COMMUNICATION

Supporting Information

Monitoring crack appearance and healing in coatings with damage self-reporting nanocapsules

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The supporting information includes:

Figure S1 - Figure S11

Table S1

Equation S1 – S4

Movie 1 – Movie 4

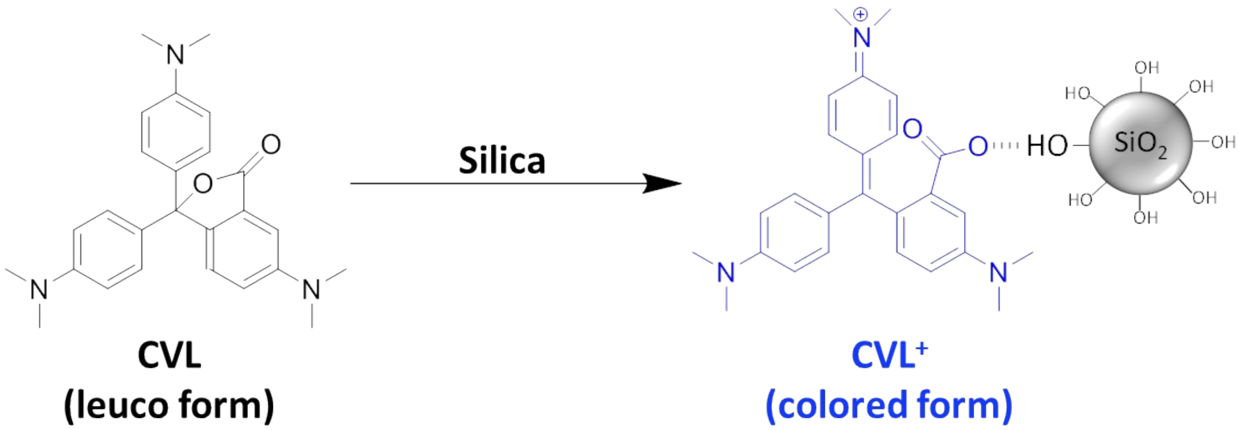

Figure S1. Chemical structures of CVL and CVL^{+}. The lactone ring of CVL can be opened by the silanol groups of silica. Then the colorless leuco form (CVL) changes its conformation to a colored form (CVL^{+}).

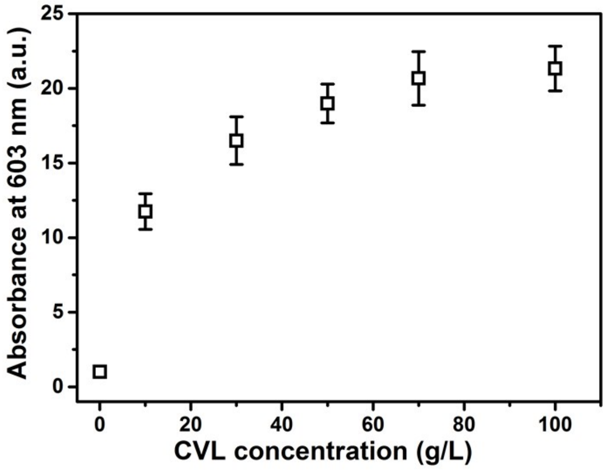

Figure S2. Absorption intensity at 603 nm for mixtures of a fixed silica amount and CVL solutions in phenyl acetate with varying concentrations.

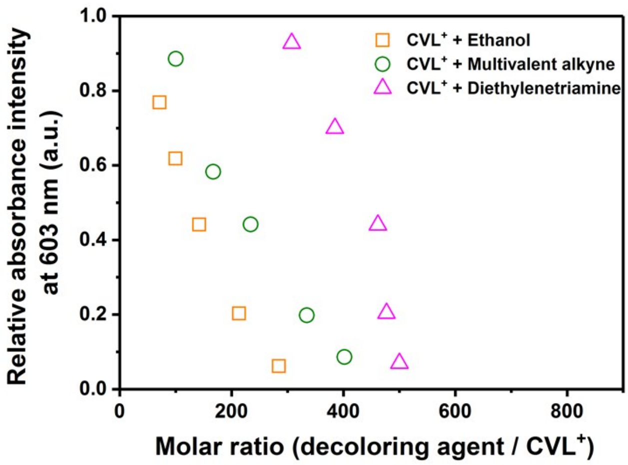

Figure S3. The relationship between color intensity and the molar ratio of decoloring agents to CVL^+.

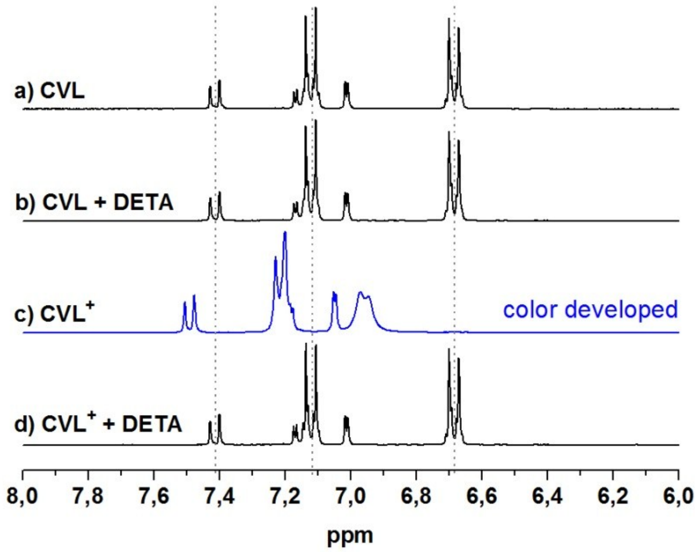

Figure S4. Solution ^{1}H NMR spectra of the aromatic protons in CVL in different conditions: a) CVL before color developing; b) CVL in presence of DETA (CVL : DETA at 1 : 2 mol ratio), no effect; c) CVL$^+$ color developing with HCl (CVL : HCl at 2.4 : 1 mol ratio); d) CVL$^+$ color deleting with DETA (CVL$^+$: DETA at 1:2 mol ratio). All spectra were acquired in acetone-d6 immediately after mixing all components.

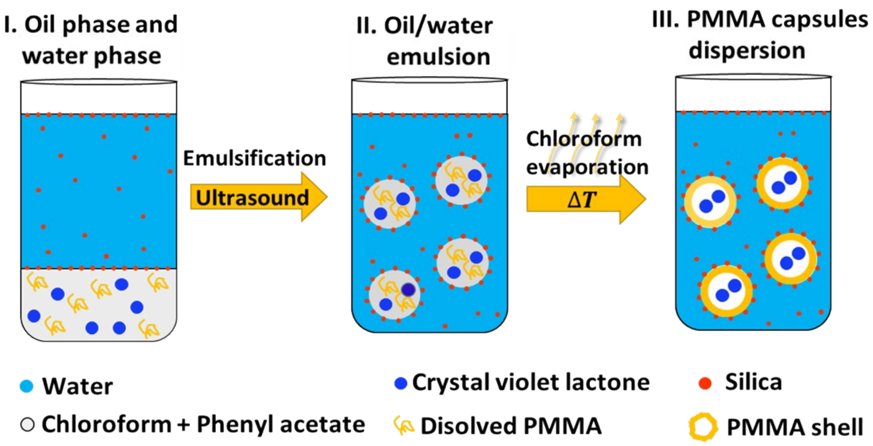

Figure S5. Schematic picture of the fabrication process of silica / CVL / PMMA nanocapsules *via* a combination of Pickering stabilized miniemulsion and solvent evaporation process.

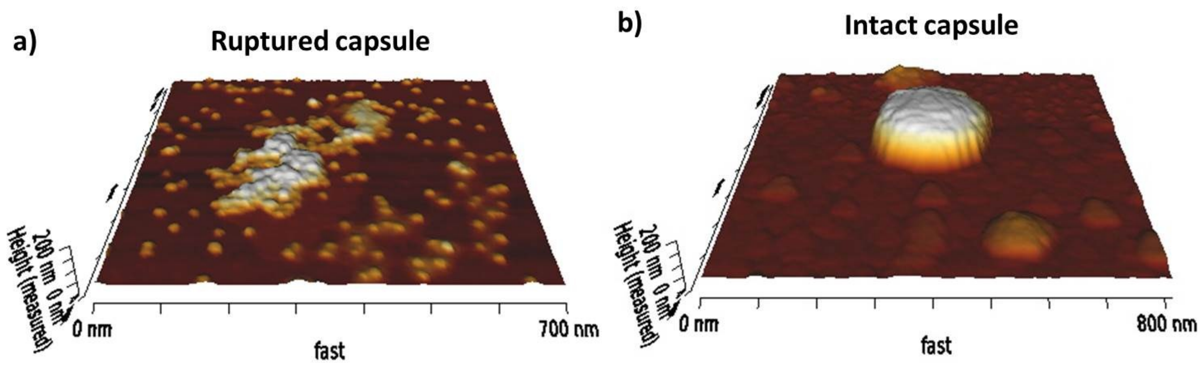

Figure S6. Atomic force microscopy of submicrocapsules with low critical buckling pressure (a) and high critical buckling pressure (b).

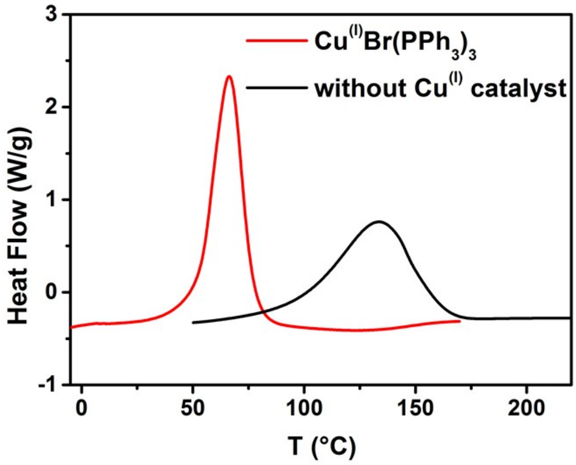

Figure S7. DSC measurements for the bulk click reaction between multivalent azide and multivalent alkyne with $Cu^{(I)}Br(PPh_3)_3$ as catalyst and without catalyst at a heating rate of 5 °C · min^{-1}.

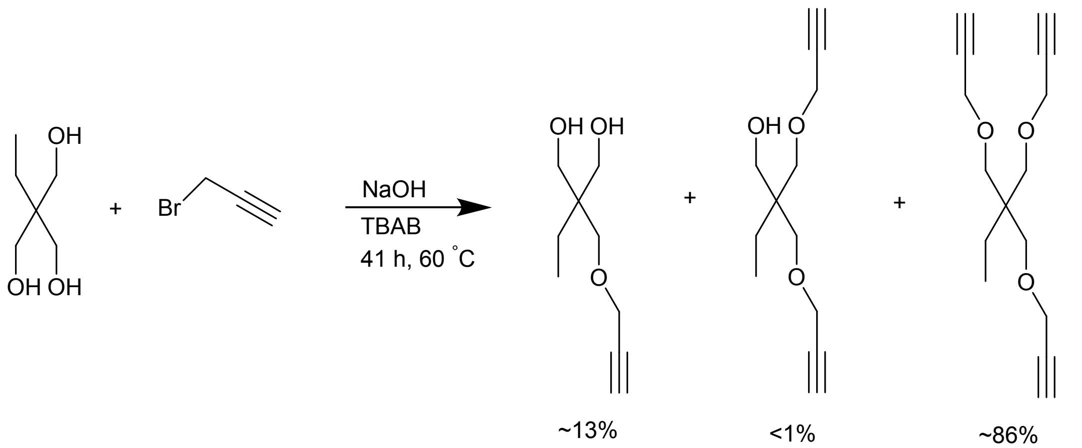

Figure S8. Synthesis of the multivalent alkyne (with one, two, three alkyne groups). The percentages were determined by GC-MS.

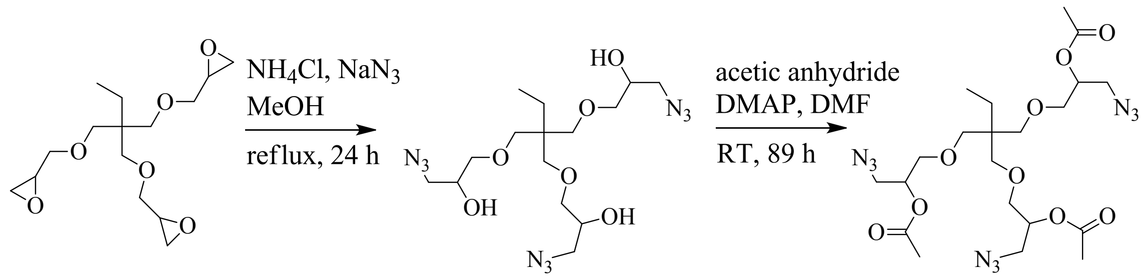

Figure S9. Synthesis of multivalent azide (((2-((2-acetoxy-3-azidopropoxy)methyl)-2-ethylpropane-1,3-diyl) bis(oxy))bis(3-azidopropane-1,2-diyl) diacetate).

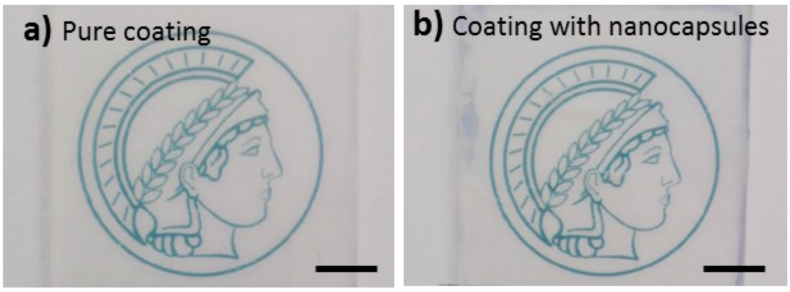

Figure S10. Optical photographs of translucent coating of water based polymeric coating (a) and the polymeric coating with self-reporting nanocapsules (b) on glass slide, respectively. Scale bars are 5 mm.

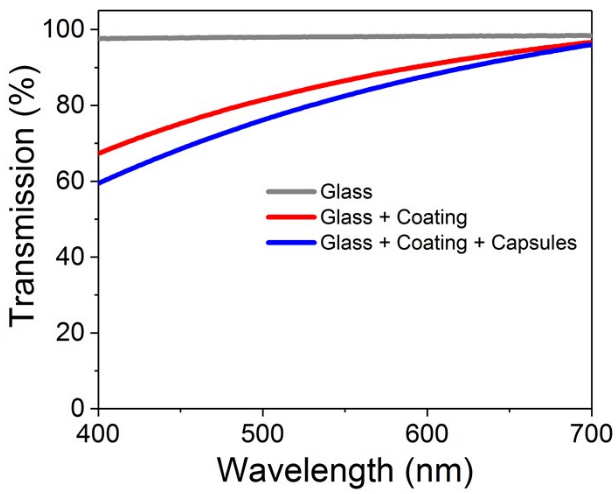

Figure S11. Optical transmission of glass slide without any coatings (grey line), polymeric coating films without (red line) and with self-reporting nanocapsules (blue line) on glass slides.

Table S1. Shell thickness and diameter of capsules with different emulsification parameters.

Sample number Entry	Polymer amount (mg)	Silica colloidal amount (g)	Ultrasound amplitude (%)	Diameter (nm)	Shell thickness of capsules (nm)
1	300	4.8	50	202 ± 80	8 ± 3
2	300	3.2	50	212 ± 76	8 ± 3
3	300	2.4	50	272 ± 137	10 ± 5
4	300	3.2	30	304 ± 130	12 ± 5
5	400	3.2	50	418 ± 112	20 ± 5
6	500	3.2	50	428 ± 87	25 ± 5
7	600	3.2	50	449 ± 125	30 ± 8
8	700	3.2	50	523 ± 160	39 ± 12
9	800	3.2	50	730 ± 215	60 ± 18
10	1000	3.2	30	834 ± 332	80 ± 32
11	1200	3.2	30	1140 ± 330	124 ± 36

The shell thickness (d) of capsules was determined by the following equation according to Zhao *et al* [1]:

$$d = R \times \left(1 - \frac{1}{\sqrt[3]{\frac{m_{polymer}}{m_{core}} \times \frac{\rho_{core}}{\rho_{polymer}}}}\right) \quad (1)$$

where R, $m_{polymer}$, m_{core}, $\rho_{polymer}$, ρ_{core} is the radius of the capsule, mass of the polymer, mass of the core, density of the polymer and density of the core, respectively.

Determination of the capillary forces during drying of the capsules

During drying of dispersions, capillary forces between the particles will occur in two ways. First during recession of the air-water interface from the outmost layer of particles down to the substrate and second during drying out of the remaining menisci. Assuming complete wetting of the particles, *i.e.* a contact angle of zero, the capillary force is proportional to the water surface tension γ and the particle radius *R* for both cases.

$$F_C = A\,\gamma\,R \tag{2}$$

The proportionality factor *A* is in both cases in the order of unity. For the case of the meniscus between two spheres, the prefactor equals $A = 2\pi$, whereas in the case of the receding water front, it is given by (eq. 16) [2]

$$A = \frac{3\sqrt{2}(1-f)^2}{\sqrt{3}-1} \tag{3}$$

with f being a factor depending on the amount of deformation of the spheres that ranges from 0 to 0.095 and is zero for zero deformation, i.e. $A = 5.8$. Therefore, both prefactors are well approximated by $A = 6$ and the capillary force for both cases takes a value of

$$F_C = 6 \cdot 0.072\frac{N}{m} \cdot 150\,nm = \;65\,nN \tag{4}$$

assuming a particle diameter of 300 nm. These forces match the range of the forces necessary to break the capsules in the AFM experiments, showing that the mechanical strength of the capsules can indeed be tuned by a proper d^2/R^2 ratio so that they either already collapse during drying or stay stable during this process.

Reference

[1] Y. Zhao, J. Fickert, K. Landfester, D. Crespy, *Small* **2012**, *8*, 2954.

[2] Visschers, M., Laven, J., & Linde, van der, R. (1997). Forces operative during film formation from latex dispersions. Progress in Organic Coatings, 31(4), 311-323.

Movie descriptions

Movie S1 Color developing

20 µL of crystal violet lactone (CVL) solution (dissolved in phenyl acetate, 10 wt.%) is taken by a pipette. Then droplets of solution are added on the silica powder. The CVL droplets develop intensive blue color when they contact with the silica. The movie speed is real speed.

Movie S2 Color deleting effect of multivalent alkyne

20 µL of multivalent alkyne is added on a blue spot where contains CVL^+. The blue color of CVL^+ fades away in an hour. The other blue spot which doesn't contact with multivalent alkyne stay the blue color. The movie speed is 128 times faster than real speed.

Movie S3 Color deleting effect of diethylenetriamine

20 µL of diethylenetriamine is added on a blue spot where contains CVL^+. The blue color of CVL^+ fades away in a minute. The other blue spot which doesn't contact with diethylenetriamine stay the blue color. The movie speed is 4 times faster than real speed.

Movie S4 Color deleting effect of ethanol

20 µL of trivalent alkyne is added on a blue spot where contains CVL^+. The blue color of CVL^+ fades away in 20 seconds. The other blue spot which doesn't contact with ethanol stay the blue color. The movie speed is real speed.