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Photoactivated acidochromic elastomeric films for on demand acidic vapor sensing

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Electronic Supplementary Information file

Geometry optimization of MCH

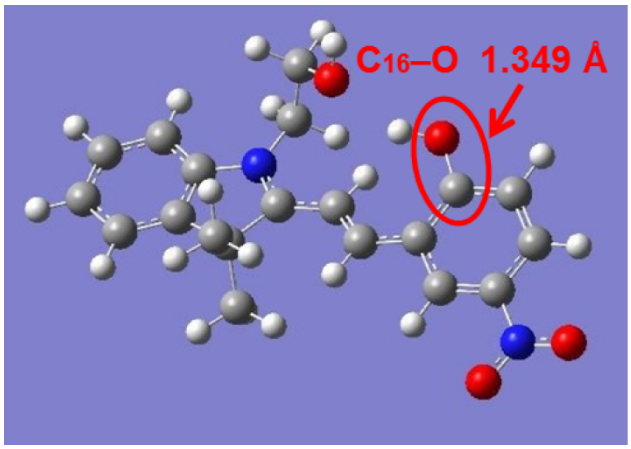

Fig. S1 Optimized structure for MCH by molecular modeling.

Photoisomerization of SP/PDMS

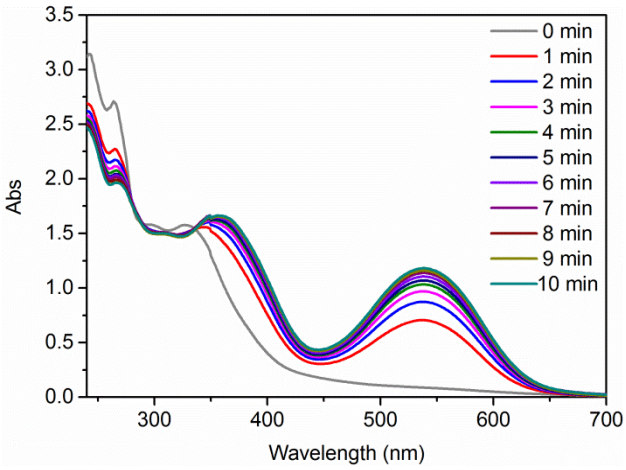

Fig. S2 Absorption spectra of a SP/PDMS film (SP = 0.5 % wt, 2.13 x 10^{-7} moles) at different irradiation times with UV light.

Thickness dependence

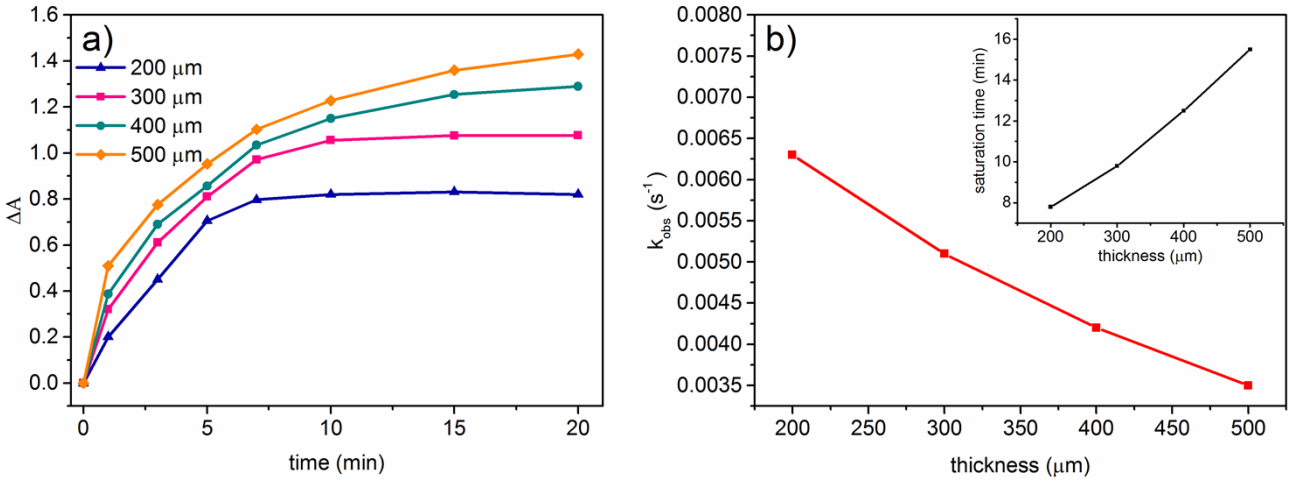

Fig. S3 a) Kinetics of protonation of SP/PDMS films with thicknesses ranging from 200 to 500 µm exposed to an excess of TFA (2.66 x 10^{-5} moles). b) Pseudo-first order rate constants (k_{obs}) as a function of the thickness of the composite SP/PDMS films. The constants were determined by the non-linear fitting of the curves in fig. S3a to the first order rate equation using Box-Lucas exponential function y = a (1-e^{-kx}). Inset: time required to reach 95% of the absorbance variation during protonation of SP/PDMS films with TFA for the range of thicknesses under investigation.

Kinetics of formation of MCH/PDMS

Under the pseudo-first order approximation the formation of the MCH complex is expressed by the following relation:

$$-\frac{d[MC]}{dt} = \frac{d[MCH]}{dt} = k_{obs}[MC] \qquad (1)$$

$$\text{with} \quad k_{obs} = k\,[HA]$$

where [MCH], [MC] and [HA] are the complex, the merocyanine and the acid concentrations respectively, k_{obs} is the observed pseudo-first order rate constant and k is the global reaction rate constant. Integration of the rate law in Equation 1 followed by linearization yields Equation 2, where t is the exposure time and A∞, A_t and A_0 are the absorbances of MCH at 417 nm at t = infinite, at a given time t and at t = 0 respectively.

$$\ln \frac{(A_\infty{}^{MCH} - A_t{}^{MCH})}{(A_\infty{}^{MCH} - A_0{}^{MCH})} = k_{obs}t \qquad (2)$$

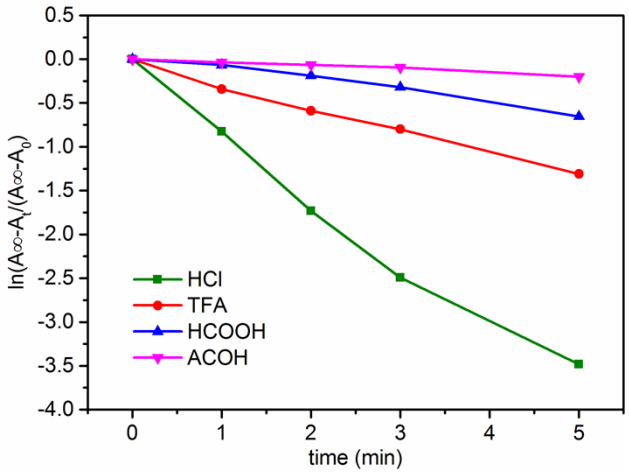

Fig. S4 Plot of $\ln(A_\infty - A_t)/(A_\infty - A_0)$ versus time for the protonation of a SP/PDMS film (SP = 0.5 % wt, 2.13 x 10^{-7} moles) with different acids.

As shown in Fig. S3, the first order kinetic law for the formation of MCH under exposure of MC to an excess of acid is demonstrated by the linear dependence of $\ln(A_\infty-A_t)/(A_\infty-A_0)$ versus t [1].

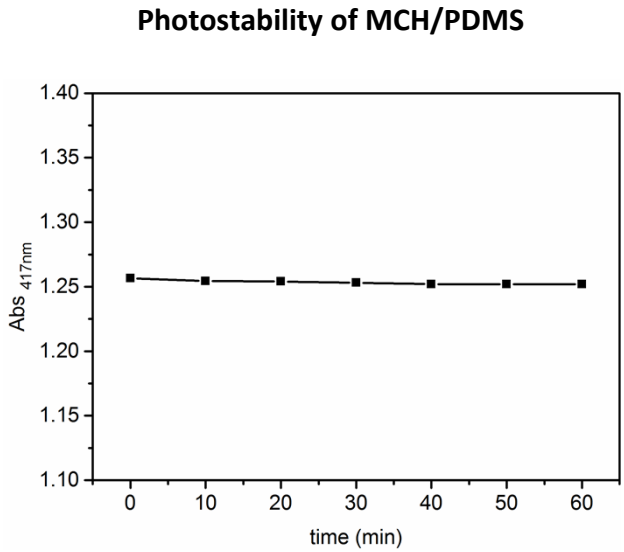

Fig. S5 Spectral variation of the MCH absorbance at 417 nm within 60 minutes after protonation of a SP/PDMS film (SP = 0.5 % wt, 2.13 x 10^{-7} moles).

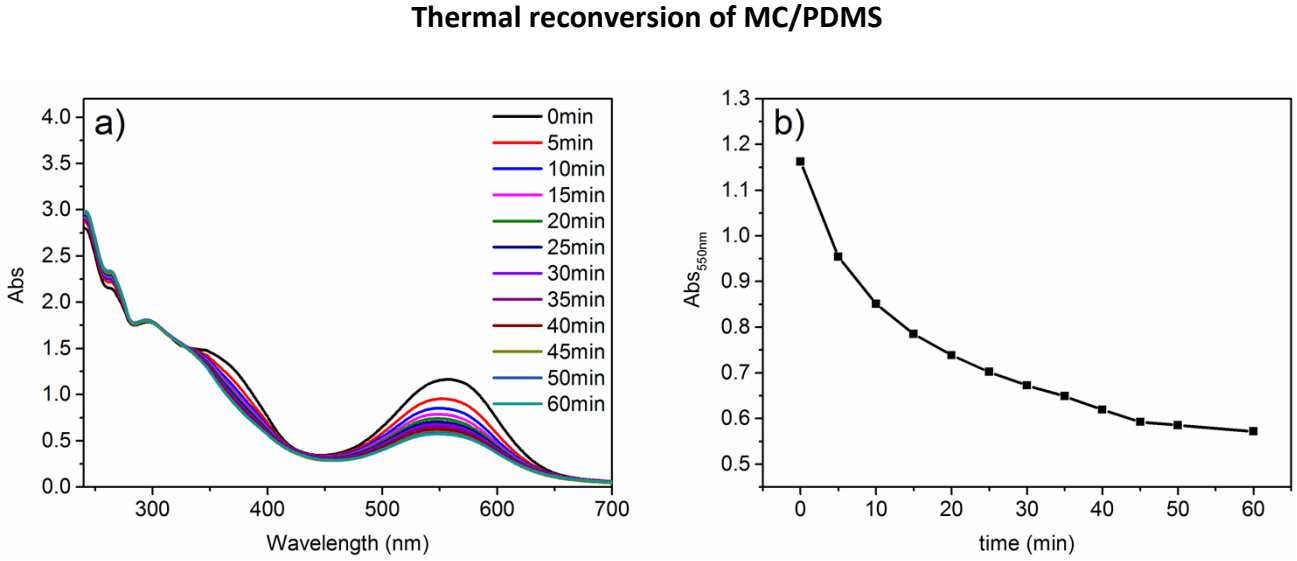

Fig. S6 a) Absorption spectra of a SP/PDMS film (SP = 0.5 % wt, 2.13 x 10^{-7} moles) 0-60 minutes after irradiation with UV light. b) Spectral variation of the MC absorbance at 550 nm within 60 minutes after UV irradiation.

Effect of the MC concentration on the acidochromic response

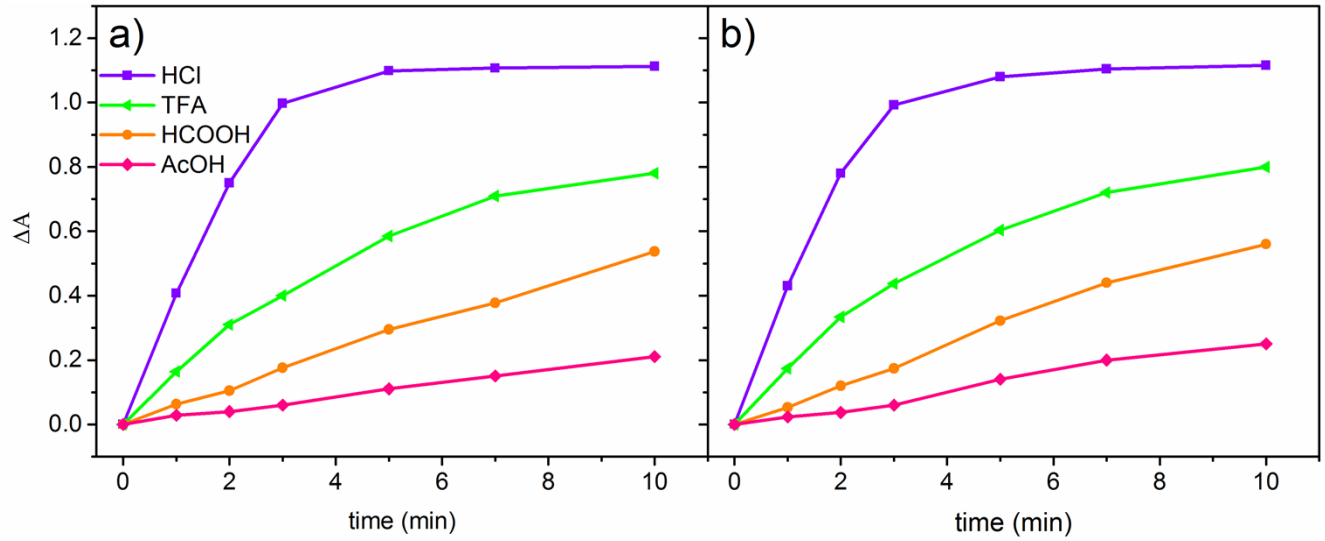

Fig. S7 a) Variation of the absorbance at 417 nm during protonation of SP/PDMS films (SP = 0.5 % wt, 2.13 x 10^{-7} moles) 20 min after UV irradiation. b) Variation of the absorbance at 417 nm during protonation of SP/PDMS films (SP = 0.3 % wt, 1.28 x 10^{-7} moles) immediately after UV irradiation. Upon photoisomerization, the relative MC ratio between 0.5% wt and 0.3% wt SP-doped PDMS films is 100:60 respectively, whereas the MC content in the 0.5 % wt SP samples is reduced to 60 % 20 minutes after UV irradiation and, therefore, it is equal to that of 0.3% wt SP films immediately after UV irradiation. As shown in the figure, the two systems exhibit an identical acidochromic behavior.

References

1 J, Zhou, F. Zhao, Y. Li, F. Zhang and X. Song, *J. Photochem. Photobiol. A*, 1995, **92**, 193-199.