Electronic Supplementary Information

Colorimetric 3D printable base-detectors exploiting halocromic core-substituted naphthalenediimides

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Material and Method: supporting information

Table S1. *DLP 3D-printing parameters for P575, P575_NDI-OH, and B_NDI-OH formulations.*

Formulation	Range name	Number of layers (-)	Layer thickness (mm)	Light intensity (mW cm^{-1})	Radiation time (s)
P575 **P575_NDI-OH**	BURN IN	2	0.1	40.00	5.0
	RANGE 1	To complete the sample	0.1	40.00	4.0
B_NDI-OH	BURN IN	2	0.1	30.00	10.0
	RANGE 1	To complete the sample	0.1	30.00	5.0

For multi-material samples, printer parameters had to be modified. This was also necessary for complex hollow geometry in order to improve printing fidelity to the cad model. The geometries and their parameters are described in Table S2.

Table S2. *DLP-3D Printing parameters for multi-material samples or characterized by a complex geometry.*

Sample geometry	Range name	Formulation	Number of layers (-)	Layer thickness (mm)	Light Intensity (mW cm^{-1})	Radiation time (s)
Honeycomb	BURN IN	P575_NDI-OH	2	0.1	40.00	5.0
	RANGE 1		46	0.1	40.00	2.5
Hollow cube	BURN IN	P575_NDI-OH	2	0.1	40.00	5.0
	RANGE 1		63	0.1	40.00	3.0
	RANGE 2		3	0.2	48.36	0.7
	RANGE 3		2	0.2	30.00	2.5
Smart lid	BURN IN	P575_UV	2	0.1	40.00	5.0
	RANGE 1		8	0.1	40.00	4.0
	RANGE 2	P575_NDI-OH	10	0.1	40.00	4.0
	RANGE 3	P575_UV	>10	0.1	40.00	4.0
Smart fluidic	BURN IN	P575_UV	2	0.1	40.00	5.0
	RANGE 1		2	0.1	40.00	4.0
	RANGE 2	P575_NDI-OH	2	0.1	40.00	7.0
	RANGE 3	P575_UV	15	0.1	40.00	4.0
	RANGE 4		3	0.1	30.00	3.5
	RANGE 5		3	0.1	40.00	4.5
	RANGE 6		21	0.1	25.00	4.5

The scaling factor (SF) for UV-Vis measurements is calculated by Equation (S1). This formula is obtained by the proportion in Equation (S2).

$$SF = \left(\frac{A^{rd}_{P575\_NDI}}{A^{nd}_{P575\_NDI}}\right); \lambda = 400\ nm \#(eq\ S1)$$

$$A^{nd}_{P575\_NDI} : A^{sd}_{sample} = A^{rd}_{P575\_NDI} : A^{rd}_{sample} \#(eq\ S2)$$

Where $A^{rd}_{P575\_NDI}$ and $A^{nd}_{P575\_NDI}$ are the absorbance value at 400 nm of a P575_NDI-OH sample respectively evaluated in the raw and in the normalized data; instead A^{sd}_{sample} and A^{rd}_{sample} are the equivalent value for a generic sample without dye.

***Table S3**. Test conditions employed to detect material response the basis.*

	Tests as a pH indicator		**Test for bases detection by sensing organic solution**
Base	NH_3	NH_3	DBU
Solvent	Water	Water	n-Hexane
Physical state of the solution	Liquid	Vapor	Liquid
Concentrations used	pH 12 [a] pH 11 [a] pH 10 [a] pH 9 [a] pH 8 [a] Distilled water	pH 12 [a] pH 11 [a] pH 10 [a] pH 9 [a] pH 8 [a] Distilled water	5 % [b] 1 % [b] 0.4 % [b] 0.2 % [b] 0.05 % [b] n-Hexane
Temperature	Room temperature	30 °C	Room temperature
Contact time	Every 2 minutes for 20 min[c]; 24 hours.	Every 2 minutes for 20 min[c]; 24 hours.	24 hours.
Sample material	P575 P575_NDI-OH	P575 P575_NDI-OH	P575 P575_NDI-OH
Printing parameters	Table S1	Table S1	Table S1
Sample thickness	0.8 ± 0.1 mm	0.5 ± 0.03 mm	0.5 ± 0.03 mm
Reversibility evaluation method	Acid aqueous liquid solution; Air exposure	Acid aqueous vapor solution; Acid organic liquid solution; Air exposure	Acid organic liquid solution; Air exposure
Samples pre-treatment before reversibility evaluation	20 minutes soaked in NH_3/H_2O liquid solution at pH 12	20 minutes exposed to NH_3/H_2O vapors at pH 12	24 hours soaked in 5% or 1% DBU/n-Hexane solution

[a]pH value is referred to liquid solution at T_{amb} and corresponds to the value described ± 0.1. [b]volumetric concentration; [c]only for solution at pH equal to 11 and 12.

***Table S4**. Reversibility evaluation method.*

	Acid aqueous solution		**Acid organic solution**	**Air exposure**
Acid agent	HCl	HCl	Benzoic acid	-
Solvent	Water	Water	n-Hexane	-
Physical state of the solution	Liquid	Vapor	Liquid	-
Concentrations used	pH=1[a]	pH=1[a]	0.1 M	-
Temperature	Room temperature	Room temperature	Room temperature	Room temperature

[a] pH value is referred to liquid solution at T_{amb} and corresponds to the value described ± 0.1.

***Table S5**. Flow rate parameters and feeding solutions employed for the fluidic application.*

	Inlet 1		**Inlet 2**		**Time**
	Solution	**Volumetric flow rate**	**Solution**	**Volumetric flow rate**	
Test a	n-hexane	250 µm min^{-1}	n-hexane	250 µm min^{-1}	30 s
Test b	n-hexane	250 µm min^{-1}	0.4 % DBU	250 µm min^{-1}	7 min e 30 s
Test c	n-hexane	250 µm min^{-1}	5 % DBU	250 µm min^{-1}	7 min
Test d	-	-	5% DBU	500 µm min^{-1}	8 min

Results and discussion: supporting information

The photophysical properties of NDIOH in different solvents were evaluated (Figure S1). Absorption spectrum of NDI-OH shows a π-π* transition around 360 nm and a charge-transfer band at 460 nm more sensitive to the environment polarity. Finally, a transition after 500 nm appears in all the solvents, excluding hexane and chloroform, probably due to the hydrogen bonding (HB) interaction between the NDIOH hydroxyl groups (HB donor) and the solvent molecules (HB acceptor).[1,2]

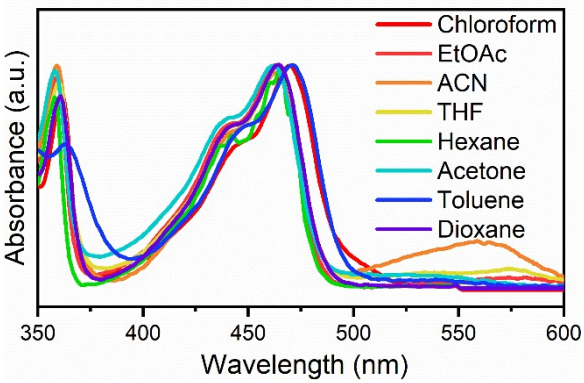

Figure S1. Absorption and emission spectra of NDI-OH in different solvents.

The four different aspects described in the paper that should be taken into account to select the most suitable monomers to develop the material are: (i) printability, (ii) miscibility with the dye, (iii) permeability to vapors, (iv) the ability to avoid dye leakage.[3,4] These characteristics depend on the dye and matrix's chemical properties, such as the resin/dye affinity, the polymeric matrix's hydrophilicity or hydrophobicity, and the polymeric network size. The final behavior of a resin can't be easily predicted because each feature influences the final results differently. For example, the resin hydrophilicity may promote vapor permeability but affect the affinity with the dye, which has two C_8 lateral chains.

To evaluate the most suitable matrix, the behavior of the dye, embedded in different resins, in contact with a basic solution (NH_3/H_2O 25% by weight) was observed in a preliminary test. The analyzed resins and the reasons beyond this choice are:

- Three PEGDA resins with three different molecular weights (250 Da, 575 Da, 700 Da): those resins were picked because increasing the molecular weight, the resin hydrophilicity increase (ethylene oxide groups prevail over acrylates ones), and also increase the polymer flexibility and permeability;[5]
- HDDA: this resin was selected for its hydrophobicity and low stiffness (T_g ~40°C), and because it may shows affinity with the dye thanks to its C_6 central chain;[6]
- Two Bisphenol A resins with different EO/phenol ratios: (BEDA EO/phenol 2) and BEMA (EO/phenol 15). The first one is more hydrophobic and stiffer than the second one because of the higher presence of the aromatic group (Bisphenol A).[7]

The preliminary testing was based on three points:

- Ease of dispersion of the dye (i.e. no or minimal use of solvent to aid dye's dispersion)
- Color change placing in contact the polymerized material with liquid basic solution and with basic vapors.
- Stability of the sample in the tested conditions

The preliminary test results show that all the materials change color after direct and indirect contact with the basic solution, from a yellow color to a red/purple one, as shown in Figure S2a. Starting from those results, it was observed and evaluated that:

- PEGDA 250 matrix does not fit the application because, during the test, it experienced an undesired reaction, probably a degradation phenomenon caused by the basic solution;
- PEGDA 575 and 700 matrices experience an evident color change without any yellowness residual (caused by protonated NDI-OH), so the analyte/dye contact is fairly promoted. Another consideration is that PEGDA 575 has higher dimensional stability and lower hygroscopicity than PEGDA 700. For that reason, PEGDA 575 matrix is preferred on PEGDA 700 one;
- HDDA and BEDA matrices neither fit the application because the original yellow color is still quite present even after prolonged contact with the alkaline solution, probably due to the matrices' hydrophobia that hinders the analyte/dye contact;
- BEMA matrix stimulates great interest because it undergoes a swift and clear color change. In fact, just a few minutes after both direct and indirect contact, it became purple.

PEGDA 575 and BEMA matrices were further analyzed by testing DLP-3D printed samples of P575_NDI-OH and B_NDI-OH formulations. During direct contact test, the B_NDI-OH sample showed a very different behavior than the formulation #6 sample. In fact, B_NDI-OH changed color very slowly, and the final color reached is not as purple as formulation #6 sample, but is red, as shown in Figure S2b.

Additional analysis revealed that the reason for those phenomena can be ascribed by the different content of acetone introduced. Theoretical explanation consists of two aspects: (i) higher acetone content causes higher polymer swelling, and (ii) faster penetration of the basis

in the matrix, which is the reason for a rapid color change. The second factor is an acetone effect on the color of PEGDA575/NDI-OH system. To verify the theoretical hypothesis, an empirical test was carried out, confirming acetone effect on formulation #6 color: adding two drops of ammonia solution to 1 ml of resin to the formulations B_NDI-OH and #6, different colors are obtained (Figure S2c).

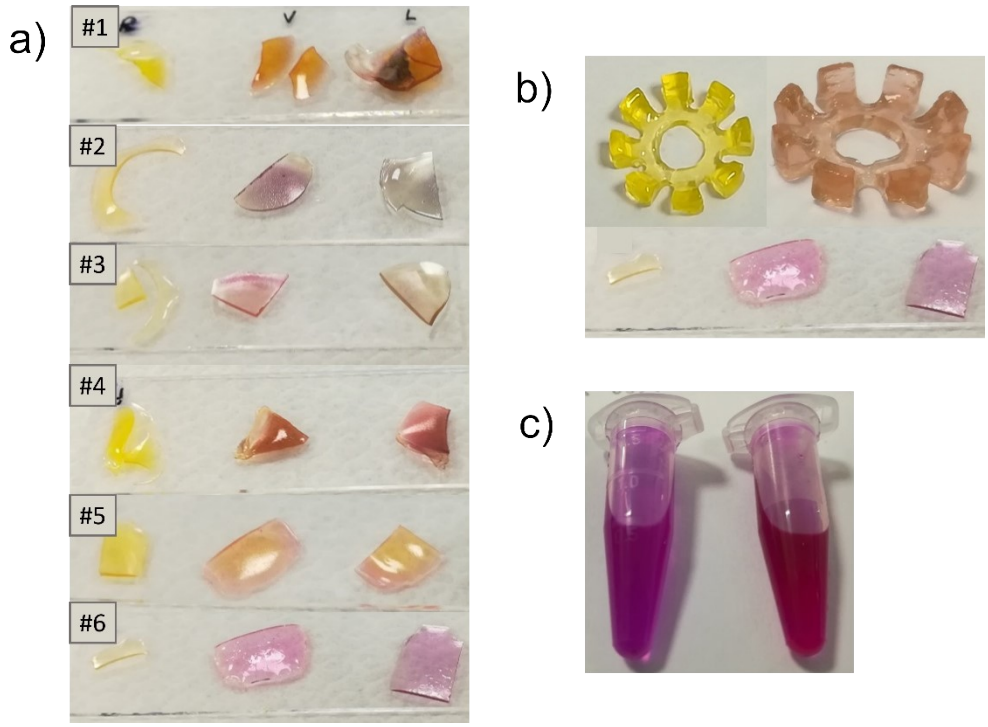

Figure S2. a) Results of preliminary test of #1 to #6 formulations' sample. In each photo, from left to right: sample as a reference of the initial color, sample after indirect contact test, sample after direct contact test; b) comparison of the final color reached by samples of B_NDI-OH (up) and #6 (down). B_NDI-OH sample was soaked for 18 hours in the alkaline solution instead #6 sample for 1 hour; c) effect of adding 2 drops of NH_3 at $25\%_{wt}$ to 1 ml of resin of the formulations B_NDI-OH (left) and #6 (right).

Acetone effect was also investigated on PEGDA 575 matrix, and acetone results to speed up the process but does not affect the final color reached after direct contact test.

The different matrices' behavior is revealed by comparing the color change phenomenon after direct contact test of two samples for both formulations (B_NDI-OH and P575_NDI-OH), one previously soaked in acetone for 10 minutes and the other as it was. On PEGDA 575 matrix, acetone speed up the process but does not affect the final color reached, unlike the acetone effect on BEMA matrix, as shown in Figure S3. For this reason, it is decided to proceed with the analysis only on PEGDA 575 matrix to avoid additional acetone variability.

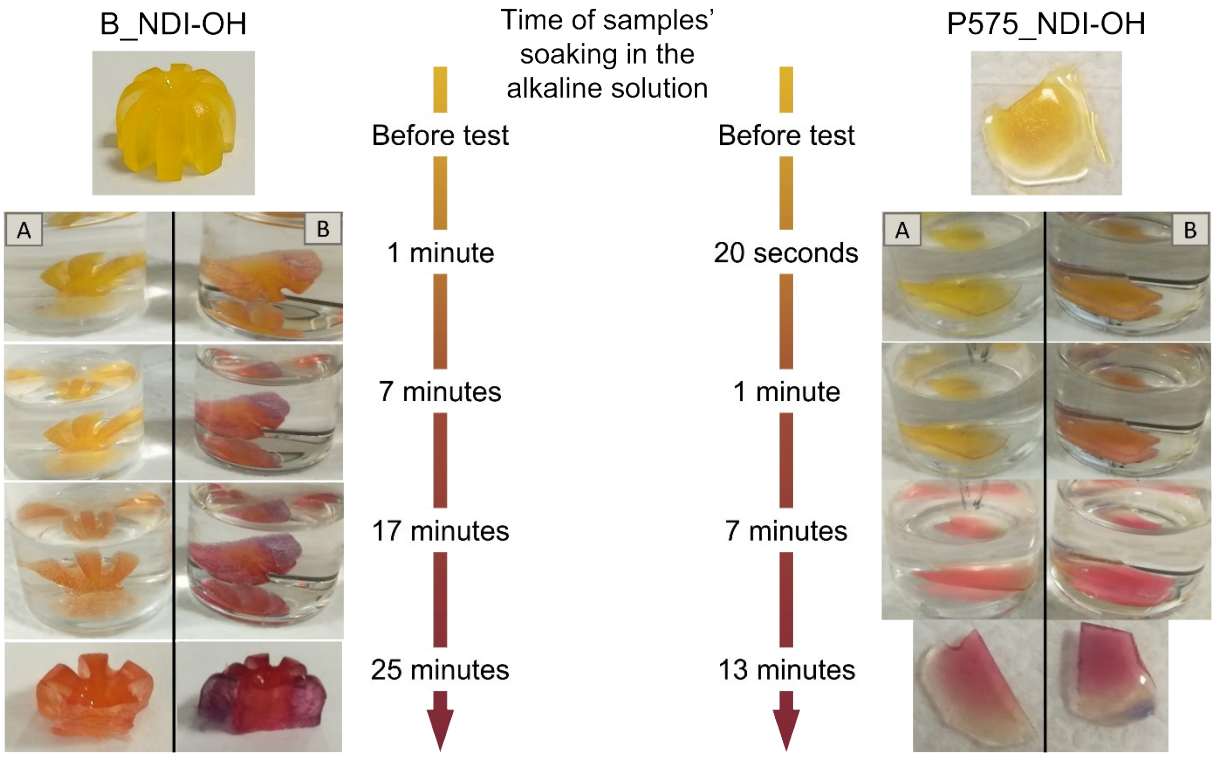

Figure S3. Effect of acetone on BEMA (left) and PEGDA 575 (right) matrices. The effect is shown by the color evolution of B_NDI-OH and P575_NDI-OH samples during direct contact test. Samples A were tested as they were. Samples B were previously soaked in acetone for 10 minutes and then tested in the alkaline solution.

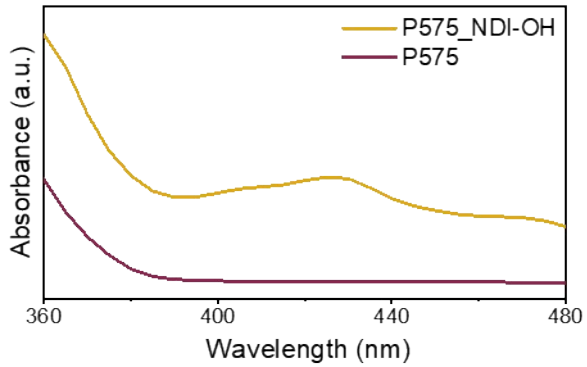

Figure S4. UV-visible absorption spectra of P575 and P575_ NDI-OH liquid formulations.

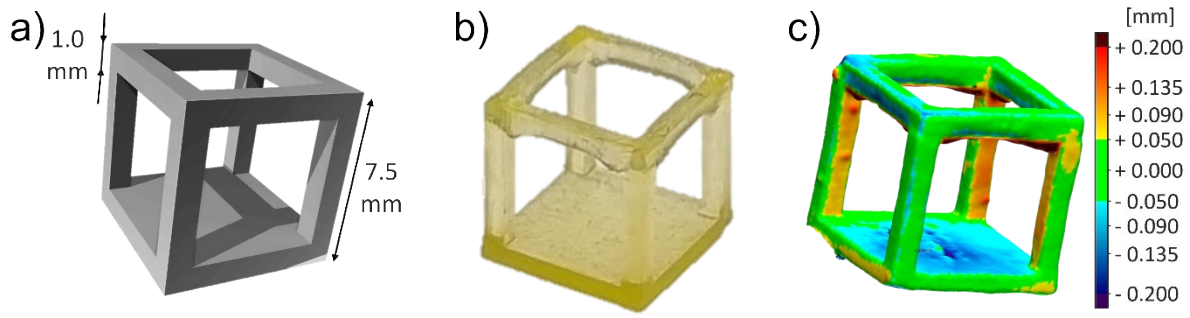

Figure S5. a) Hollow cube CAD model; b) P575_NDI-OH 3D-printed sample with hollow cube geometry; c) printing fidelity heat-map obtained comparing 3D-scanned model and the original CAD model.

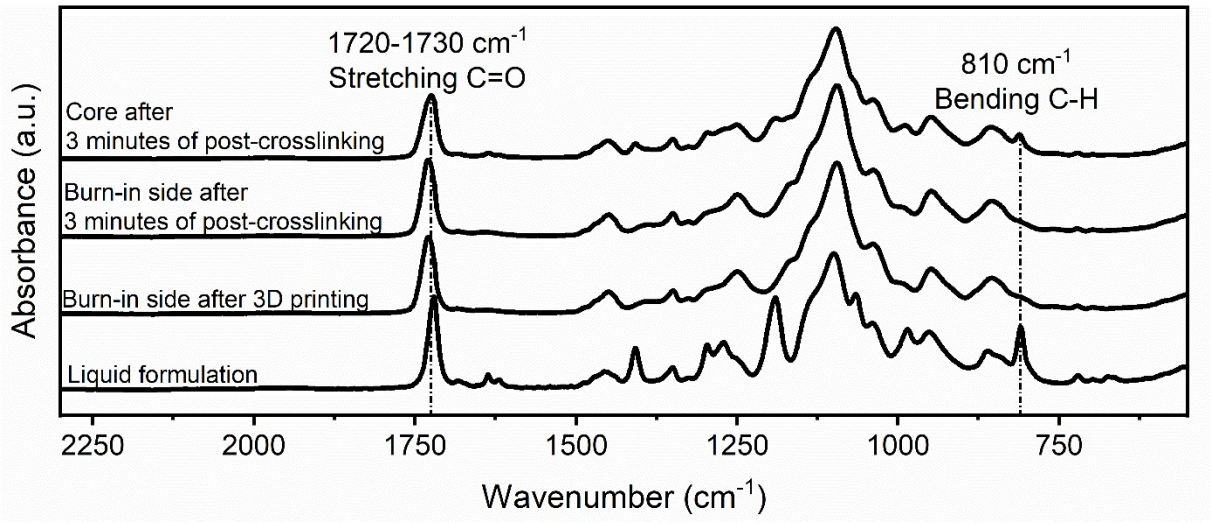

Figure S6. ATR analyses results of P575 samples.

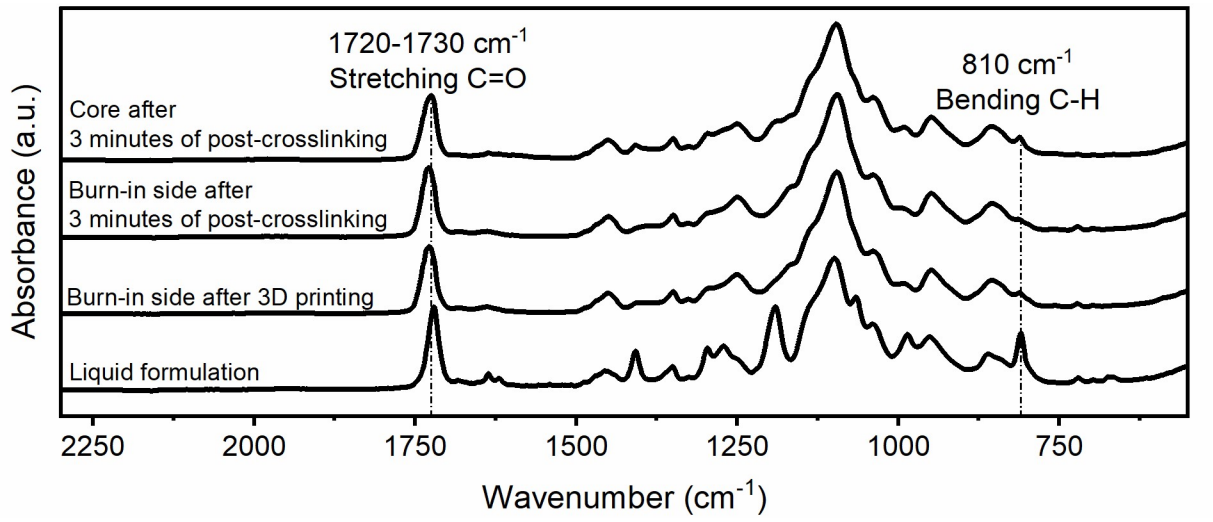

Figure S7. ATR analyses results of P575_NDI-OH samples.

Both P575 and P575_NDI-OH samples give photoinitiator leakage after prolonged immersion in water (Figure S8). In fact, P575 and P575_NDI-OH samples show an absorption decrease in the UV range after 24 hours of soaking in water, and these variations match an increase in the water's absorption. The variation in the visible range of P575_NDI-OH is not related to the dye release since no variation is detected in water's absorption and can be connected to the matrix swelling; in fact, the alteration is similar to what is observed by increasing samples thickness (Figure S9b).

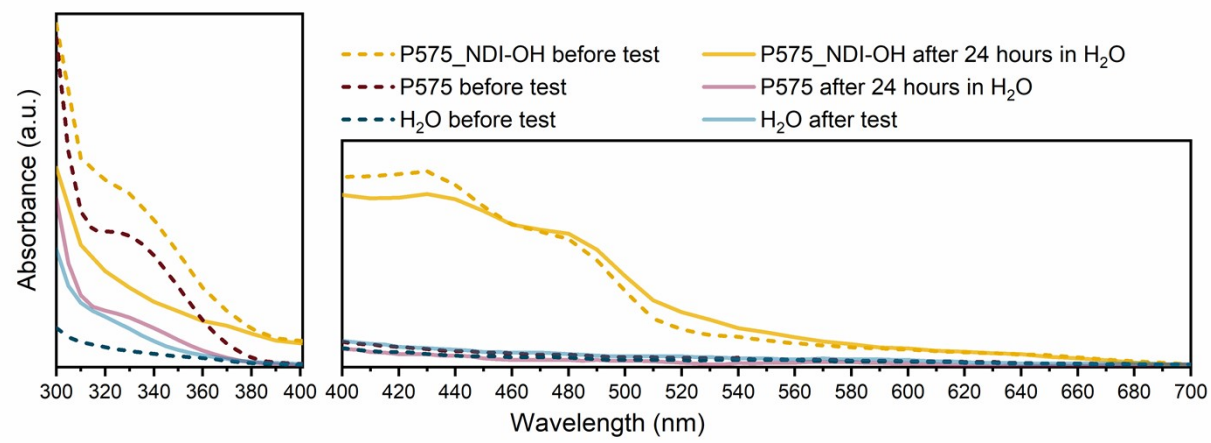

Figure S8. UV-Visible absorption spectra of P575 and P575_NDI-OH samples before and after gel content test in water media.

The choice of the optimal thickness for the samples was made by experimental studies. P575_NDI-OH samples having different thicknesses were studied in order to evaluate the optimal value that allows both visual color observation and clear and not noisy UV-Visible spectroscopy results. The results are reported in Figure S9. A thickness of 0.5 mm was selected as optimal because it is a trade-off value between clearly visible absorption peaks and fast colorimetric response. However, for samples tested in liquid aqueous solutions, the thickness was increased up to 0.8 mm to guarantee the integrity of the samples.

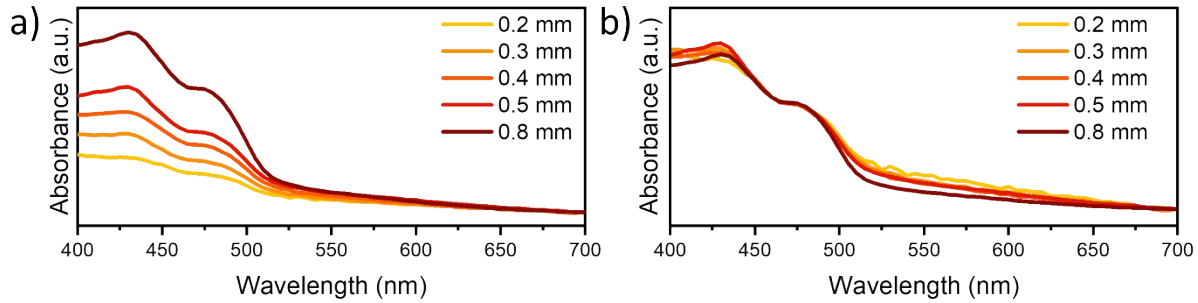

Figure S9. Visible absorption spectra of P575_NDI-OH samples with a thickness between 0.2 and 0.8 mm: a) not normalized curves; b) Curves normalized at 460 nm.

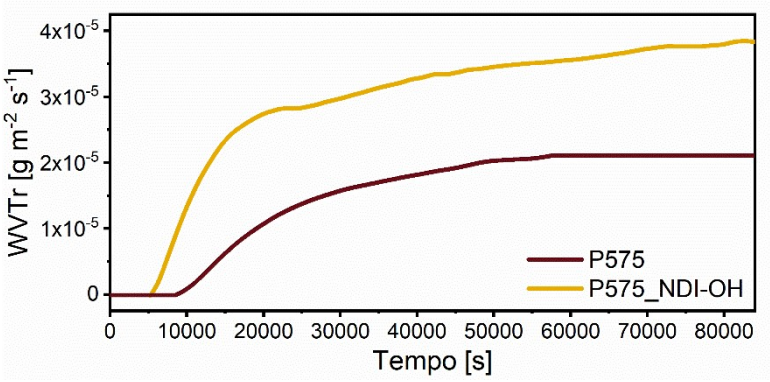

Figure S10. Transmission rate of P575 and P575_NDI-OH samples.

Table S6. *Permeability values calculated for P575 and P575_NDI-OH samples.*

	Permeability ($cm^2\ s^{-1}\ bar^{-1}$)
P575	$1.31\ 10^{-10}$
P575_NDI-OH	$2.18\ 10^{-10}$

Table S7*. P575 and P575_NDI-OH samples' swelling test results.*

	Swelling (%)		
Solvent	**P575_NDI-OH**	**P575**	**Remarks**
Dimethyl sulfoxide	15.6	6.8	-
Ethylene Glycol	0.0	0.0	No Swelling
Toluene	5.9	4.9	Extensive cracks after 10 minutes
Acetonitrile	11.5	4.0	Extensive cracks after 10 minutes
Propylene Carbonate	4.5	6.8	-
n-Hexane	0.0	0.0	No Swelling
Dimethylformamide	7.5	7.8	DMF caused P575_NDI-OH sample's slight color change
Acetone	5.0	5.3	Extensive cracks after 20 minutes
Isopropanol	3.6	3.0	-
Ethanol	8.9	2.4	-

Solvents effects on P575_NDI-OH are shown in Figure S8 and Figure S11, respectively for H_2O and n-hexane. In both cases, only the photoinitiator leakage after prolonged contact is detected, and no color variation is observed.

Concerning target species (NH_3 and DBU) effects on P575 samples, Figure S11a and Figure S12 show that only DBU cause a slight absorption variation in the blue range for wavelength shorter than those involved in the NDI-OH color change process, so that effect is negligible for the material application. This effect it's caused by the light absorption of the absorbed DBU into the polymeric matrix, as confirmed by DBU absorbance spectra reported in Figure S11b.

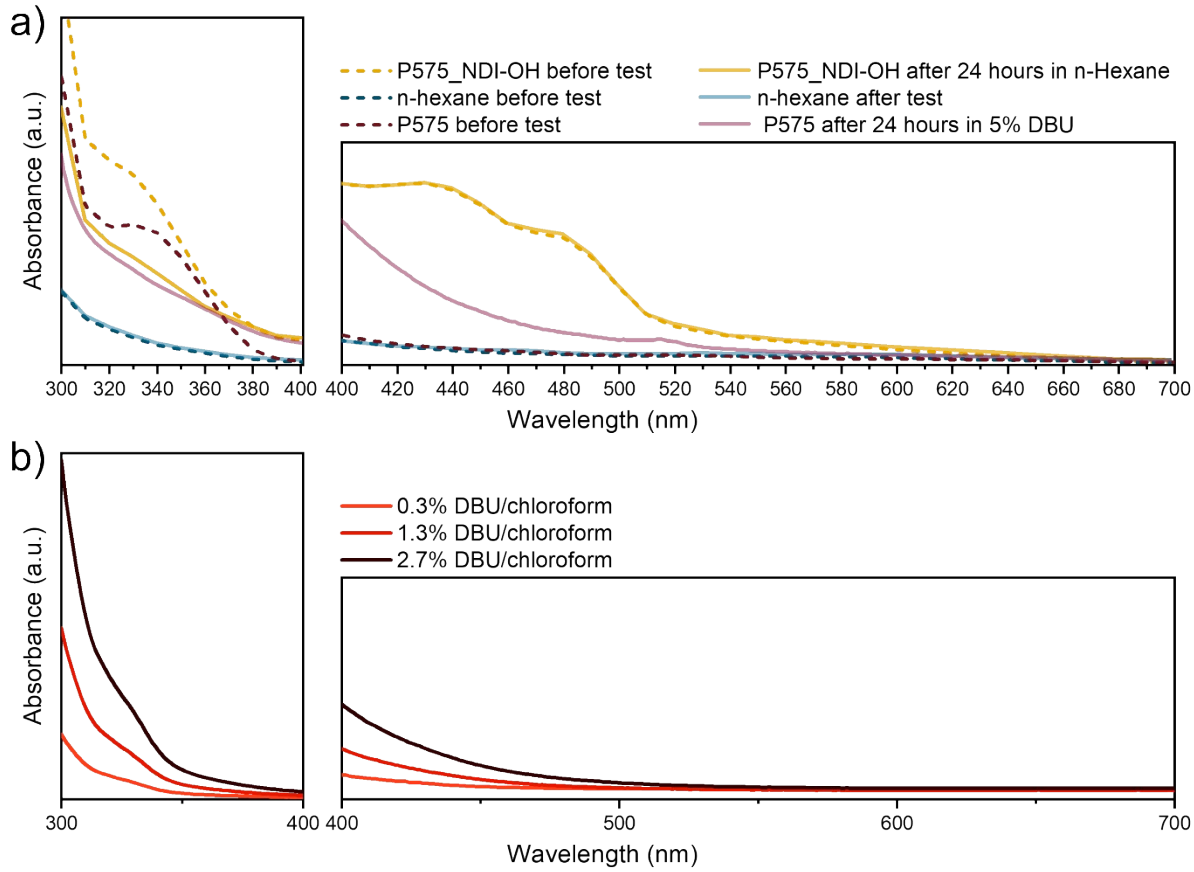

Figure S11. UV-Visible absorption spectra of P575 and P575_NDI-OH samples tested for 24 hours in 5% DBU solution and n-hexane, respectively.

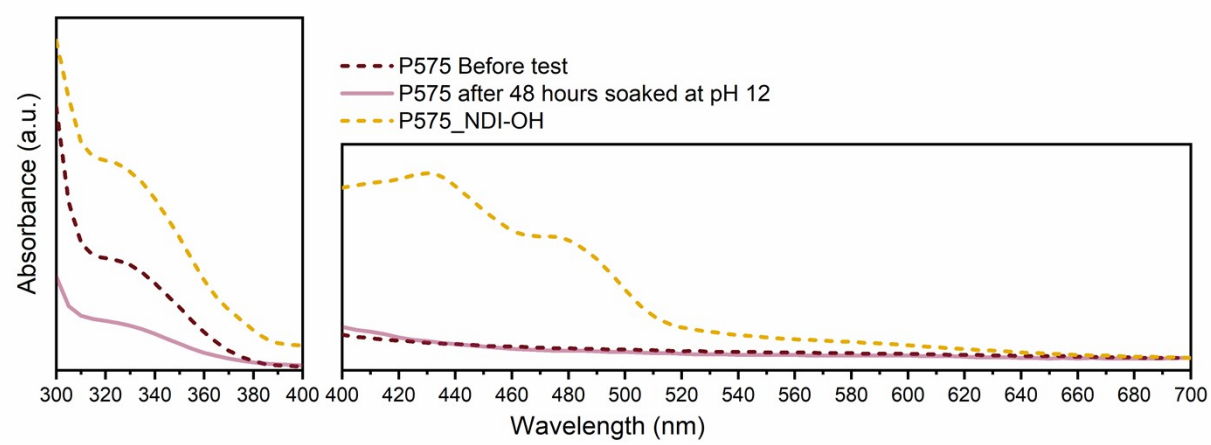

Figure S12. UV-Visible absorption spectra of a P575 sample tested for 48 hours in NH_3/H_2O solution at pH 12. The P575_NDI-OH sample spectrum is reported as a reference to compare the magnitude of the P575 spectra variation intensity.

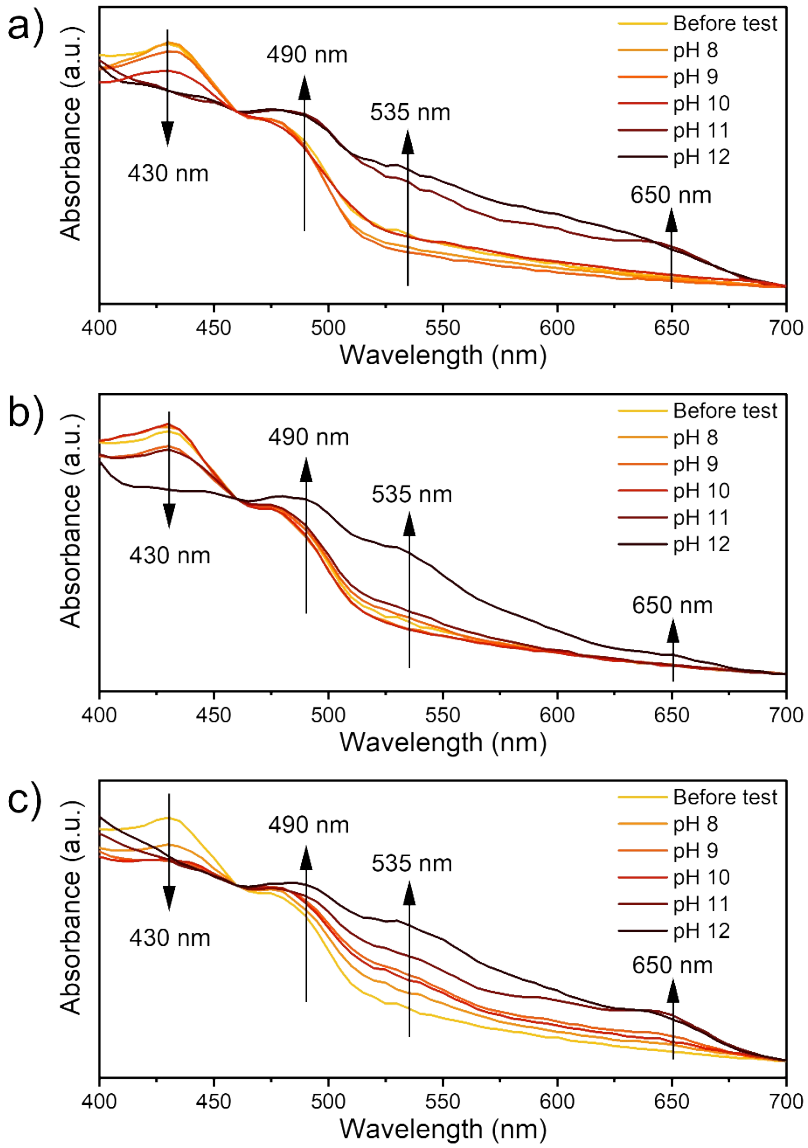

Figure S13. Visible absorption spectra of P575_NDI-OH samples tested with NH_3/H_2O solutions at different pH for: a) 24 hours by direct contact test; b) 18 minutes by indirect contact test; c) 24 hours by indirect contact test.

The kinetics of color evolution confirms the hypothesis of the photoinitiator's leakage in liquid media since the UV absorption decrease is observed only after prolonged direct contact tests.

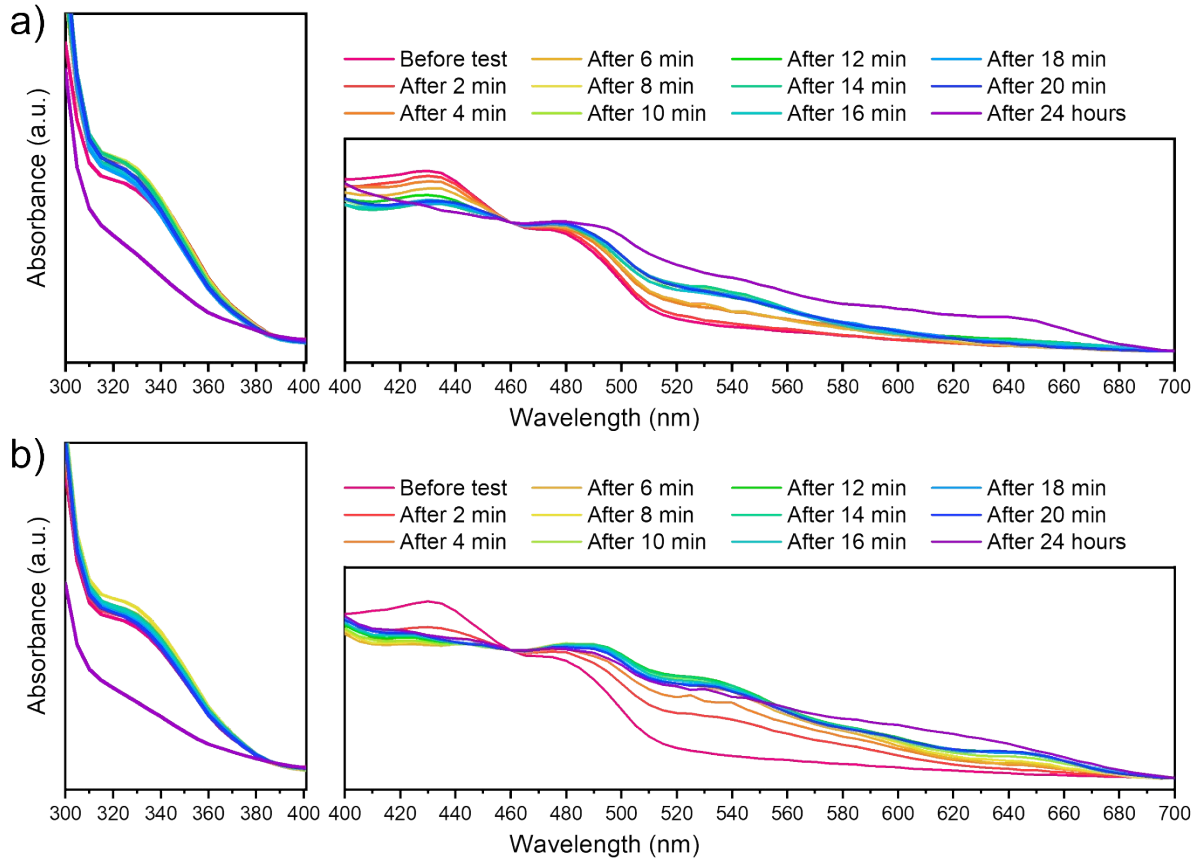

Figure S14.UV-Visible absorption spectra mapping the kinetics of a P575_NDI-OH sample's color change during direct contact tests in solutions at: (a) pH 11; (b) pH 12.

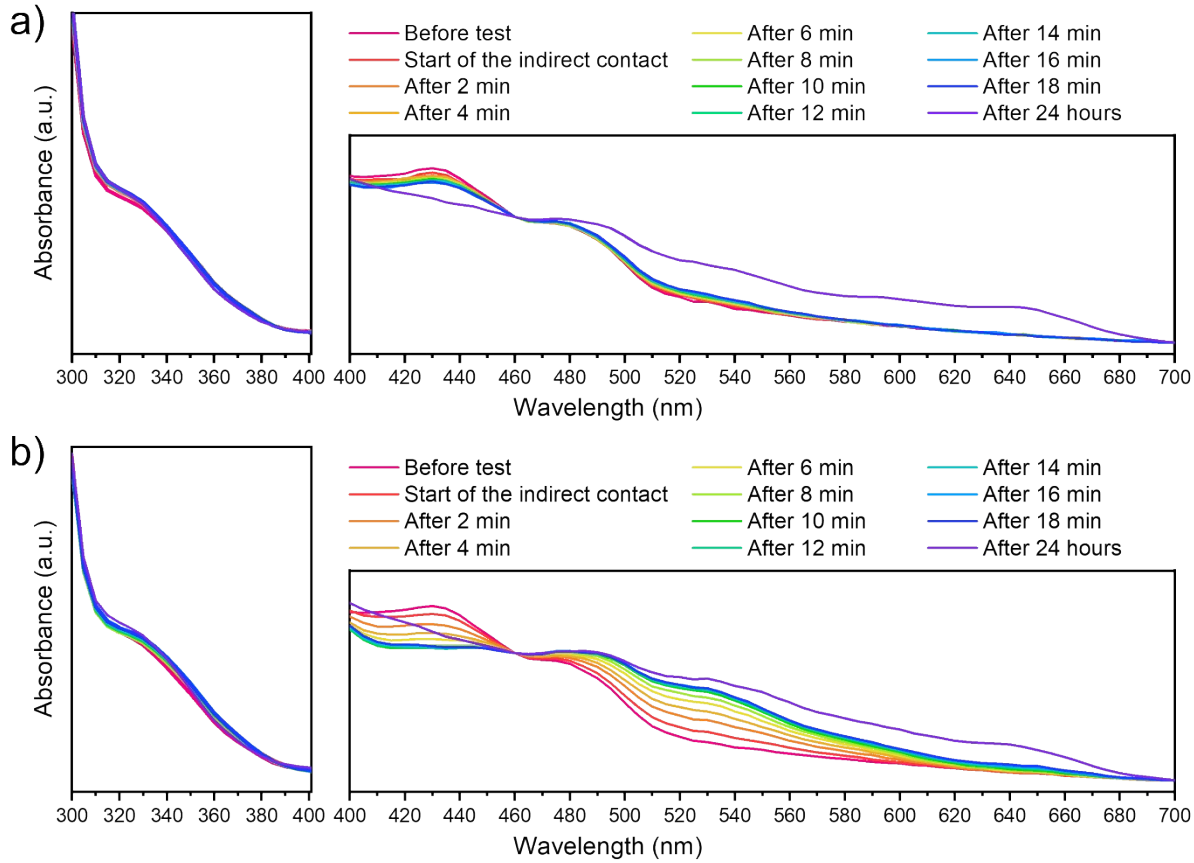

Figure S15. UV-Visible absorption spectra mapping the kinetics of a P575_NDI-OH sample's color change during indirect contact tests in solutions at: (a) pH 11; (b) pH 12.

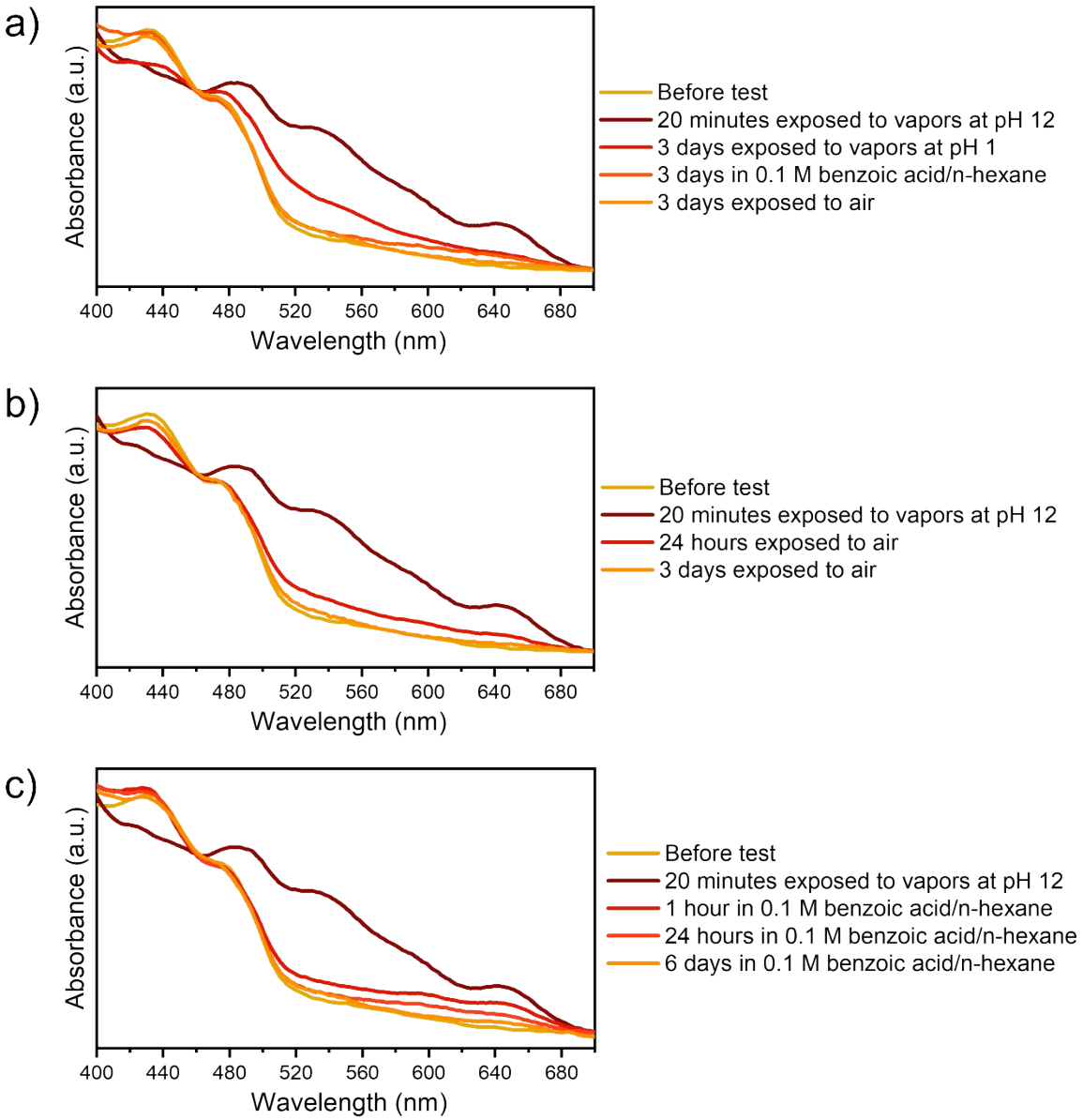

Figure S16. Visible absorption spectra of a P575_NDI-OH sample previously exposed for 20 minutes to NH_3/H_2O vapors at pH 12 and then (a) the process reversibility through 3 days in different media, (b) exposed to air, (c) soaked in a 0.1 M benzoic acid/n-hexane liquid solution.

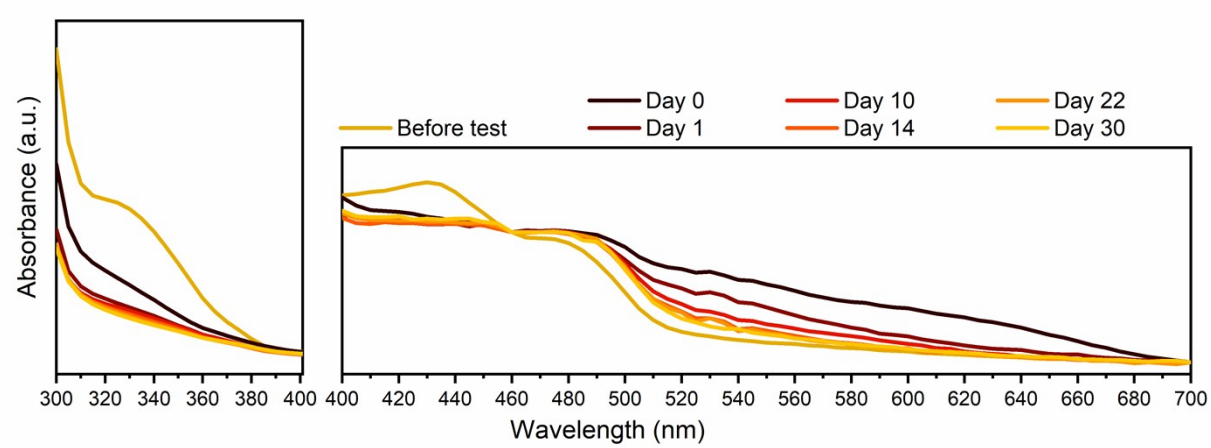

Figure S17. UV-visible absorption spectra of P575_NDI-OH sample's evolution by exposing it to air after being soaked in liquid NH_3/H_2O solutions at pH 12.

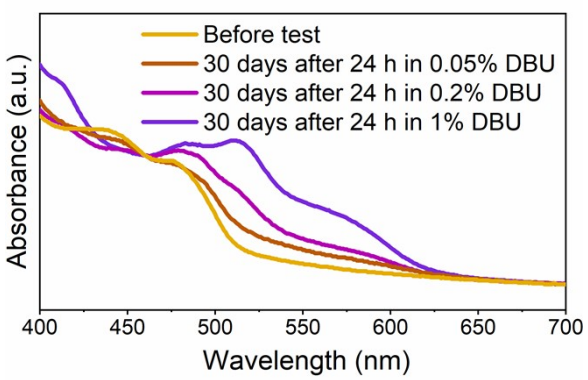

Figure S18. UV-Visible absorption spectra of P575_NDI-OH samples' evolution by exposing it to air after being soaked in DBU/n-hexane.

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