Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

SUPPORTING INFORMATION

Supramolecular assembly by time-programmed acid autocatalysis

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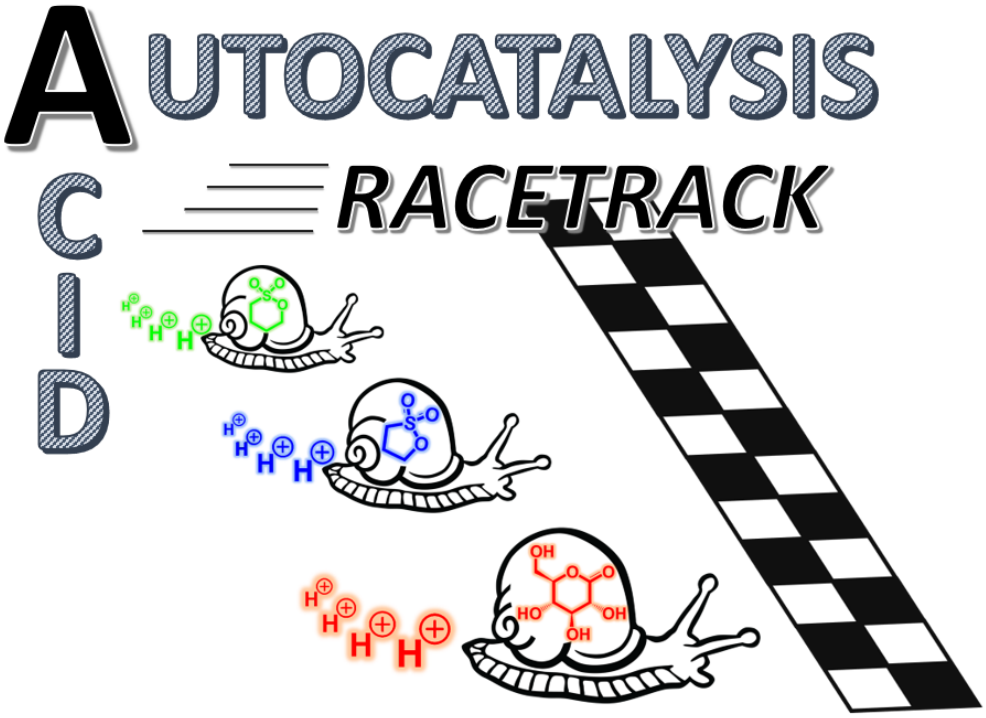


EXPERIMENTAL

Reagents. Sodium bromate (puriss. p.a., ≥99.5% RT), sodium sulfite (≥98%), δ-gluconolactone (meets USP testing specifications), 1,3-propanesultone (98%), 1,4-butanesultone (≥99%), lactic acid (~90%, titrimetric), 1-methyl imidazole (≥99%, purified by redistillation) and 3-aminopropanoic acid (99%) were purchased from Sigma-Aldrich (Switzerland). 3,4,9,10-Perylenetetracarboxylic dianhydride (PTCDA, 98%) was purchased from Acros Organics (Belgium). 1-Propanesulfonic acid (99%) was obtained from Fluka (Switzerland). Unless otherwise stated, all chemicals were of analytical or reagent grade purity and used as received. Water was purified by means of a MilliQ system (resistivity ≥ 18 MΩ). All the experiments were carried out at room temperature (22°C).

pH Measurements. A Hanna Instruments (USA) HI5222-02 benchtop pH-meter was used together with a HI1330B glass body combination pH microelectrode from the same Company. The pH-meter was calibrated with standard buffer solutions (pH values: 1.670, 4.010, 7.010 and 10.01) before each set of analysis. The pH-electrode was cleaned after each analysis by repeated immersion in water, the excess water gently removed with hairless paper and immediately immersed in the solution to analyze. The pH-meter was interfaced with a computer through the software HI92000 – 5.0.38 (Hanna Instruments, USA) to allow continuous recording of pH values with a time interval of 1 s.

UV-Visible spectrophotometry (UV-Vis). UV-Vis measurements were performed with a Cary 60 UV-vis spectrophotometer (Agilent). Standard quartz cuvettes with an optical path of 1 cm were used. The absorbance data were recorded with a time interval of 1 s. Mixing was provided with a Cimarec i Mini stirrer (Thermo Scientific) and a PTFE-coated magnetic bar (3x8 mm) rotating at ~500 rpm.

Fourier-transform infrared spectroscopy (FTIR). FTIR in attenuated total reflectance (ATR) conditions were performed with a Bruker Alpha P spectrophotometer equipped with a diamond window. Spectra were acquired with a 4 cm^{-1} resolution.

Dynamic light scattering (DLS). DLS measurements were performed with an ALV/CGS-3 Goniometer (ALV-Gmbh) and analysed with the software from the same company (version 3.0). The reagents were mixed, the solution was quickly passed through a 0.22 μm filter and poured in a glass test-tube previously rinsed with water. The tube was closed, washed with toluene, and placed inside the toluene-filled chamber of the setup. The measurement started after one minute (for temperature equilibration to 25 ºC); one run of 10 seconds was acquired every minute. Each run was independently fitted by the software using a second-order cumulant method, and the resulting hydrodynamic radius is reported here. The time origin $t = 0$ was set as the time when the reagents were first mixed.

Scanning electron microscopy (SEM). SEM was performed with a Hitachi SU5000. Sample preparation: the reaction mixture containing the precipitated aggregates was centrifuged (7000 rpm, 10 min), the supernatant discarded and the fluffy pellet gently redispersed in water. A small amount of properly diluted aqueous suspension was dropped on a small piece of (100)-cut silicon wafer (previously hydrophilized by treating them at 90°C for 1 h with acidic piranha solution. *Caution!*). The samples were allowed to dry in open air at room temperature. To facilitate imaging, the silicon substrates were mounted on conductive carbon tape and sputtered with 4 nm of Pt/Pd alloy.

Typical experimental protocols. Sodium bromate stock solution: 3.32 g (22 mmol) $NaBrO_3$ were dissolved in 40 mL water. Sodium sulfite stock solution: 0.756 g (6 mmol) Na_2SO_3 were dissolved in 40 mL water. All stock solutions were made fresh before each experiment and stored for no longer than three hours at room temperature avoiding direct light.

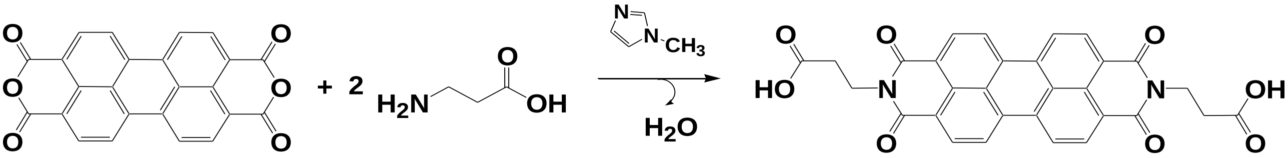
Reactions were carried out at room temperature (23 ± 1 °C), using 15 mL-glass vials as reaction vessels and PTFE-coated magnetic stirrer bars (5x20 mm) rotating at 500 rpm to provide mixing. The measurements were performed in open-to-air vessels. Equal amounts of the stock solutions (usually 4 mL each) were mixed together and water was added (usually 1 mL) to adjust the volume. A proper amount (see Table S1) of the chosen cyclic ester was dissolved in 1 mL water and the resulting solution was added to the reaction mixture. The final reaction volume was fixed as 10 mL.

For the supramolecular self-assembly experiments, 0.0014 g of PDIacid (see through) were dissolved in 1 mL of water with 5 μL of NaOH 2 M. The resulting homogeneous red solution was diluted 1:10 with the bromate-sulfite reaction mixture, to have a final PDIacid concentration of 25 μM.

Table S1. Amounts of the cyclic esters and model acids used.

Final concentration (mM)	*δ-Gluconolactone (g)*	*1,3-Propanesultone (μL)*	*1,4-Butanesultone (μL)*	*Lactic acid (μL)*	*Propanesulfonic acid (μL)*
10	0.0178	9	-	8.2	10
20	0.0356	17.5	-	16.4	20
30	0.0534	26.3	-	24.6	30
50	0.0890	44	-	41	50
100	0.178	88	102.3	82	99

Synthesis of (3-aminopropanoic acid)-perylene-3,4:9,10-tetracarboxylic acid diimide (PDIacid). The procedure was adapted from the literature[1]. In particular, 1-methyl imidazole was used instead of imidazole, resulting in both high product yield and simpler work-up.



In a three-neck 100 mL-round bottom flask, equipped with a magnetic stirrer, water condenser and nitrogen inlet, 1.376 g (3.507 mmol) of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) and 2.5 g of 3-aminopropanoic acid (28.06 mmol) are suspended in 25 mL of 1-methyl imidazole. The resulting mixture is heated under nitrogen in an oil bath at 100°C for 4 h. The reaction mixture is allowed to cool to room temperature and added to 100 mL of ethanol under stirring. Then, 300 mL of 2 M HCl are added slowly under stirring and cooling with a water bath. The resulting suspension is left overnigth under stirring, then it is centrifuged at 8000 rpm for 15 min. The solid is washed three times with water, two times with ethanol and eventually is dried under vacuum. Yield: 90%. The product was characterized by ATR-FTIR (Figure S0). Calculated molecular mass ~561 g mol^{-1}.

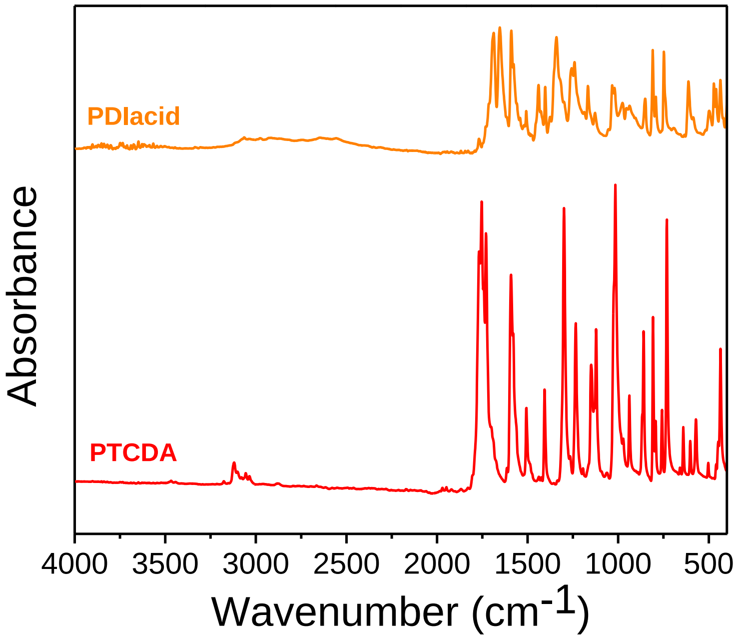


Figure S0. Normalized ATR-FTIR spectra of the product PDIacid and of the starting material PTCDA. The success of the synthesis if confirmed by the disappearance of the strong absorption at ca. 1750 cm^{-1} (anhydride carbonyl), together with the appearance of strong absorptions around 1689 cm^{-1} and 1653 cm^{-1} (asymmetric and symmetric vibrations of the imide carbonyl), in the spectrum of PDIacid.[2]

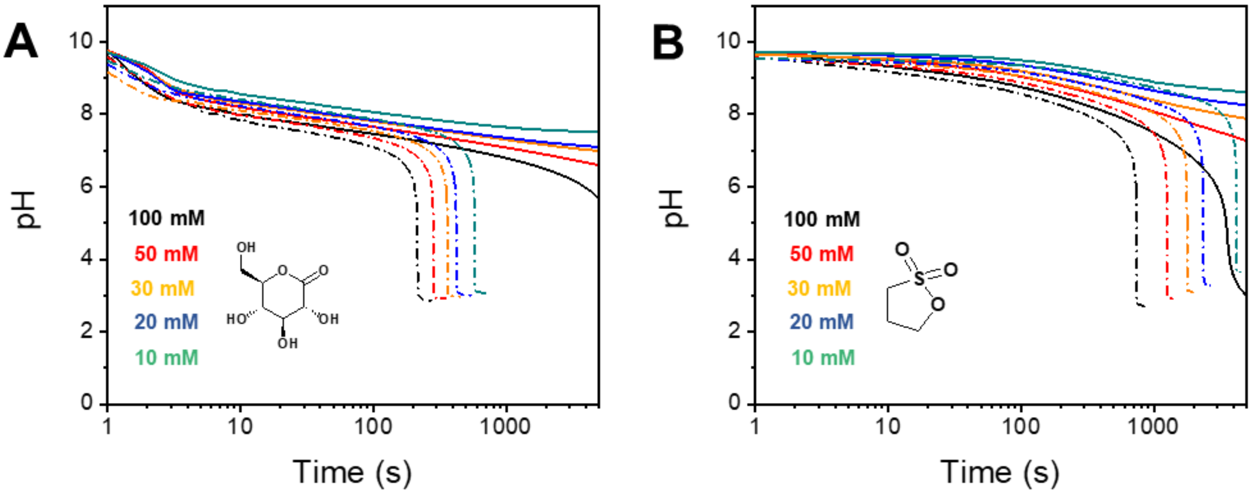


Figure S1. Evolution of pH over time for different concentrations of acid generators added to a 60 mM sodium sulfite solution: (a) δ-gluconolactone, (b) 1,3-propanesultone. For comparison, the curves obtained for the bromate-sulfite reaction (220 mM bromate, 60 mM sulfite) are also shown (dash-dot lines).

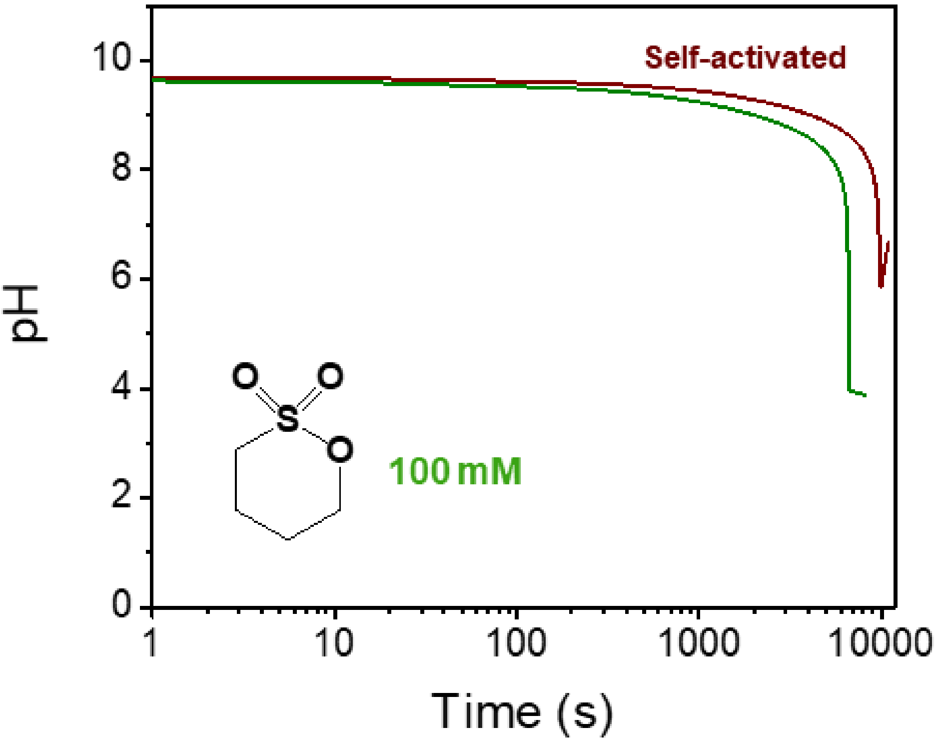


Figure S2. Effect of 1,4-butanesultone (100 mM) on the pH-time evolution of the bromate-sulfite reaction. The self-activated reaction is shown for comparison.

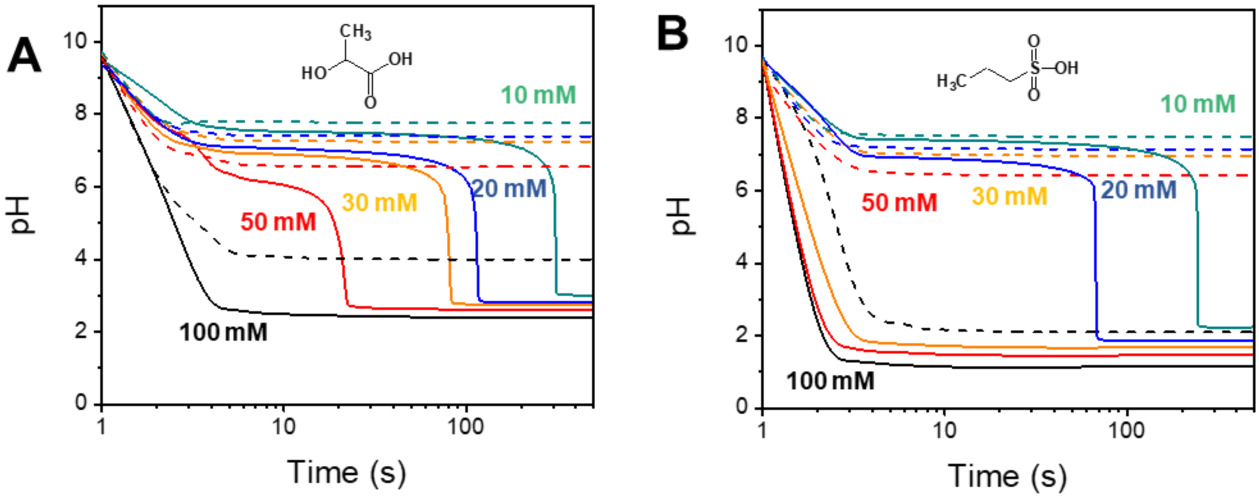


Figure S3. Control experiments using model acids: effect of different concentrations of (a) lactic acid and (b) 1-propanesulfonic acid on the pH evolution of the bromate-sulfite reaction (220 mM bromate, 60 mM sulfite). For comparison, the results obtained with a 60 mM sodium sulfite solution are also shown (dashed lines).

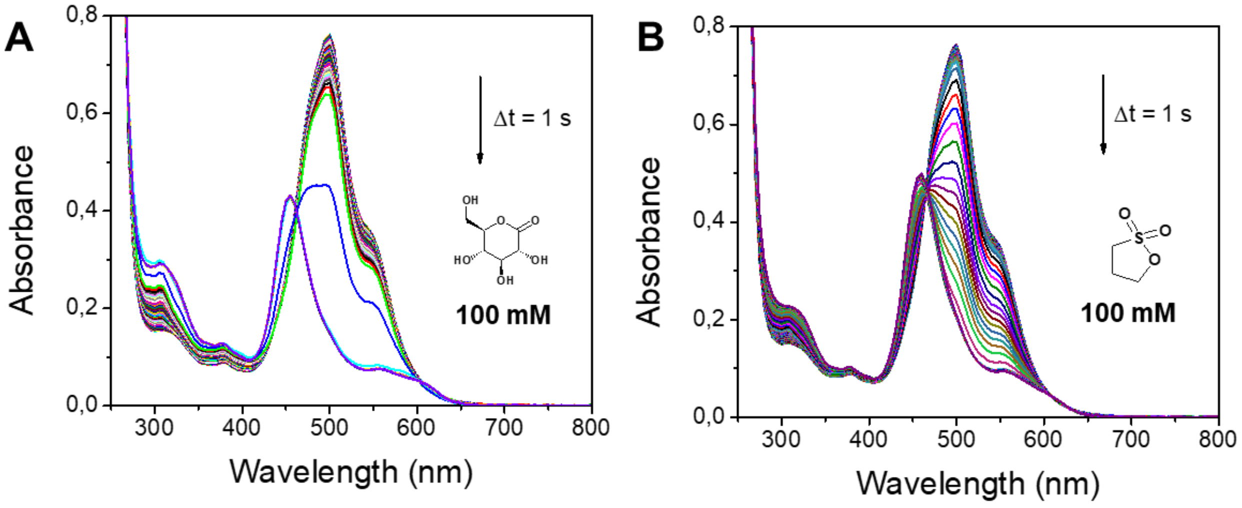


Figure S4. Evolution of UV-Visible spectra over time for the BS reaction with 25 μM PDIacid and 100 mM of (a) δ-gluconolactone (GL), (b) 1,3-propanesultone (PrS). The spectra have been acquired with a frequency of 1 s^{-1} to demonstrate the rapid change in the photophysical properties of PDIacid as a result of protonation.

REFERENCES

1 A. Datar, K. Balakrishnan and L. Zang, *Chem. Commun.*, 2013, **49**, 6894–6896.

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