Electronic Supporting Information (ESI)

Supramolecular logic with macrocyclic input and competitive reset

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1) General remarks

Materials. All reagents for the synthesis of **1** were from Aldrich and used as received. Cadaverine dihydrochloride was purchased from Aldrich in the highest purity available (>98%) and used without further purification. Cucurbit[7]uril (CB7) was prepared in >95% purity, following described synthetic procedures.[1-3]

Absorption and Fluorescence Measurements. Absorption measurements were performed with a Varian Cary 4000 spectrophotometer and fluorescence spectra were recorded on a Cary Eclipse fluorimeter. The solutions of **1** and CB7 were freshly prepared with ultrapure water, and the pH was adjusted using HCl and NaOH. Special care was taken to minimize the amount of NaOH, because excessive [Na^+] may adversely affect the formation of CB7 host-guest complexes.[4,5] Fluorescence titrations at constant pH were performed by successive addition of CB7 to a solution of **1** in a 1-cm quartz cuvette. The resulting data were fitted with a 1:1 binding model, using Origin 7.0 software (OriginLab Corporation, Northampton, MA). Special care was taken to avoid dilution effects in the course of the experiment. Fluorescence spectra were obtained for selective excitation of the naphthalimide part of **1** (λ_{exc} > 325 nm). pH Titration curves were recorded by following the fluorescence signal at λ_{max} = 395 nm. The Job's plot analysis was performed by systematic variation of the molar fraction of **1** at a constant total concentration of guest and host. The fluorescence quantum yields were determined with 9-methylanthracene in deaerated ethanol as standard (Φ_f = 0.33).[6]

Isothermal Titration Calorimetry. The microcalorimetric measurements were performed on an isothermal titration calorimeter (VP-ITC) from MicroCal Inc., USA. The ITC instrument was periodically calibrated using the internal electric heater.

Titration experiments were carried out at 25°C in aqueous solution. Each experiment consisted of 15–25 consecutive injections (5–10 μL) of host solution (0.3–0.4 mM) injected into the microcalorimetric reaction cell, filled with probe solution (20 μM), placed specifically into the reaction cell due to its limited solubility. All solutions were degassed prior to titration. Heats of dilution were subtracted from each data set. Mean values were measured from at least two experiments with errors given as standard deviation (±1σ). The data were analyzed using a 1:1 binding model in Origin 7.0 software.

High Resolution Mass Spectrometry (HRMS) was done with a MicroTOF focus mass spectrometer (Brucker Daltonics) fitted with an electrospray ionisation (ESI) source. External calibration was achieved with 0.1 M sodium formate solution. The sample was prepared in 50:50 water/ethanol mixture and measured in a negative mode.

Mass Spectrometry of Complex CB7•1 was done on a Ion-trap mass spectrometer fitted with an ESI source (Bruker Daltonics HCT Ultra). MS operating conditions (negative/positive mode) had been optimized using polyethylene glycol solution with a capillary temperature of 300ºC, a dry gas flow rate of 5 L/min and a nebulizer pressure of 10 psi. The sample of host and guest was prepared in water and measured in a positive mode.

Preparation of *N*-[2-(2-benzimidazoyl)ethyl]-4-sulfonato-1,8-naphthalimide (1) 122 mg (0.52 mmol) of 2-(2-aminoethyl)benzimidazole dihydrochloride were added to 166 mg (0.52 mmol) of 4-sulfonato-1,8-naphthalic anhydride potassium salt and 0.15 mL (1 mmol) of triethylamine in 10 mL ethanol. The reaction mixture was refluxed for 13 hours. The colourless precipitate, which formed during this time, was filtered, washed with ethanol, and vacuum-dried to give 172 mg of the product (67% yield).

^{1}H NMR (400 MHz, DMSO-d_6) δ/ppm: 13.39 (br s, 1H), 9.26 (dd, J = 8.6 Hz, J = 1.2 Hz, 1H), 8.45 (dd, J = 7.3 Hz, J = 1.2 Hz, 1H), 8.43 (d, J = 7.6 Hz, 1H), 8.21 (d, J = 7.6 Hz, 1H), 7.88 (dd, J = 8.6 Hz, J = 7.3 Hz, 1H), 7.53 (m, 2H), 7.22 (m, 2H), 4.50 (t, J = 7.2 Hz, 2H), 3.28 (t, J = 7.2 Hz, 2H).

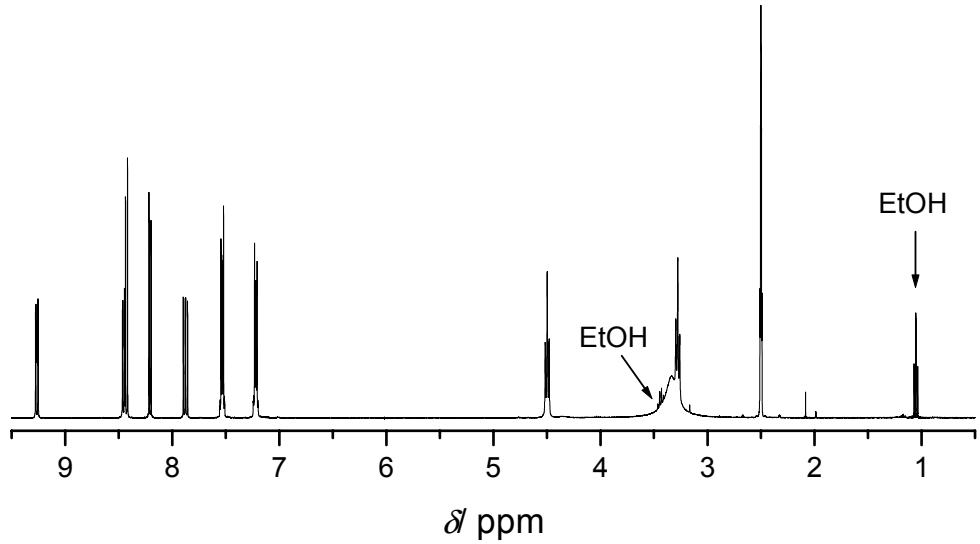


Figure S1. ^{1}H-NMR spectrum of **1** in dimethylsulfoxide-d_6.

^{13}C NMR (100 MHz, DMSO-d_6) δ/ppm: 163.5, 163.1, 152.1, 149.9, 136.5, 134.1, 130.2, 130.0, 128.1, 127.5, 126.6, 124.9, 122.7, 122.3, 122.0, 114.2, 38.1, 26.5.

HRMS: calcd for $C_{21}H_{14}N_3O_5S$ (anion), 420.0660; found, 420.0636.

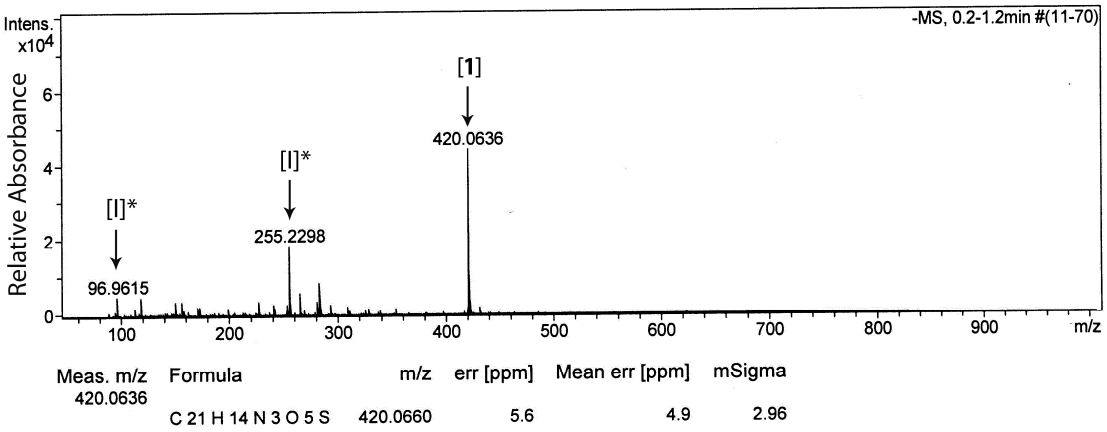


Figure S2. High resolution mass spectrum of **1** (negative mode). [I]* stands for standard sample preparation impurity recognized as a fragment of a derivative of the fatty acid palmitone.[7]

2) Thermodynamic of photoinduced electron transfer (PET)

The assumption of intramolecular PET as fluorescence quenching mechanism of the signalling unit in **1** is founded on the fact that 1,8-naphthalimide chromophores are generally potent electron acceptors in the singlet-excited state (E_{red} = −1.0 V *versus*

SCE in acetonitrile for *N*-ethyl-1,8-naphthalimide as model,[8] $E^*(S_1)$ = 3.4 eV; determined for **1** from the intersection point of normalized absorption and fluorescence spectra). This enables strongly exergonic PET thermodynamics, even with moderate electron donors like benzimidazole (E_{ox} = 1.3 V *versus* SCE in acetonitrile),[9] *i.e.*, ΔG_{PET} *ca.* −1.2 eV (calculated with $\Delta G_{PET} = E_{ox} - E_{red} - E^* + \Delta G(\varepsilon)$; $\Delta G(\varepsilon) \approx -0.1$ eV for water[10]).

3) UV/Vis absorption spectra of 1 upon addition of CB7

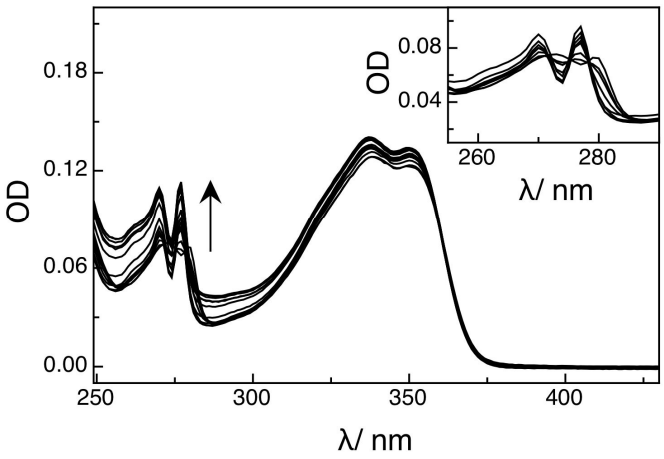


Figure S3. UV/Vis titration of 10 μM **1** with up to 2 mM CB7 at pH 7.

4) Determination of binding constant with CB7 by fluorescence titration at pH 7

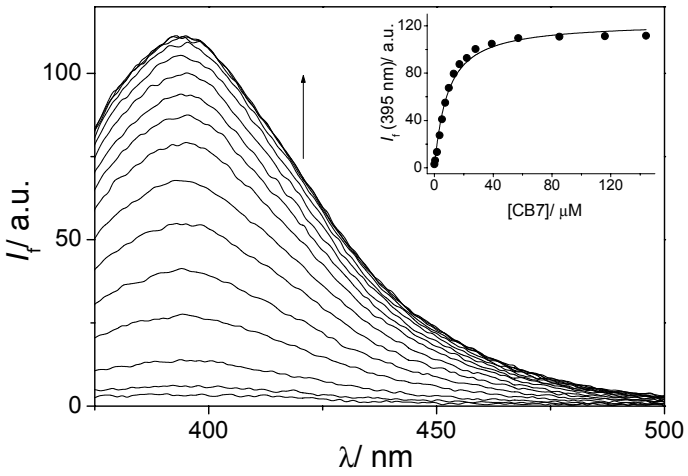


Figure S4. Fluorescence titration of **1** (2 μM) with CB7 (up to 144 μM) at pH 7. The inset shows the corresponding titration curve and 1:1 binding fit (solid line) with $K_b = (1.3 \pm 0.1) \times 10^5$ M^{-1}.

5) Job's plot analysis

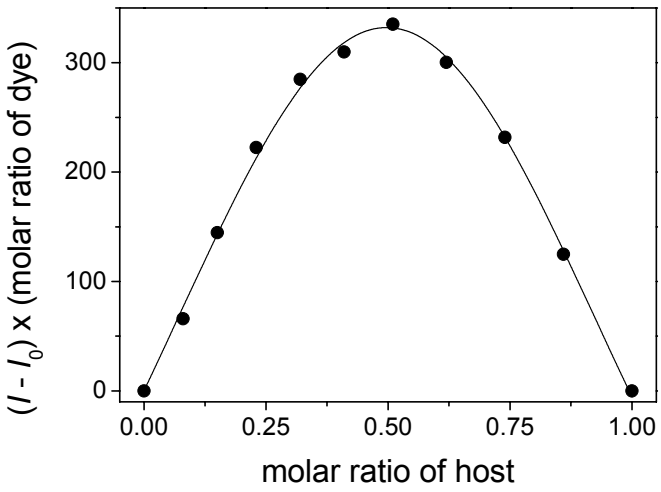


Figure S5. Fluorescence Job's plot of **1** with CB7 (pH 7, λ_{exc}= 360 nm, λ_{em}= 395 nm). *I* is the observed fluorescence intensity in presence of varying mole fractions of CB7 and I_0 is the intrinsic fluorescence of dye in absence of CB7.

6) Isothermal titration calorimetry (ITC)

The ITC titration data revealed an enthalpic contribution of $\Delta H^{o} = -17.1$ kJmol^{-1} and an entropic gain of $T\Delta S^{o}$ = 14.6 kJmol^{-1} for complex formation at pH 3.5 (Figure S6). From these values it can be deduced that complexation is enthalpically and entropically driven. The enthalpic contribution is related to hydrophobic effects and ion-dipole interactions between protonated **1** and CB7 carbonyl portals. The entropic gain is caused by the desolvation of the guest upon inclusion in the host cavity. Similar effects have been observed for the complexation of other guests by CB7.[4,11]

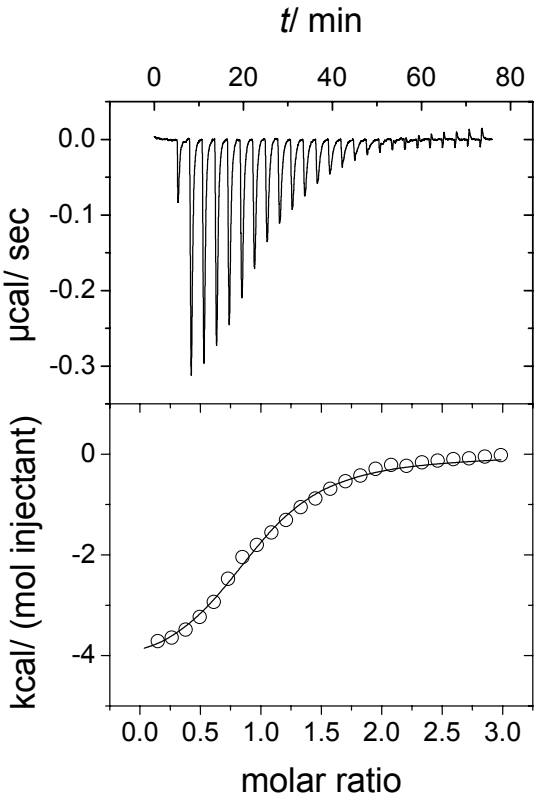
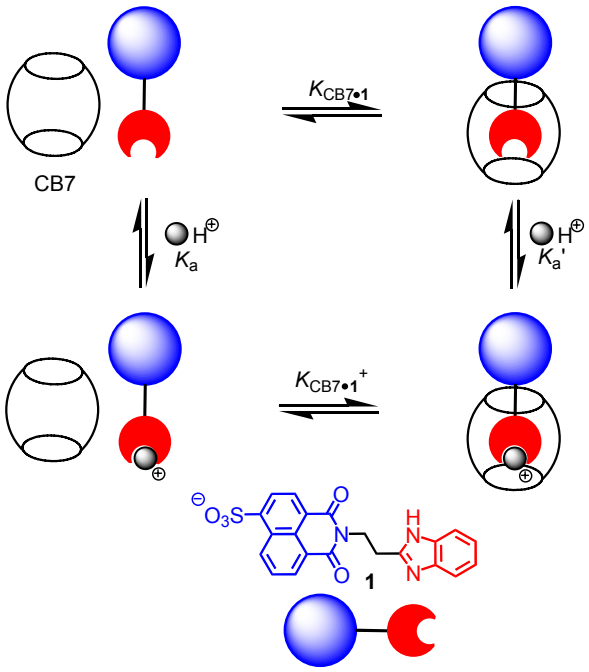


Figure S6. Calorimetric titration of **1** with CB7 (25°C, pH 3.5). The top plot shows the instrumental power function versus time (injected aliquots). The bottom plot shows the heat of reaction obtained from the integration of the calorimetric traces, plotted against the host/guest molar ratio.

7) Fitting according to four-state-model



Scheme S1. Four-state-model involving the free and complexed **1** in protonated and unprotonated forms.

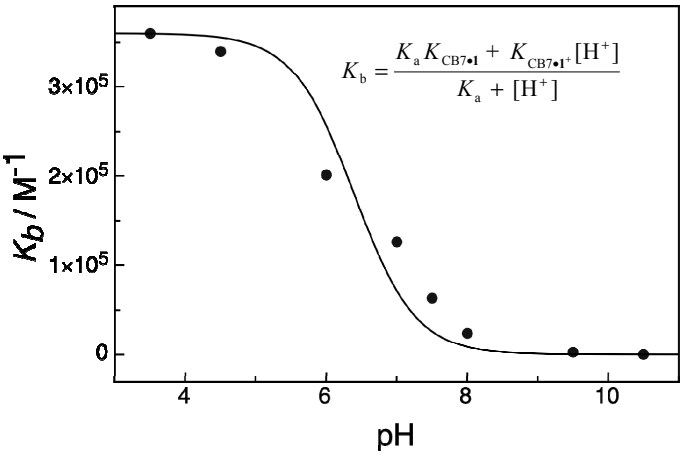


Figure S7. Variation of the binding constant K_b of **1** by CB7 upon changing of pH. The solid line represents the fit according to the four-state-model (Scheme S1, above). The experimental data are compiled in Table S1 (below). The inset shows the corresponding fitting function.

Table S1. Binding constants of **1** by CB7 at different pH, measured by fluorescence spectroscopy and isothermal titration calorimetry.

pH	K_b/ M^{-1}[a]	
	Fluorescence	Isothermal calorimetry
3.5		$(3.6 \pm 0.1) \times 10^5$
4.5		$(3.4 \pm 0.1) \times 10^5$
6.0	$(2.0 \pm 0.4) \times 10^5$	
7.0	$(1.3 \pm 0.1) \times 10^5$	
7.5		$(6.3 \pm 0.5) \times 10^4$
8.0	$(2.4 \pm 0.5) \times 10^4$	
9.5	$(2.5 \pm 0.8) \times 10^3$	
10.5	0 (no binding)	

[a] Mean values measured from at least two experiments at 25ºC in aqueous solution, error given as standard deviation (±1σ).

8) Mass spectrum of complex CB7•1

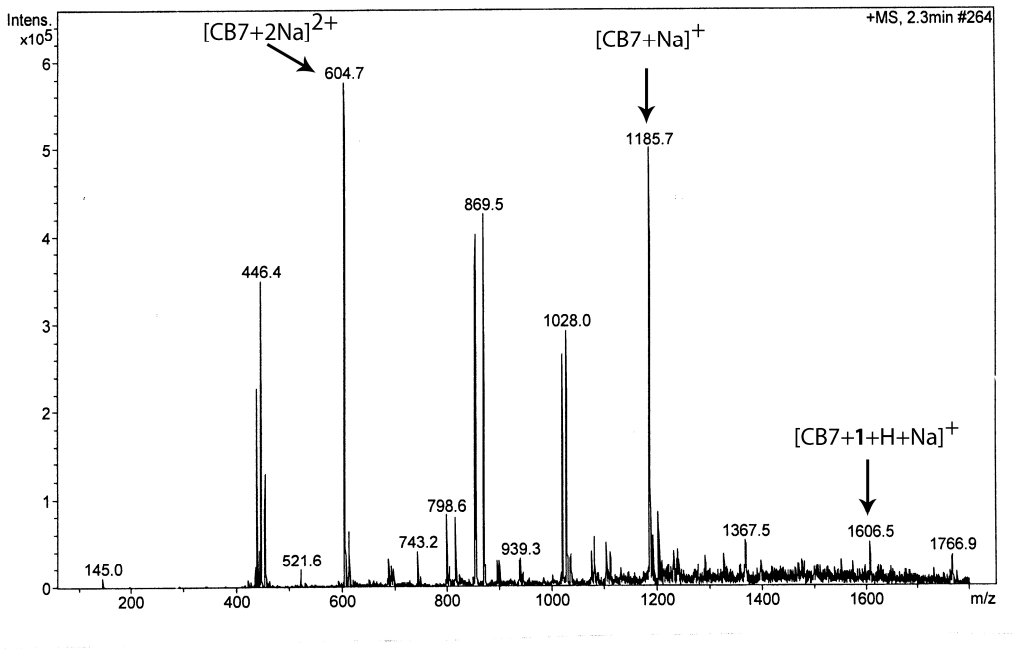


Figure S8. ESI mass spectrum of a mixture of 10 μM **1** and 100 μM CB7 (positive mode).

9) Logic gates (threshold for all gates: $I_f = 0.25$, 2 μM **1**, 200 μM CB7); see also Table 1 in manuscript.

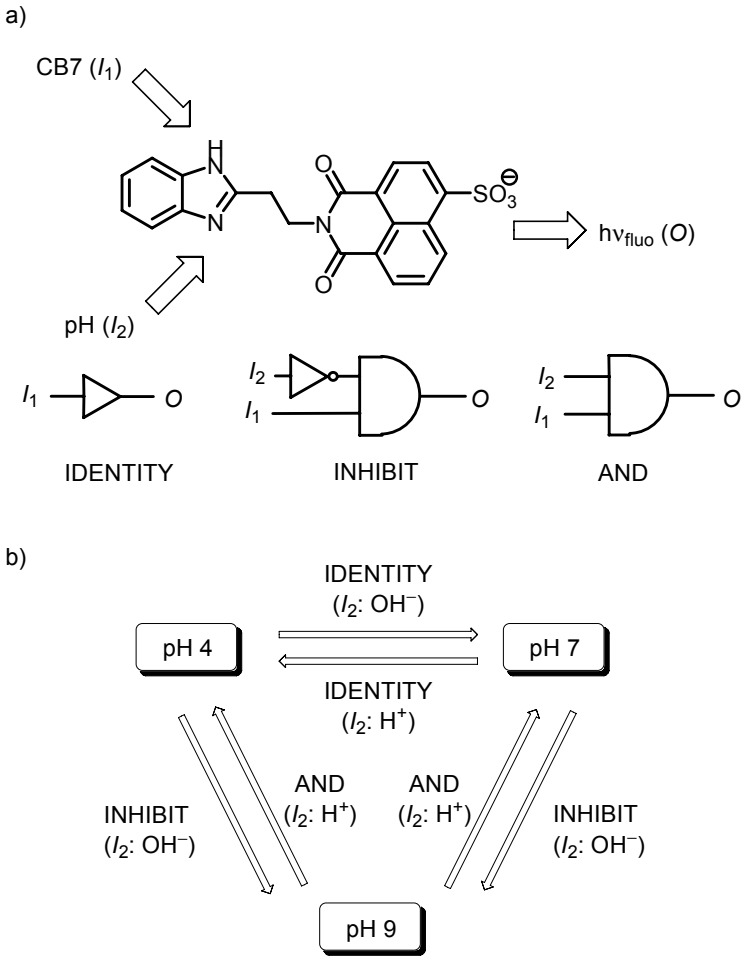
initial pH = 4.0; **logic gate: IDENTITY (I_1)**		
I_1: CB7	I_2: OH^- (pH = 7.0)	O: I_f (395 nm) normalized
0	0	0 (0.17)
1	0	1 (1.00)
0	1	0 (0.05)
1	1	1 (0.93)

initial pH = 4.0; **logic gate: INHIBIT**		
I_1: CB7	I_2: OH^- (pH = 9.0)	O: I_f (395 nm) normalized
0	0	0 (0.17)
1	0	1 (1.00)
0	1	0 (<0.01)
1	1	0 (0.07)

initial pH = 7.0; **logic gate: IDENTITY (I_1)**		
I_1: CB7	I_2: H^+ (pH = 4.0)	O: I_f (395 nm) normalized
0	0	0 (0.05)
1	0	1 (0.93)
0	1	0 (0.17)
1	1	1 (1.00)

initial pH = 7.0; **logic gate: INHIBIT**		
I_1: CB7	I_2: OH^- (pH = 9.0)	O: I_f (395 nm) normalized
0	0	0 (0.05)
1	0	1 (1.00)
0	1	0 (<0.01)
1	1	0 (0.08)

initial pH = 9.0; **logic gate: AND**		
I_1: CB7	I_2: H^+ (pH = 4.0)	O: I_f (395 nm) normalized
0	0	0 (<0.01)
1	0	0 (0.07)
0	1	0 (0.17)
1	1	1 (1.00)



Scheme S2. a) Representations of the different reconfigurable logic gates (IDENTITY, INHIBIT, AND) based on **1** with CB7 and pH changes as chemical input signals. b) Reconfiguration of the three logic gates in dependence on the initial situation (pH at the corners of the triangle) and the application of acid or base as input I_2. Note that input I_1 corresponds to the addition of CB7 in all cases.

References

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