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Electronic Supplementary Information for:

Optical Calorimetry in Microfluidic Droplets

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Supplementary Figure 1: Titration of EDTA with CaCl₂. Binding of CaCl2 to EDTA was measured at 25 °C in 100 mM Tris-HCl (pH 7.5), 0.015% (w/v) Triton X-100. The sample cell (200 μ L) contained EDTA (500 μ M), and the injection syringe contained 5 mM CaCl₂.



Supplementary Figure 2: Microphotograph of the color change of TLC microparticles in response to temperature. 5x objective, ≈2 sec exposure. Water/0.015% Triton X-100.

Supplementary Table 1: Mixing rates at various flow conditions. ** Some binding of fluo-4 to Ca²⁺ occurs prior to droplet generation

Combined aqueous flow rate (µl/min)	Novec 7500 flow rate (µl/min)	Total fluid flux (µl/sec)	Droplet generation rate (Hz)	Linear flow rate (mm/s)	Distance for 90% mixing (mm)	Time for 90% mixing (ms)
22.5	37.3	0.997	716	83.9	0.75	9
15	37.3	0.872	477	73.4	0.70	10
12	37.3	0.822	382	69.2	**	NA
9	37.3	0.772	286	64.9	**	NA
6	37.3	0.722	191	60.7	**	NA



Supplementary Figure 3: Microphotograph (2 s exposure, individual droplets are invisible) showing time-averaged fluorescence arising from mixing inside droplets formed by combining equal volumes of CaCl2 (5 mM), EDTA (1 mM), and Fluo-4 (54 μ M), in MOPS (20 mm, pH 7.2). Aqueous streams were in the same configuration as described in Figure 6 of the article.

Name	Value	Units	Description		
T _{ref}	298.15	[K]	Reference temperature		
[EDTA] ₀	0.05	[mol/liter]	Initial concentration of EDTA		
[CaCl ₂] ₀	1	[mol/liter]	Initial concentration of CaCl ₂		
D _{EDTA}	1.09E-09	[m^2/s]	Diffusivity of EDTA in water		
D _{CaCl2}	1.09E-09	[m^2/s]	Diffusivity of CaCl ₂ in water		
k	1.00E+07	[1/((mol/liter)*s)]	reaction kinetic rate constant		
ΔH	-50578	[J/mol]	Heat of reaction, measured using ITC		
<i>K</i> _{Novec}	0.06477	[W/m*K]	Thermal conductivity of Novec 7500 at $T_{\rm ref}$		
K _w	0.607	[W/m*K]	Thermal conductivity of water at <i>T</i> _{ref}		
C _{pNovec}	1128.455	[J/kg*K]	Specific heat capacity of Novec 7500 at $T_{\rm ref}$		
C _{pw}	4138	[J/kg*K]	Specific heat capacity of water at $T_{\rm ref}$		
$ ho_{ m Novec}$	1613.6875	[kg/m ³]	Density of Novec 7500 at $T_{\rm ref}$		
ρ _w	997	[kg/m ³]	Density of water at T _{ref}		

Supplementary Table 2: Parameters used in the COMSOI model. Value of ΔH was obtained from ITC measurements. Values for Novec 7500 from product data sheet (http://multimedia.3m.com/mws/media/65496O/3mtm-novectm-7500-engineered-fluid.pdf).



Supplementary Figure 4: Concentration profiles of EDTA (initial 50 mM) and CaCl₂ (initial 1 M) over time for the 'with spacer' condition (for t = 0 through t = 100 ms at 10 ms time steps).



Supplementary Figure 5: Concentration profiles of EDTA (initial 50 mM) and CaCl2 (initial 1 M) over time for the 'no spacer' condition (for t = 0 through t = 100 ms at 10 ms time steps).

