Supplement

S.1. Equilibration times with the surrounding RH

As mentioned in the main text, when preparing thin films with sucrose concentrations > 67 wt % sucrose (which corresponds to solutions supersaturated with respect to crystalline sucrose) first a droplet containing 60 wt % sucrose in water and trace amounts of dye was placed on a siliconized hydrophobic slide (Hampton Research) using a micropipette. Next, the hydrophobic slide containing the droplet was placed into a flow cell or sealed glass container with a set RH. The slide containing the droplet was left inside the flow cell or container and given enough time to come to equilibrium with the surrounding RH. To determine the time required to come to equilibrium we first calculated the characteristic time for mixing of water by molecular diffusion within a droplet ($\tau_{diff,water}$) using the following equation (Seinfeld and Pandis, 2006; Shiraiwa et al., 2011):

$$\tau_{diff,water} = \frac{R_{droplet}^2}{\pi^2 D_{H2O}} \quad \text{(S1)}$$

Where $R_{droplet}$ is the radius of the droplet and D_{H2O} is the diffusion coefficient of water molecules in a sucrose-water solution. Equation S1 corresponds to the time at which the concentration of water at centre of the droplet deviates by less than 1/e from anywhere else in the droplet. To ensure that enough time was allowed for the surrounding RH to come to equilibrium with the droplets in our experiment, the time the droplets were exposed to a give RH (t_{exp}) was at least a factor of 2.5 greater than $\tau_{diff,water}$. In some experiments we also varied t_{exp} from a factor of approximately 2.5 to 5.5 greater than $\tau_{diff,water}$, and in these experiments we did not see a systematic decrease in the measured diffusion coefficients of the organic dyes, suggesting that using t_{exp} values of 2.5 greater than $\tau_{diff,water}$ was sufficient to equilibrate the droplets with surrounding gas phase water vapor. In (Tables S1-S3) $t_{diff,water}$ and t_{exp} used in each experiment is given. When calculating $\tau_{diff,water}$ we used diffusion coefficients of water in sucrose-water solutions reported by Price et al. (2014).

S.2 Fluorescence signal as a function of dye concentration in sucrose-water films

In a separate set of experiments, we measured the fluorescence signal as a function of the dye concentration in sucrose-water films. Thin films (50 wt % sucrose in water) were prepared as describe in the main text with a range of dye concentrations (see Figures S1-S3).

For the measurements with fluorescein and calcein, we used a Leica TCS SP5 II confocal laser scanning microscope with a 10x 0.4 NA objective, a pinhole of 53.07 μm and an Ar 488 nm laser. Fluorescence intensity was measured over an area of 140 μm x 140 μm. For the measurements with rhodamine 6G, we used a Zeiss Axio LSM 5 MP laser scanning microscope with a 10x 0.3 NA objective, a pinhole of 80 μm, and a 543 nm HeNe laser. Fluorescence intensity was measured over an area of 200 μm x 200 μm. Average fluorescence intensity per pixel was recorded and plotted in Figures S1-S3.

Tables

Table S.1. Selected parameters used in fluorescein FRAP experiments and resulting diffusion coefficients.

a_w	Thin film #	Droplet radius (µm)	$\tau_{diff,water}$	t_{exp}	Photobleach size (µm x µm)	Measured diffusion coefficients of organic dye ($\mu m^2/s$)
0.88	1	350	N/A[a]	N/A[a]	30 x 30	6.46
	2	350	N/A[a]	N/A[a]	30 x 30	6.73
	3	350	N/A[a]	N/A[a]	30 x 30	7.94
0.80	1	350	11 min	30 min	30 x 30	2.10
	2	350	11 min	1 hrs	30 x 30	0.94
	3	350	11 min	1.5 hrs	30 x 30	1.69
0.70	1	350	55 min	2.5 hrs	15 x 15	0.0618
	2	350	55 min	3.75 hrs	15 x 15	0.110
	3	350	55 min	5 hrs	15 x 15	0.111
0.60	1	350	5.2 hrs	14 hrs	5 x 5	0.00358
	2	350	5.2 hrs	21 hrs	5 x 5	0.00425
	3	350	5.2 hrs	28 hrs	5 x 5	0.00384
0.52	1	350	1.5 days	4 days	5 x 5	0.000145
	2	350	1.5 days	6 days	5 x 5	0.000324
	3	350	1.5 days	8 days	5 x 5	0.000391
0.38	1	150	2.6 days	10 days	5 x 5	2.23E-5
	2	150	2.6 days	10 days	5 x 5	5.45E-6
	3	150	2.6 days	10 days	5 x 5	9.00E-6

[a] Droplets with an a_w 0.88 were prepared gravimetrically, and hence $\tau_{diff,water}$ and t_{exp} are not applicable (N/A) in this case.

Table S.2. Selected parameters used in rhodamine 6G FRAP experiments and resulting diffusion coefficients.

a_w	Thin film #	Droplet radius (µm)	$\tau_{diff,water}$	t_{exp}	Photobleach size (µm x µm)	Measured diffusion coefficients of organic dye ($\mu m^2/s$)
	1	350	N/A[a]	N/A[a]	36 x 36	34.67
	2	350	N/A[a]	N/A[a]	36 x 36	16.53
	3	350	N/A[a]	N/A[a]	36 x 36	43.66
0.85	1	350	N/A[a]	N/A[a]	36 x 36	1.53
	2	350	N/A[a]	N/A[a]	36 x 36	1.30
	3	350	N/A[a]	N/A[a]	36 x 36	1.04
0.80	1	350	11 min	1 h	36 x 36	0.545
	2	350	11 min	1 h	36 x 36	0.607
	3	350	11 min	1 h	36 x 36	0.418
0.75	1	350	17 min	1 h	36 x 36	0.0586
	2	350	17 min	1 h	36 x 36	0.0841
	3	350	17 min	2 hrs	36 x 36	0.0794
0.60	1	140	0.85 hrs	3 hrs	10 x 10	0.00187
	2	125	0.67 hrs	3 hrs	10 x 10	0.00567
	3	90	0.35 hrs	3 hrs	10 x 10	0.00266
0.52	1	190	11 hrs	6 d 15 hrs	5 x 5	0.000286
	2	150	7 hrs	6 d 15 hrs	5 x 5	0.000204
	3	200	12 hrs	6 d 15 hrs	5 x 5	0.000143
0.38	1	75	1 d	6 d	5 x 5	2.52E-06
	2	60	17 hrs	12 d	5 x 5	2.25E-06
	3	100	2 d	93 d	5 x 5	7.11E-07
	4	75	1 d	93 d	5 x 5	7.55E-07

[a] Droplets with an a_w of 0.93 and 0.85 were prepared gravimetrically, and hence $\tau_{diff,water}$ and t_{exp} are not applicable (N/A) in these cases.

Table S.3. Selected parameters used in calcein FRAP experiments and resulting diffusion coefficients.

a_w	Thin film #	Droplet radius (µm)	$\tau_{diff,water}$	t_{exp}	Photobleach size (µm x µm)	Measured diffusion coefficients of organic dye ($\mu m^2/s$)
0.88	1	350	N/A[a]	N/A[a]	30 x 30	4.32
	2	350	N/A[a]	N/A[a]	30 x 30	3.95
	3	350	N/A[a]	N/A[a]	30 x 30	3.27
0.80	1	350	11 min	30 min	15 x 15	0.158
	2	350	11 min	1 hrs	15 x 15	0.440
	3	350	11 min	1.5 hrs	15 x 15	0.229
0.70	1	350	34 min	2.5 hrs	5 x 5	0.0209
	2	350	34 min	3.75 hrs	5 x 5	0.0161
	3	350	34 min	5 hrs	5 x 5	0.0206
0.60	1	350	2.5 hrs	14 hrs	5 x 5	0.00104
	2	350	2.5 hrs	21 hrs	5 x 5	0.00227
	3	350	2.5 hrs	28 hrs	5 x 5	0.00243
0.52	1	150	5 hrs	7 days	5 x 5	0.000371
	2	150	5 hrs	7 days	5 x 5	0.000448
	3	150	5 hrs	7 days	5 x 5	0.000322
0.38	1	150	2 days	10 days	5 x 5	6.72E-6
	2	150	2 days	10 days	5 x 5	1.61E-5
	3	150	2 days	10 days	5 x 5	3.05E-6

[a] Droplets with an a_w 0.88 were prepared gravimetrically, and hence $\tau_{diff,water}$ and t_{exp} are not applicable (N/A) in this case.

Figures

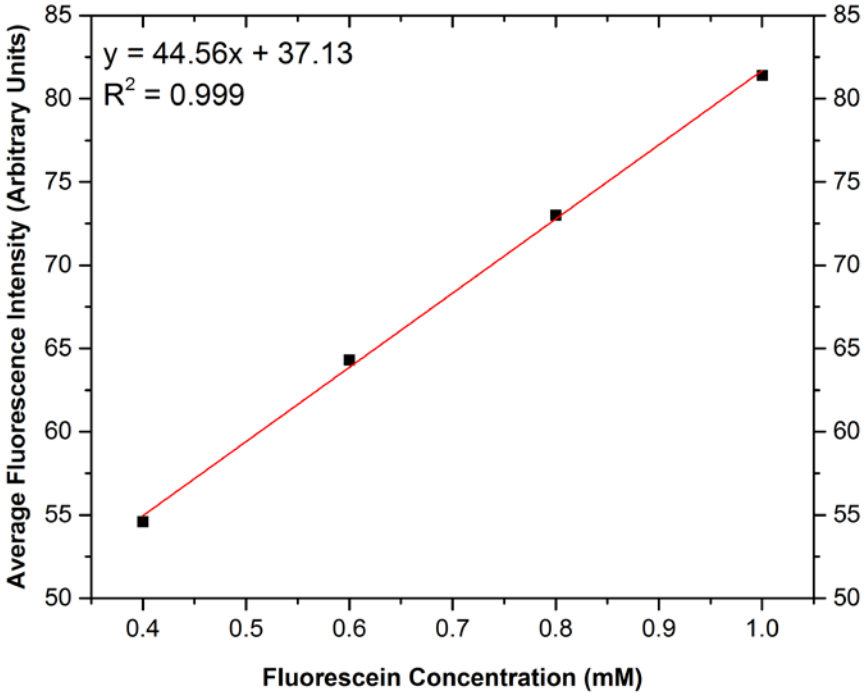

Figure S1. Average fluorescence intensity as a function of fluorescein concentration in 50 wt % sucrose solutions. The red line is a result of a linear fit to the data.

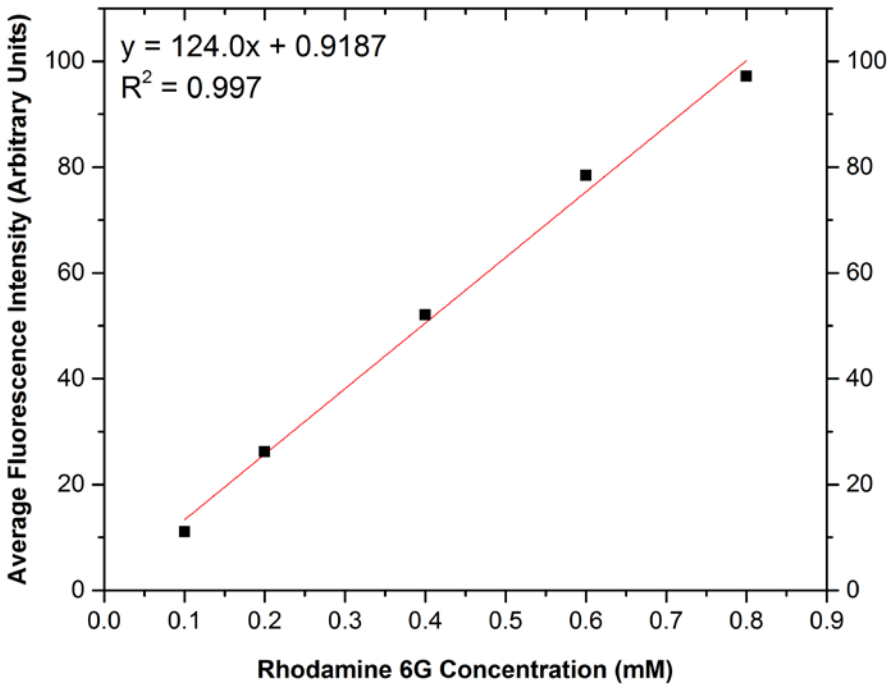

Figure S2. Average fluorescence intensity as a function of rhodamine 6G concentration in 50 wt % sucrose solutions. The red line is a result of a linear fit to the data.

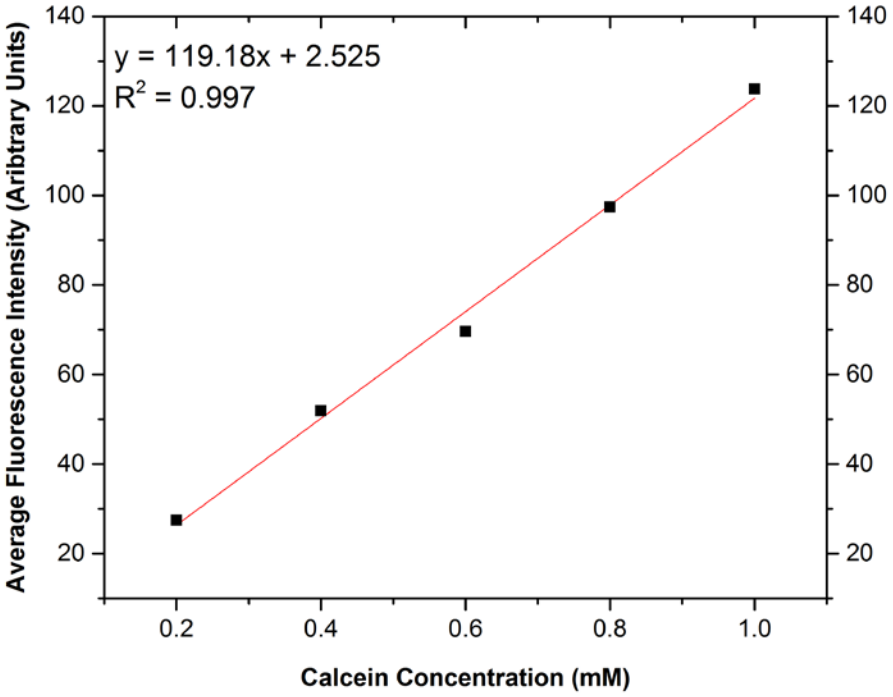

Figure S3. Average fluorescence intensity as a function of calcein concentration in 50 wt % sucrose solutions. The red line is a result of a linear fit to the data.

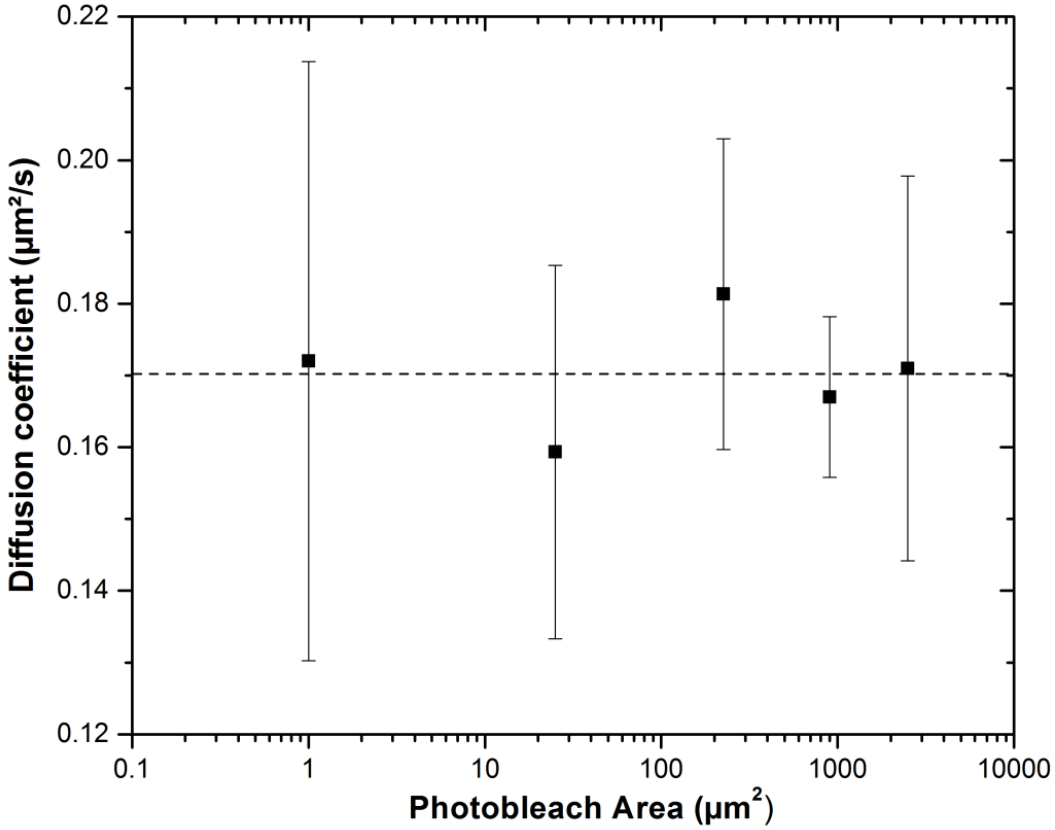

Figure S4. Measured diffusion coefficients of calcein in sucrose-water films conditioned at a_w of 0.80 using bleach sizes of 1x1 μm (photobleach area of 1 μm^2), 5x5 μm (photobleach area of 25 μm^2), 15x15 μm (photobleach area of 225 μm^2), 30x30 μm (photobleach area of 900 μm^2) and 50x50 μm (photobleach area of 2500 μm^2). The dashed line represents the average value of the data points (black squares).

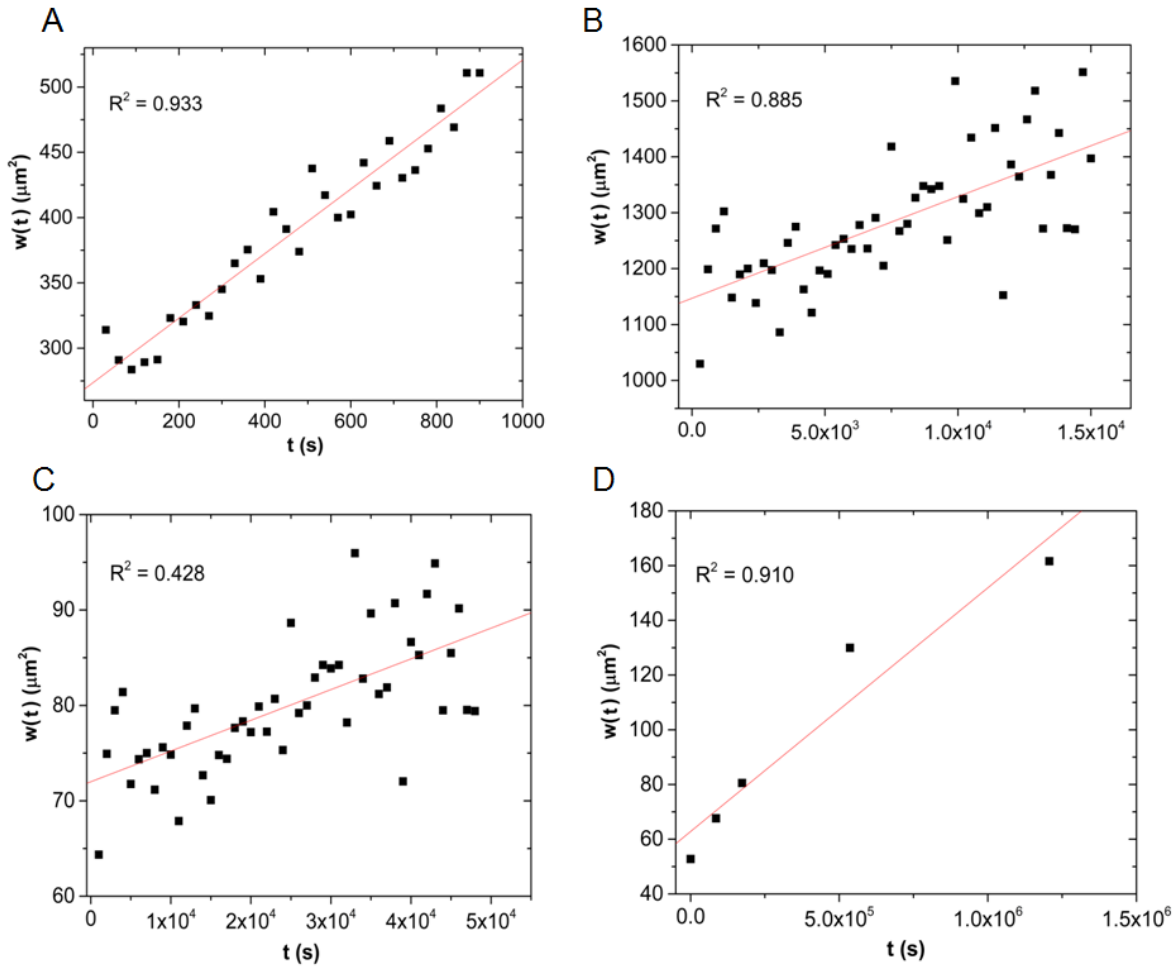

Figure S5. Example plots of *w(t)* versus time using fluorescein at the following a_w values: 0.70 (A), 0.60 (B), 0.52 (C) and 0.38 (D). The black squares represent measured data points, and the red line is a linear fit to the data.

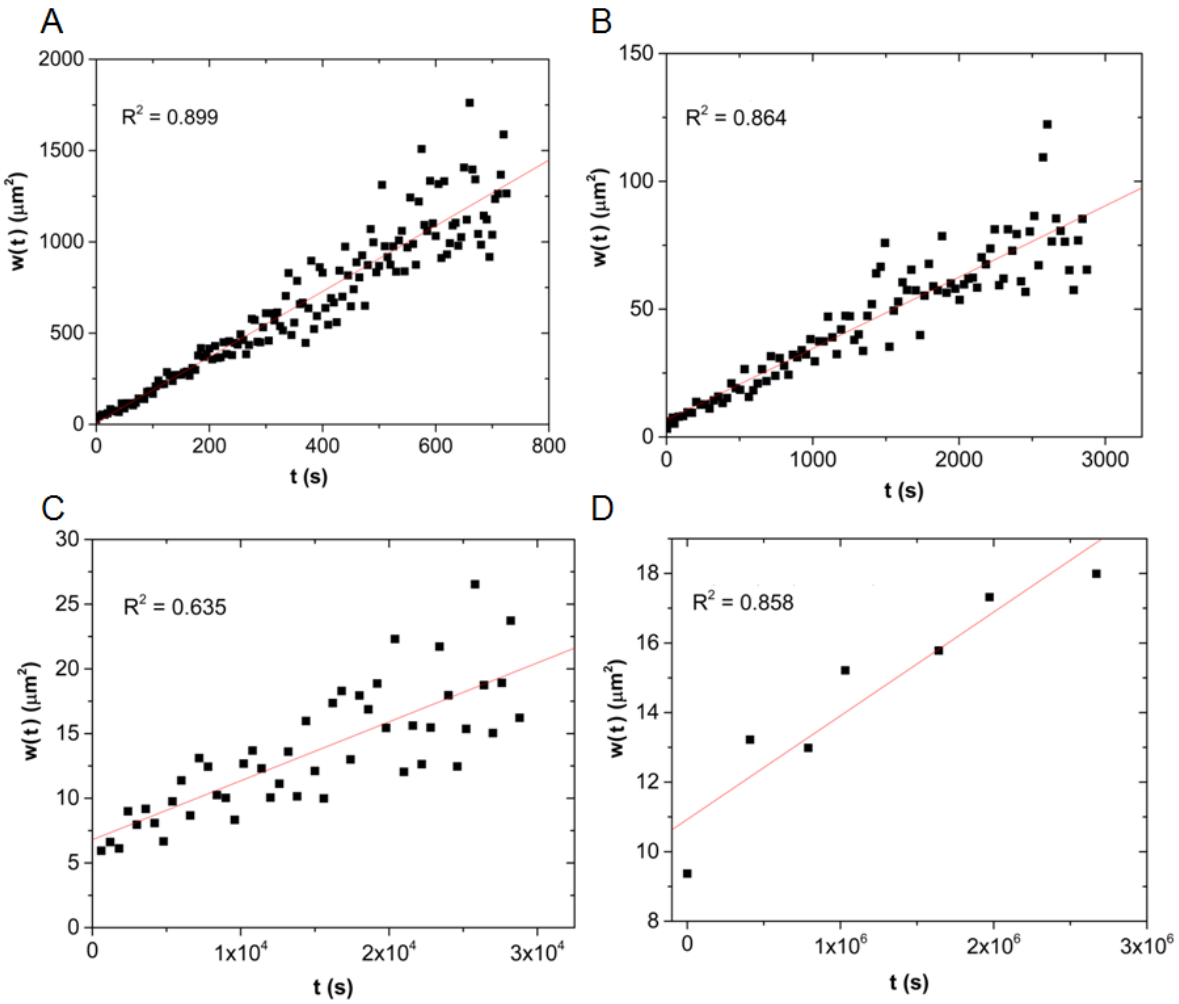

Figure S6. Example plots of *w(t)* versus time using rhodamine 6G at the following a_w values: 0.70 (A), 0.60 (B), 0.52 (C) and 0.38 (D). The black squares represent measured data points, and the red line is a linear fit to the data.

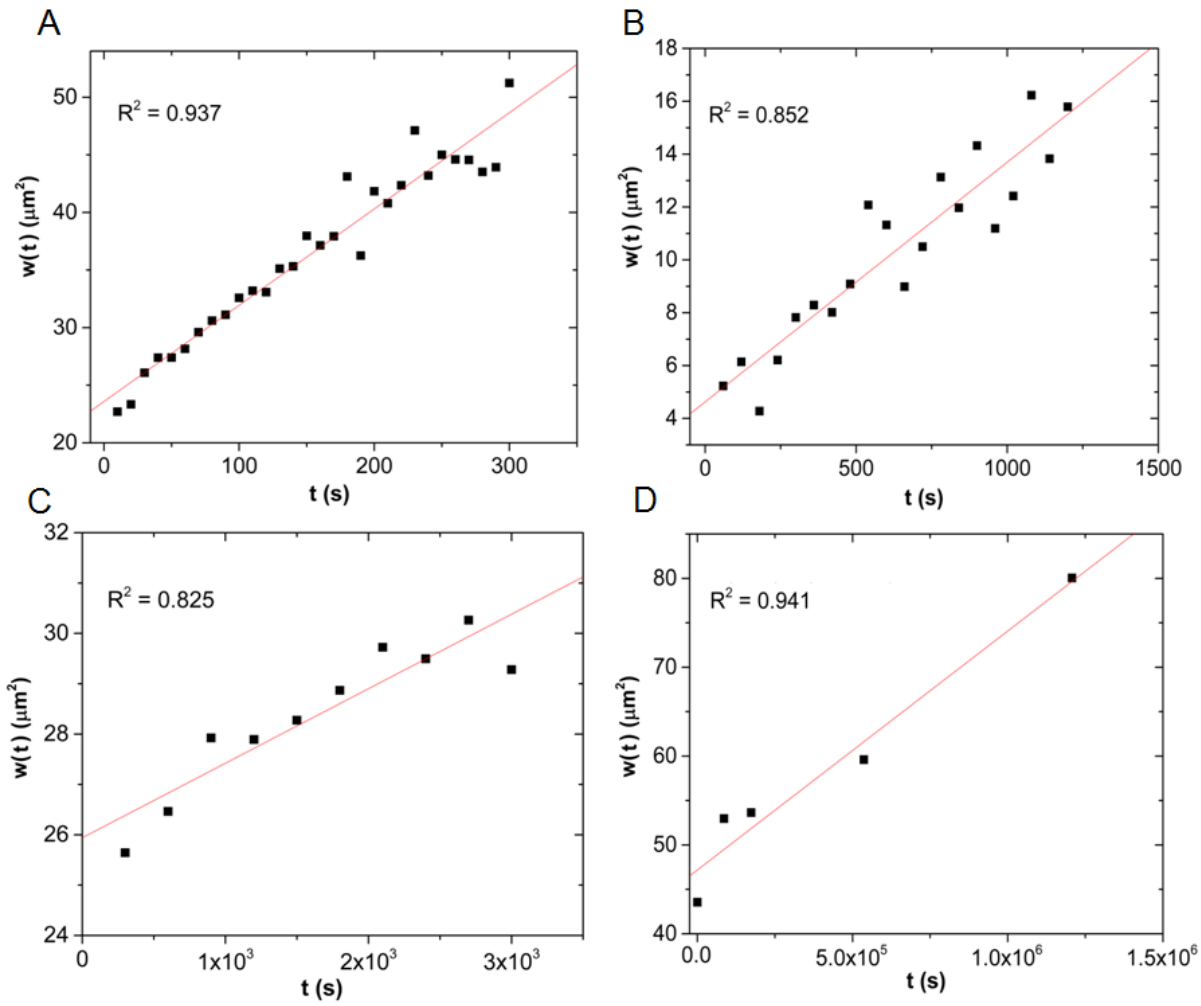

Figure S7. Example plots of *w(t)* versus time using calcein at the following a_w values: 0.70 (A), 0.60 (B), 0.52 (C) and 0.38 (D). The black squares represent measured data points, and the red line is a linear fit to the data.