

Supporting Information

Micellar catalysis in aqueous - ionic liquids systems

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1. Materials and Methods

Commercially available reagents and solvents were used as received from Sigma Aldrich unless otherwise specified. Ionic liquids [C₈mim]Cl, [C₁₀mim]Cl, [C₁₂mim]Cl, and [C₁₄mim]Cl were prepared from freshly distilled *N*-methylimidazole and alkylchloride according to literature. Solid [C₁₂mim]Cl, and [C₁₄mim]Cl were crystallized from THF until colorless crystals were obtained. All ionic liquids were dried for at least 24-48 h at 80 °C and 0.01 mbar before use and were stored under Argon. The purity of all ionic liquids was checked by ¹H and ¹³C NMR spectroscopic analysis and was found to be >99 wt%. *N*-Benzylmaleimide was prepared as previously reported and analytical data were in accordance with literature.¹ Based on its low solubility in water, *N*-benzylmaleimide was handled as stock solution in acetonitrile (91.17 mM). 1,3-Cyclohexadiene was distilled on a weekly basis and stored under Argon at -20 °C.

Doubly-distilled deionised water was obtained from a Millipore Milli-Q water purification system (Millipore, USA). All ionic liquid-aqueous solutions were left under shaking with 360 min⁻¹ at 25 °C for 24 h to equilibrate.

UV-vis spectroscopy was performed on a Shimadzu UV1800 spectrometer equipped with a thermostat at 25 °C for 60 min.

Dynamic Light Scattering was performed on Malvern Nano Zetasizer. Samples were equilibrated at 25 °C and measured in back-scattering mode for 10-15 runs with 10 seconds. At least three consistent measurements per solution and reaction were recorded.

¹H and ¹³C NMR spectra were recorded on a Bruker AC 200 at 200 and 50 MHz, respectively, using the solvent peak as reference. J values are given in Hz.

GC-MS analyses were conducted on a VOYAGER Quadrupole (Thermo Finnigan) directly interfaced to a GC 8000 TOP gas chromatograph using a BGB-5 (30 m x 0.32 mm i.d., 1.0 µm film thickness) cross-bonded dimethyl polysiloxane capillary column. The oven program temperature was 80 °C (2 min)//10 °C min⁻¹//280 °C (2 min). Source and transfer line temperatures were set at 200 and 280 °C, respectively.

2. MD simulations of 50 mM [C₁₂mim]Cl

MD simulations of 50 mM [C₁₂mim]Cl in water were done according to the following parameters:

	number	Force field parameter
C ₁₂ mim	10	J. Phys. Chem. B 108(2004), 2038
Cl	10	J. Chem. Phys. 100 (1994), 9050
water	11000	J. Chem. Phys. 79(1983), 926

time step	1 fs
simulation period	2 ns
simulation boxlength	69.3 Å
real space cutoff	12 Å
Ewald κ	0.41 Å ⁻¹
thermostat	300 K $\tau = 0.1$ ps (normal atoms) 1 K $\tau = 0.005$ ps (Drude particles)
Drude mass	0.2 amu
Drude force constant	500 kcal/mol Å ²
α (carbon)	1.2886 Å ⁻³ (J. Phys. Chem. A 102(1998), 2399)
α (nitrogen)	0.97157 Å ⁻³ (J. Phys. Chem. A 102(1998), 2399)

3. Experimental procedures

3.1. Kinetics measurement

Freshly distilled 1,3-cyclohexadiene (diene) was dissolved in an ionic liquid/aqueous solution to obtain a 24 mM solution (**Solution A**). A concentrated stock solution of *N*-benzylmaleimide (dienophile) in acetonitril was added to an ionic liquid/aqueous solution and equilibrated for 1 min (**Solution B**).

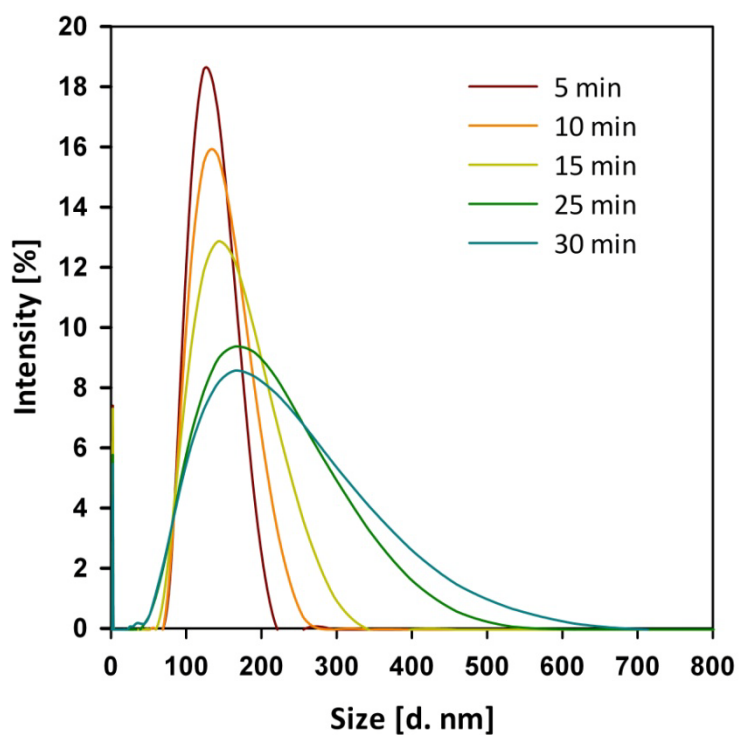
Equal volumina of **Solution A** (0.5 ml corresponding to 0.012 mmol diene) and of **Solution B** (0.5 ml corresponding to 0.0002 mmol dienophile) were combined in a fused quartz glass cuvette of 1.00 cm path length and quickly mixed with a Pasteur pipette. The solution was immediately transferred into the photometer and followed at 298 nm for 60 min using the diene solution (**Solution A**) as reference.

Rate constants k' were obtained according to the pseudo-first order model:

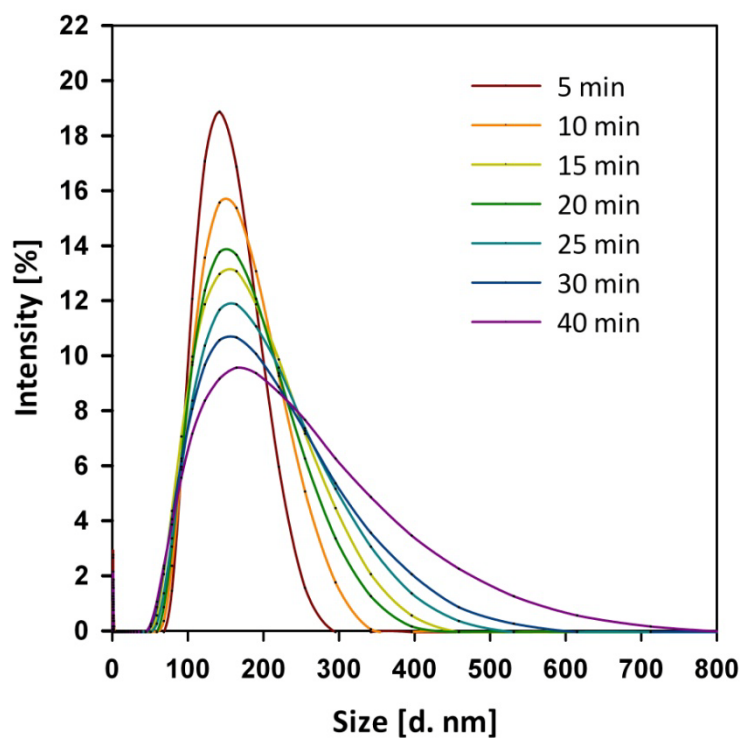
$$\begin{aligned}
 r &= k \cdot [A] \cdot [B] \\
 r &= k' \cdot [A] \\
 \frac{d([A])}{d(t)} &= -k' \cdot ([A]) \\
 \frac{d([A])}{[A]} &= -k' \cdot d(t)
 \end{aligned}
 \qquad
 \begin{aligned}
 \ln([A]) - \ln([A]_0) &= -k' \cdot t \\
 \ln\left(\frac{[A]}{[A]_0}\right) &= -k' \cdot t \\
 [A] &= [A]_0 \cdot e^{-k' \cdot t}
 \end{aligned}$$

All reported rate constants are the average of at least five kinetic measurements under each experimental condition.

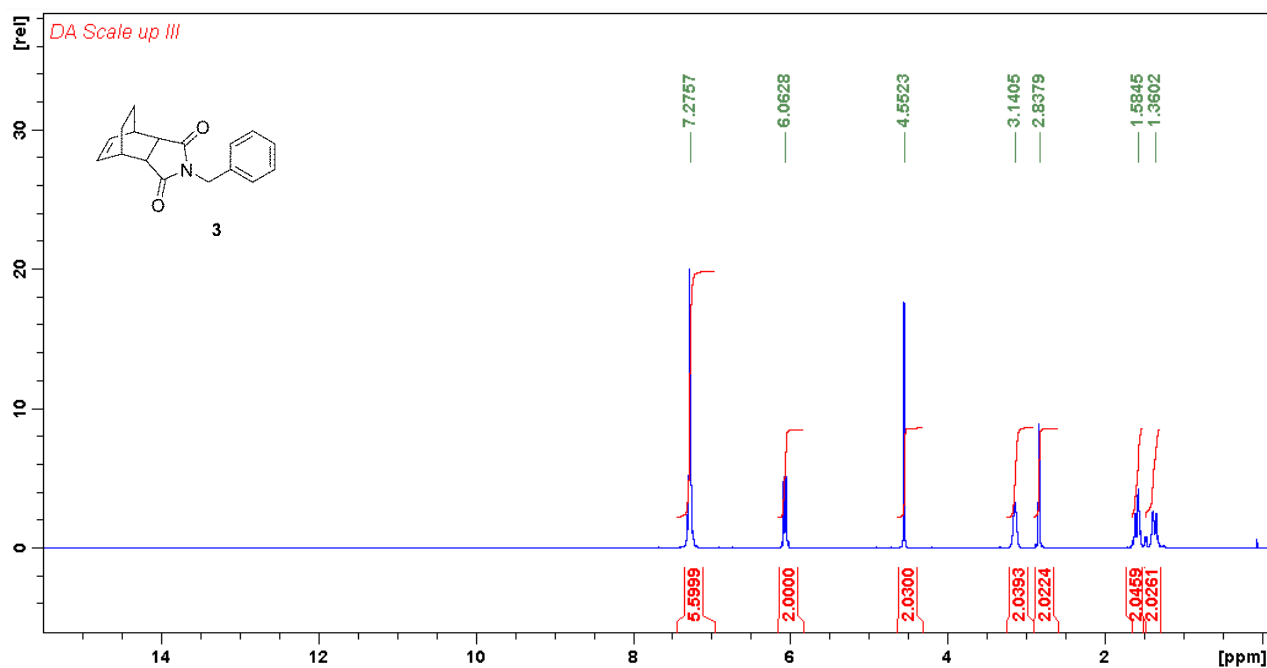
4. Fig. S2: Size distribution by intensity in the course of the Diels-Alder reaction in a 50 mM $[C_{12}mim]Cl$ solution



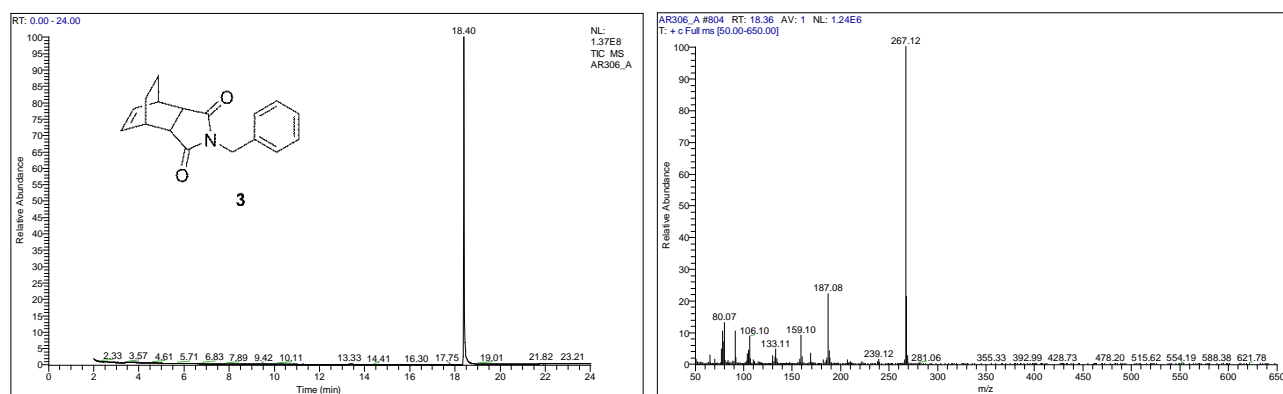
5. Fig. S3: Size distribution by intensity in the course of the Diels-Alder reaction in a 50 mM $[C_{14}mim]Cl$ solution



6. Fig. S4: Copy of ^1H -NMR spectrum of the Diels-Alder product **3** isolated via crystallization from a 100 mM $[\text{C}_{10}\text{mim}]\text{Cl}$ solution



7. Fig. S5: Copy of GC-MS trace of the Diels-Alder product **3** isolated via crystallization from a 100 mM $[\text{C}_{10}\text{mim}]\text{Cl}$ solution



¹ N. Matuszak, G. G. Muccioli, G. Labar, D. M. Lambert, *J. Med. Chem.*, 2009, **52**, 7410.