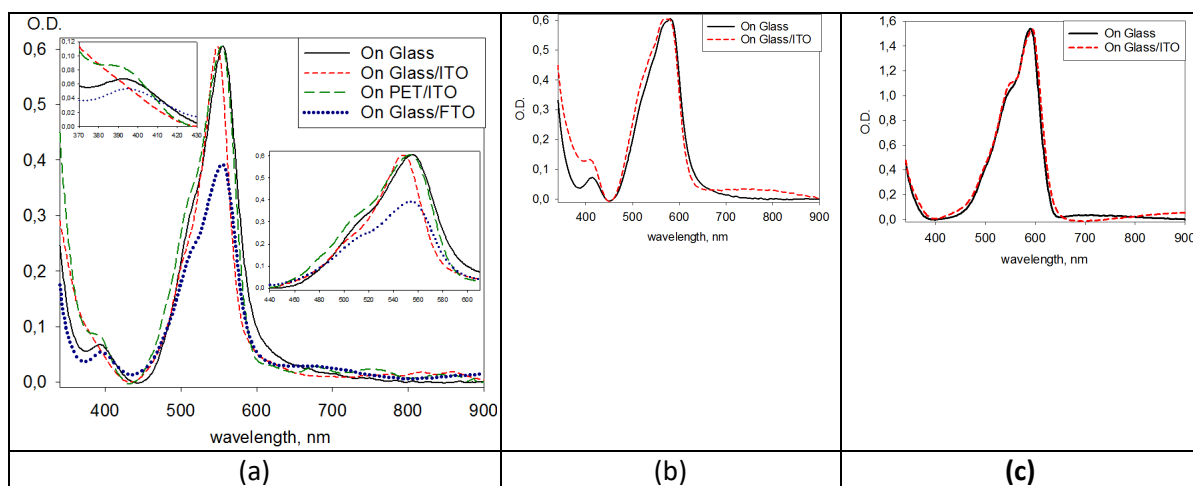
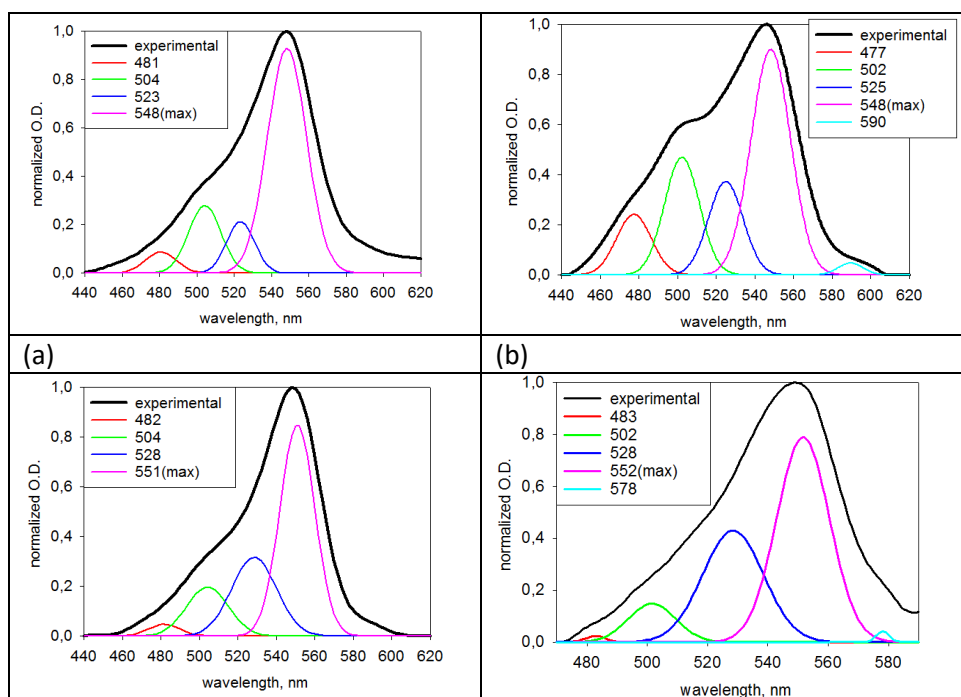


Figure S11. Absorption spectra of films deposited on various substrates (a) SubPzS₃H₀, (b) SubPzS₂H₄, (c) SubPcS₀H₁₂.



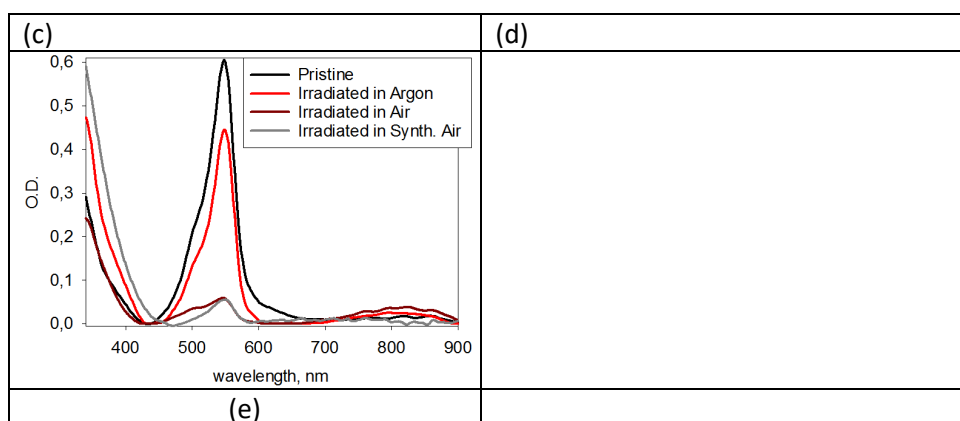


Figure S12.I. Deconvolution of Q-band in the spectrum of **SubPzS₃H₀** film on glass/ITO initial (a) and exposed to direct sunlight: in air (b), in argon (c), in synthetic air (d); comparison of all spectra (e).

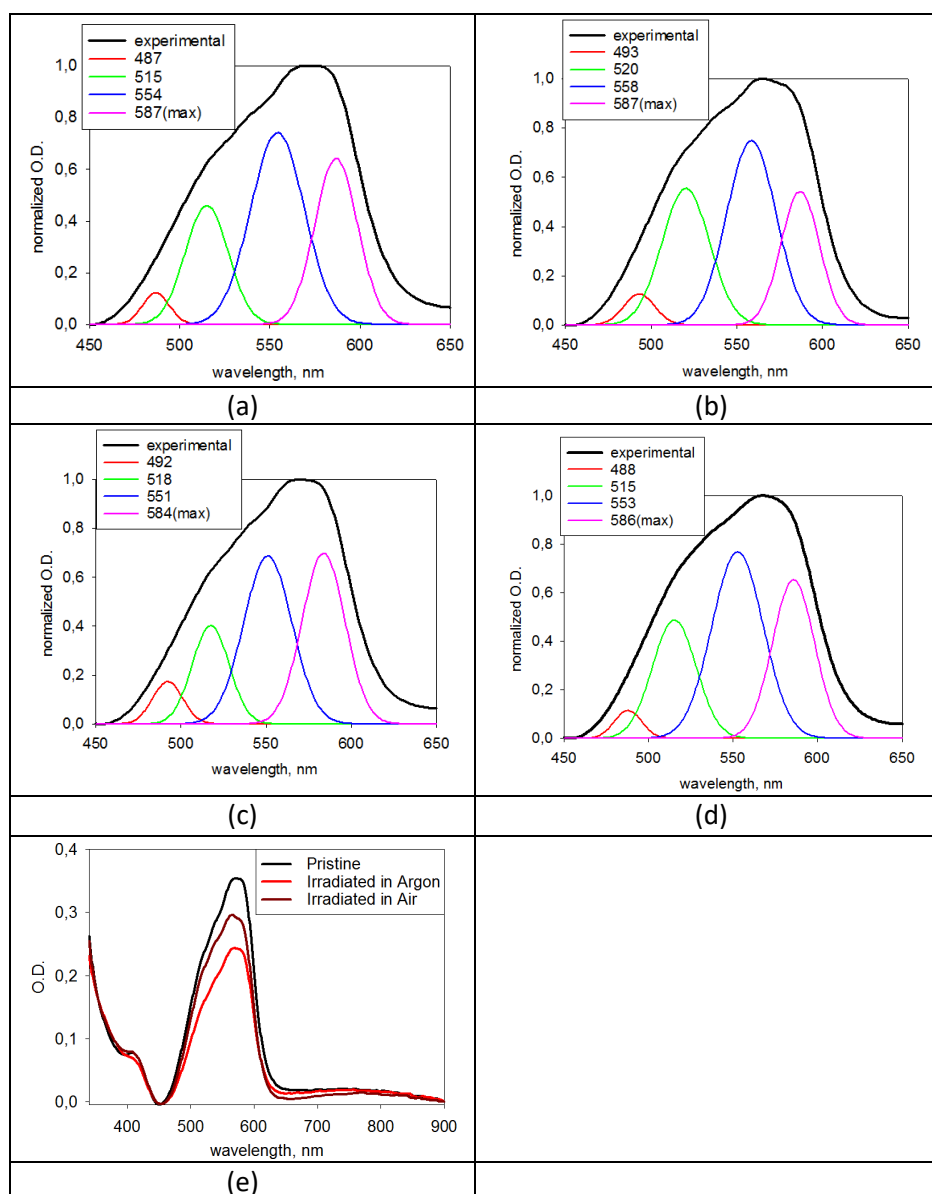


Figure S12.II. Deconvolution of Q-band in the spectrum of **SubPzS₂H₄** film on glass/ITO initial (a) and exposed to direct sunlight: in air (b), in argon (c); in synthetic air (d); comparison of all spectra (e).

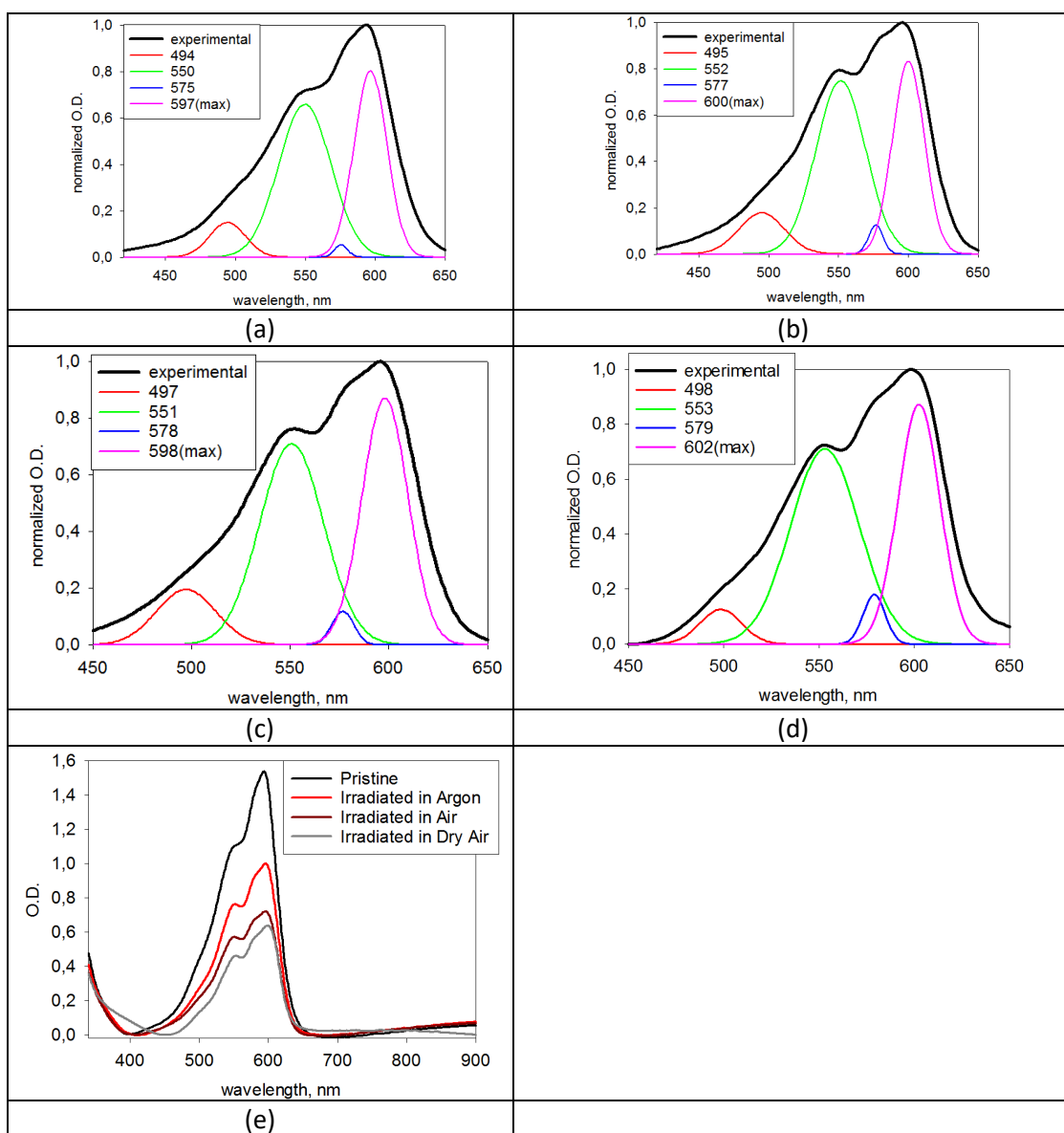


Figure S12.III. Deconvolution of *Q*-band in the spectrum of **SubPcS₀H₁₂** film on glass/ITO initial (a) and exposed to direct sunlight: in air (b), in argon (c); in synthetic air (d); comparison of all spectra (e).

Table S1.

The relative intensities of subpeaks according to the deconvolution results in Figures S5, S9, S12, S13.

Substrate →		Glass				Glass/ITO				PET/ITO		
	Peak	Initial	Ar	Dry Air	Air	Initial	Ar	Dry Air	Air	Initial	Ar	Air
SubPzS ₃ H ₀	P1	0.14	0.15	0.13	0.09	0.09	0.06	0.03	0.27	0.17	0.14	0.27
	P2	0.38	0.34	0.31	0.27	0.31	0.23	0.19	0.52	0.43	0.46	0.48
	P3	0.23	0.26	0.27	0.24	0.28	0.37	0.54	0.41	0.34	0.23	0.25
	P4	1	1	1	1	1	1	1	1	1	1	1
	P5	-	-	-	-	-	-	0.05	0.05	0.02	0.09	0.09
SubPzS ₂ H ₄	P1	0.22	0.27	-	0.16	0.19	0.25	0.17	0.23	-	-	-
	P2	0.53	0.51	-	0.70	0.72	0.58	0.75	1.02	-	-	-
	P3	0.77	0.69	-	0.97	1.16	0.98	1.18	1.38	-	-	-
	P4	1	1	-	1	1	1	1	1	-	-	-
	P5	-	-	-	-	-	-	-	-	-	-	-
SubPcS ₀ H ₁₂	P1	0.22	0.20	-	0.22	0.19	0.23	0.15	0.21	-	-	-
	P2	0.96	0.80	-	0.91	0.82	0.82	0.82	0.90	-	-	-
	P3	0.14	0.24	-	0.23	0.07	0.12	0.21	0.15	-	-	-
	P4	1	1	-	1	1	1	1	1	-	-	-
	P5	-	-	-	-	-	-	-	-	-	-	-

P4 – the main subband, P1,P2,P3,P5 – subbands in Figures S5, S9, S12, S13, from left to right; green color – increased intensity, red color – decreased intensity, relative to the initial intensity value before light exposure

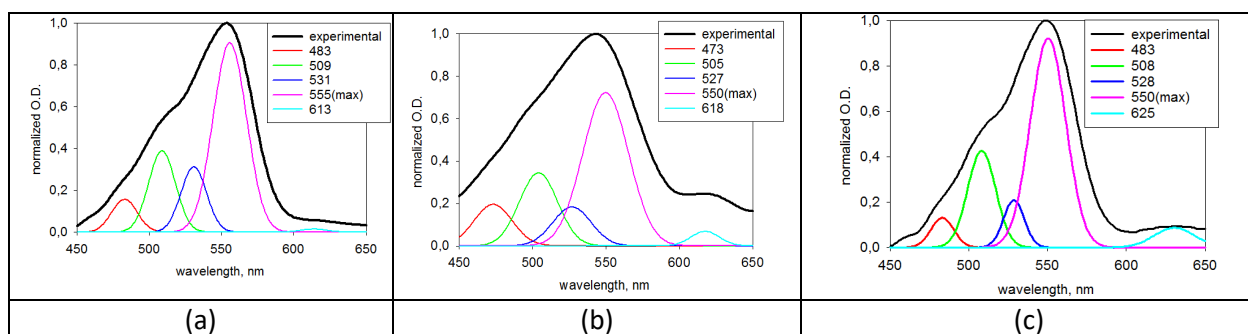


Figure S13. Deconvolution of *Q*-band in the spectrum of **SubPzS₃H₀** film on **PET/ITO** initial (a) and exposed to direct sunlight: in air (b), in argon (c).