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Supporting Information

Influence of the Cation in Lithium and Magnesium Polysulphide Solutions in Dependence of the Solvent Chemistry

Georg Bieker, Julia Wellmann, Martin Kolek, Kirsi Jalkanen, Martin Winter**,#, and Peter Bieker*

MEET Battery Research Centre, Institute of Physical Chemistry, University of Münster, Corrensstrasse 28/30, 48149 Münster, Germany.

#Helmholtz Institute Münster (HI MS), IEK12, Forschungszentrum Jülich GmbH, Corrensstrasse 46, 48149 Münster, Germany.

*E-mail: peter.bieker@uni-muenster.de

**Co-corresponding author: Martin.Winter@uni-muenster.de, m. winter@fz-juelich.de

Preparation of the Mg and Li polysulphide solutions

The Mg polysulphide solutions were prepared as 1.0 mM stock solutions by stirring $[Mg(N\text{-}MeIm)_6]S_8$ or $[Mg(DMSO)_6]S_8$ at 40°C for 7 d in the investigated solvents.

In order to increase accuracy upon weighing the sulphur and Li_2S powders, the "LiS_8" solutions were prepared at a higher concentration of 10 mM. Stoichiometric amounts of Li_2S and sulphur were stirred in the investigated solvent at 40 °C for 4 d, after which the solutions were diluted to 1 mM and stirred for another 3 d at 40°C. The total preparation time of 7 d is comparable to the preparation of the Mg polysulphide solutions. However, due to their slower dissolution rate, the 10 mM "Li_2S_8" samples in ACN and $Pyr_{14}TFSI$ were stirred for 9 d at 40°C in order to achieve a complete dissolution. After a complete dissolution, also these solutions were diluted to a concentration of 1.0 mM and stirred for another 3 d at 40°C.

The Mg and Li 1.0 mM stock solutions were diluted to 0.5 mM, 0.2 mM, and 0.1 mM samples directly before measuring the UV/Vis absorption spectra.

UV/Vis studies

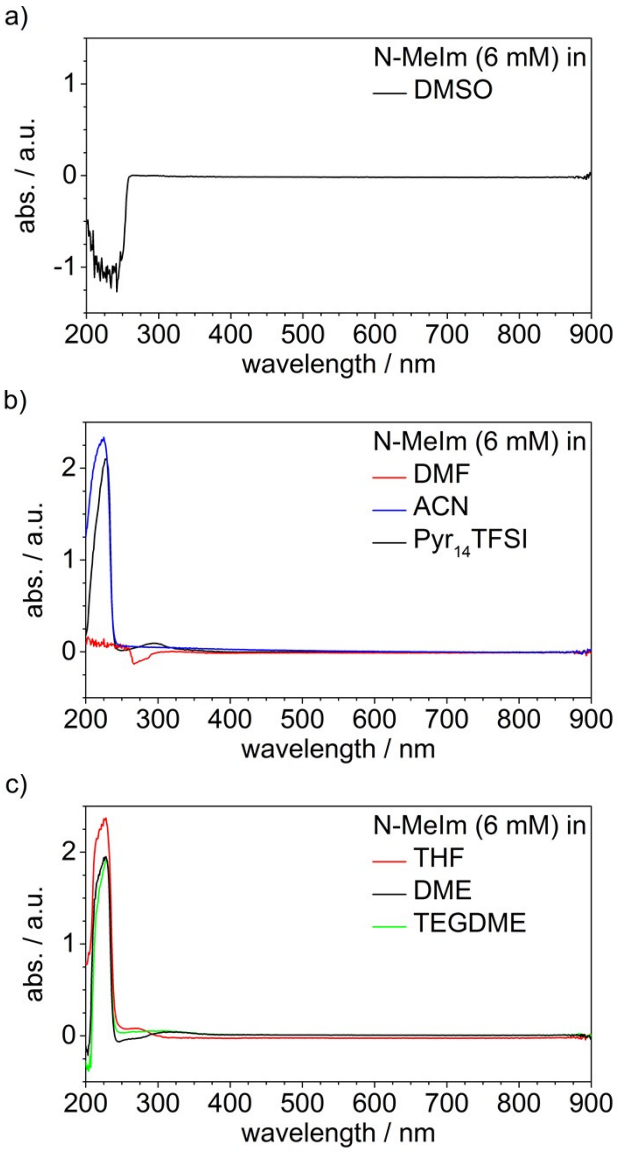

Figure S1: UV/Vis spectra of N-MeIm (6 mM) in a) DMSO, b) DMF, ACN, and $Pyr_{14}TFSI$, and c) THF, DME, and TEGDME.

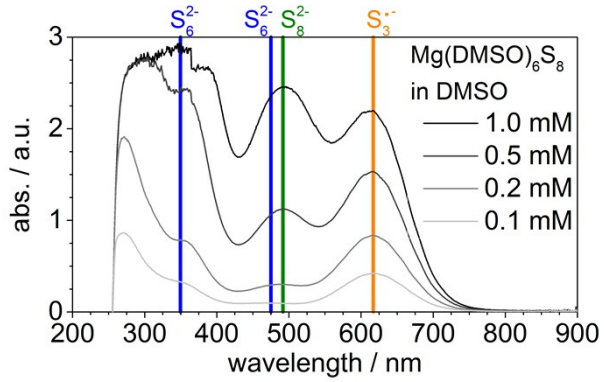

Figure S2: UV/Vis spectra of $Mg(DMSO)_6S_8$ solutions in DMSO.

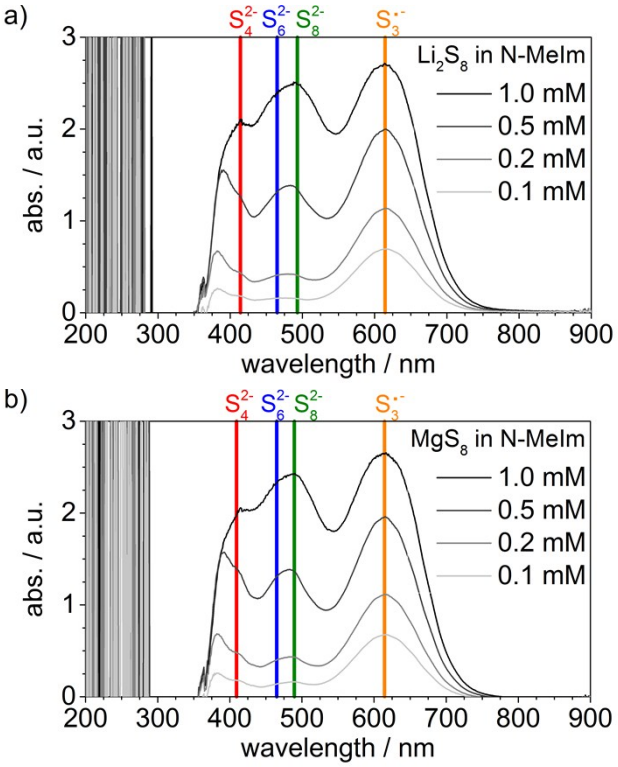

Figure S3: UV/Vis spectra of a) Li_2S_8 and b) MgS_8 solutions in N-MeIm.

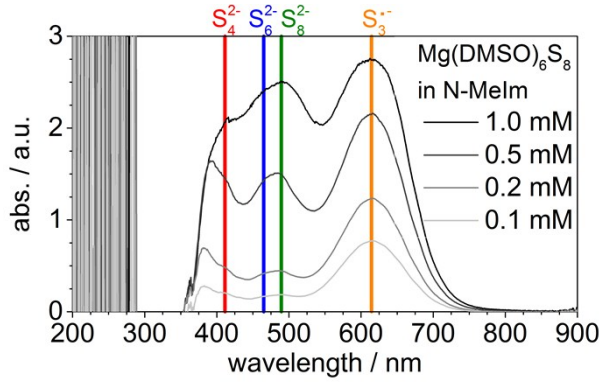

Figure S4: UV/Vis spectra of $Mg(DMSO)_6S_8$ solutions in N-MeIm.