Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Electronic Supplementary Information

Design and evaluation of stir bar designs for single-mode microwave reactors†

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Assembly of stir bars

As stir bar core, a stack (8 × 4 × 4 mm total dimension) of 4 nickel-coated Sm_2Co_{17} magnets (HKCM Engineering e.K., 4 × 4 × 2 mm each) was glued together with high-temperature silicone. The coating dispersion was prepared as follows: To 800 µL PTFE-dispersion in water (60%, Sigma-Aldrich) in a conical 1 mL Eppendorf vial, a mixture of 10 mg glass flour, 20 mg thixotroping agent (pyrogene silica, R&G Faserverbundwerkstoffe GmbH) was added to the dispersion in order to reduce the necessary number of dip/dry steps necessary to generate a comprehensive coating layer. This mixture was dispersed on a vortex mixer at medium speed (to avoid incorporation of air-bubbles) to achieve a gel-like consistency and used for dipping the magnet, taking up the dispersion on its surface. This step was followed by drying for 10 min at 70 °C. The dip/dry was repeated 3-4 times and sintered at around 340 °C for 30 min on a suitable hotplate. The exact temperature on the hotplate was monitored with a (type K) thermocouple thermometer. In cases where cracks appeared upon cooling, a single dip/dry/burn stage was added to seal residual imperfections.

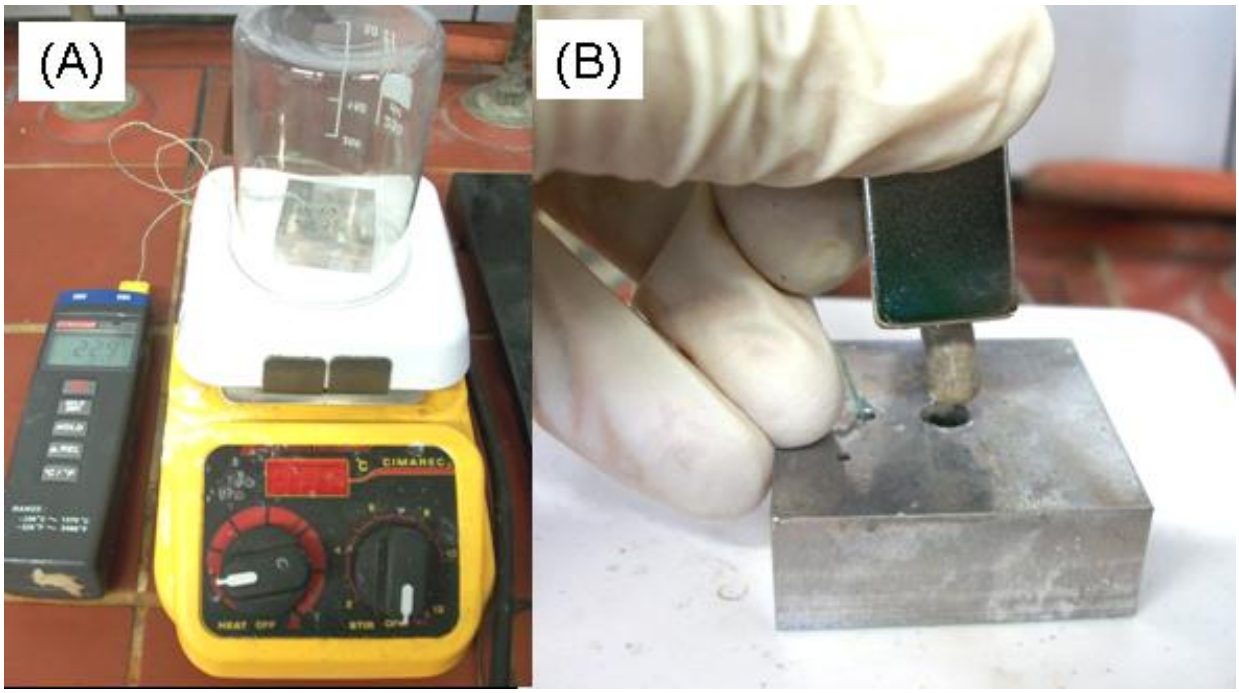

Fig. S1 Thermal treatment of the PTFE-dip-coating deposited on the Sm_2Co_{17} magnet core (8 × 4 × 4 mm + coating). The stir bar was heated to above 340 °C for 30 min using an aluminum block (12 × 40 × 40 mm with a 10 × 6 mm cylindrical hole) as mold (optional, picture (A)). Exact temperature monitoring was assured with a type K thermocouple thermometer. Picture (B) shows the removal of the cooled down cylindrical stir bar (10 × 5.5 mm) from the mold with the help of a magnet. Alternatively, the stir bar is pushed out from the backside of the aluminum block via a small hole on the bottom of the mold.

A u-shaped double-blade was cut from a 1.6 mm PTFE sheet (Bohlender GmbH) and attached to the coated magnet through a small mounting-hole made with a hole punch tool (4-5 mm diameter). Two small holes and C-cuts were added on the blades as additional turbulence-inducing elements.

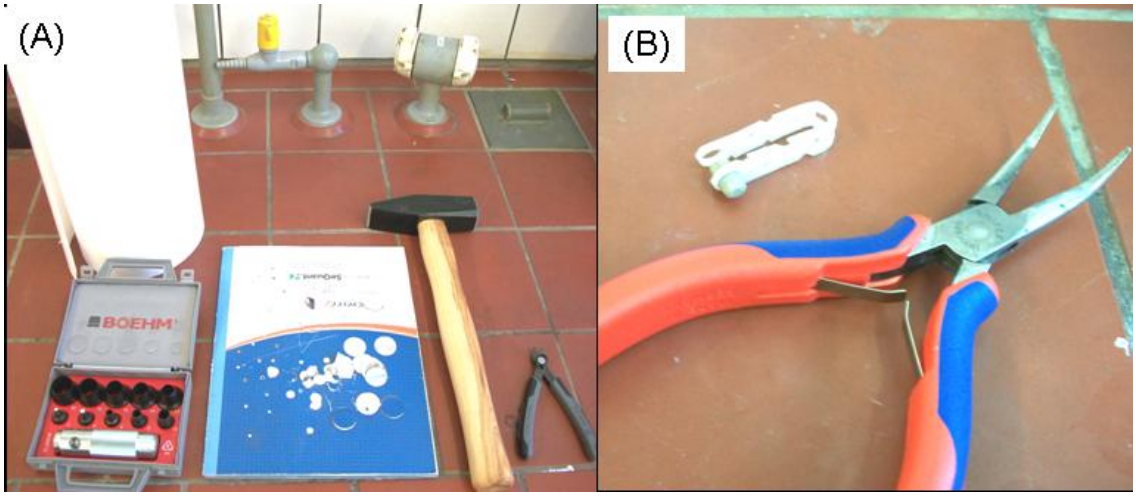

Fig. S2 Tools and materials used for making a u-shaped double-blade extension from PTFE sheet. Holes where made using a hole punching set, whereas cuts where made with the help of a paper-cutting machine and a side-cutter (A). A long-nose plier was used for shaping the PTFE sheet cutout (B).

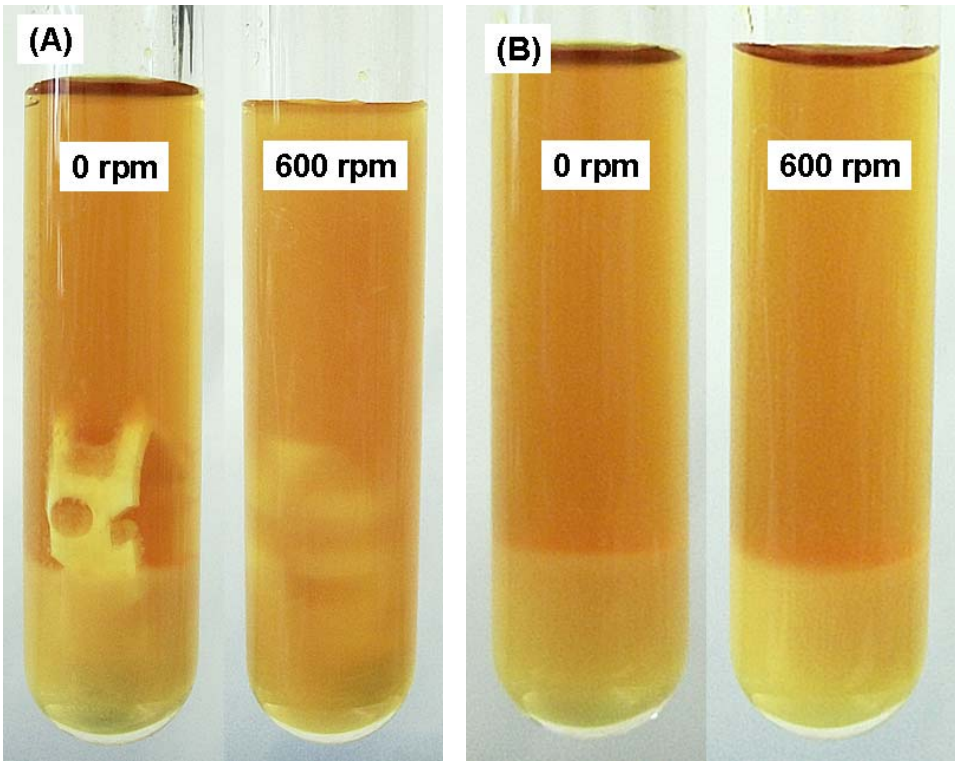

Fig. S3 Preliminary "offline" stirring experiment for the S_NAr of 1,2-dichloro-4-nitrobenzene with 4-methoxyphenol (1.1 equiv.) employing an insoluble base (K_2CO_3, 1.5 equiv.) in 5 ml DMA. Picture (A) shows the reaction mixture containing the vertical blade stirrer in OFF state and at 600 rpm on a magnetic stirrer/hotplate, while picture (B) shows the reaction mixture containing a standard 10 x 6 mm cylindrical stir bar under the same conditions.

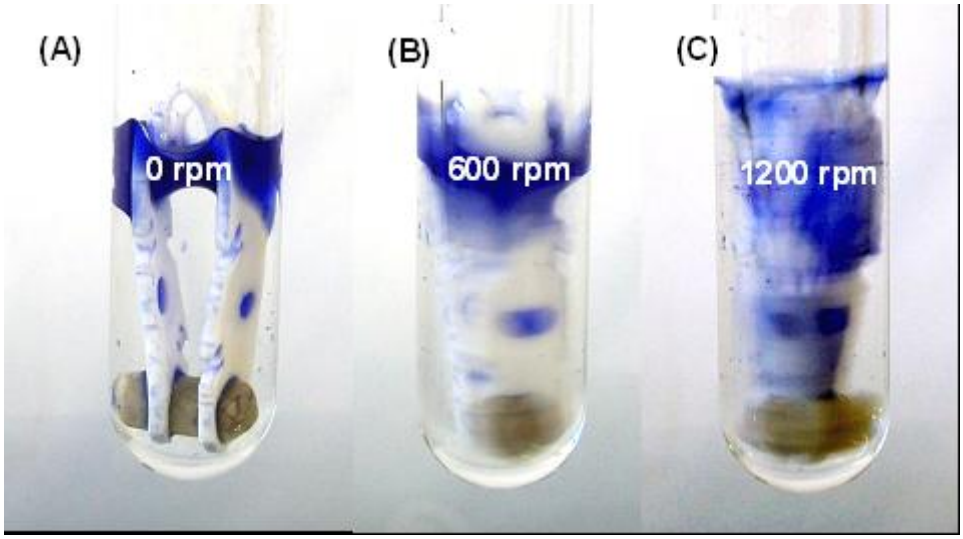

Fig. S4 Preliminary "offline" stirring experiment for the oxidation of cyclohexene to adipic acid with hydrogen peroxide using the vertical blade stirrer (Scheme 2). The upper phase consists of 405 µL cyclohexene containing azulene, whereas the lower phase represents 2 mL 25% hydrogen peroxide. The pictures show the mixture without stirring (A), at 600 rpm (B) and at 1200 rpm (C).

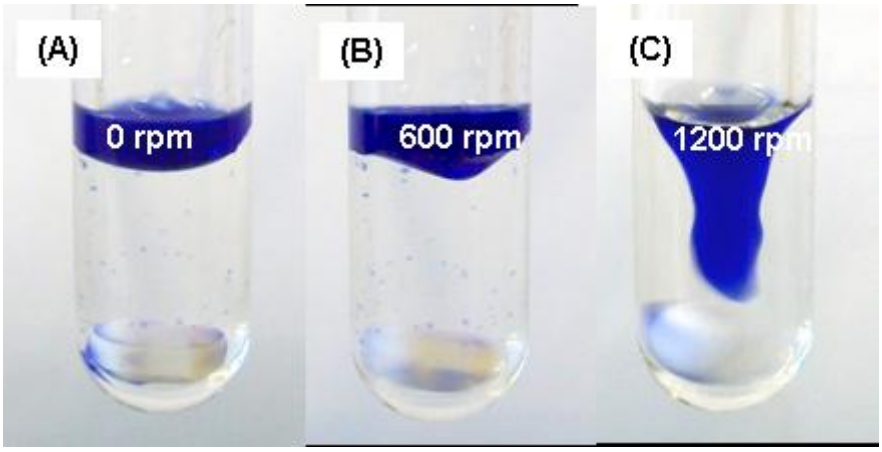

Fig. S5 Preliminary "offline" stirring experiment for the oxidation of cyclohexene to adipic acid using hydrogen peroxide using a standard 10 × 6 mm PTFE-coated stir bar. The upper phase consists of 405 µL cyclohexene containing azulene, whereas the lower phase represents 2 mL 25% hydrogen peroxide. The pictures show the mixture without stirring (A), at 600 rpm (B) and at 1200 rpm (C).

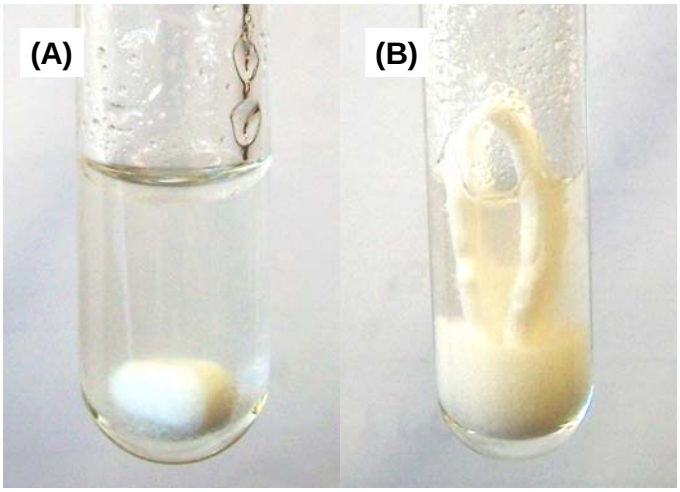

Fig. S6 Images of 10 mL microwave vessels containing the adipic acid reaction mixture taken after the reaction was performed and additional cooling (1 h at 0 °C). The reaction conditions for both experiments were identical (140 °C for 30 min, 600 rpm), the only difference was the stir bar being used. The left picture (A) shows the biphasic reaction mixture being stirred with a standard stir bar. The mixture is still biphasic (cyclohexene phase on top of the water phase) and hardly any precipitated adipic acid is visible. The right reaction mixture (B) was stirred with a vertical blade stirrer, a homogeneous reaction mixture containing precipitated adipic acid is shown.