

Supporting Information

Halide coordinated homoleptic $[\text{Fe}_4\text{S}_4\text{X}_4]^{2-}$ and heteroleptic $[\text{Fe}_4\text{S}_4\text{X}_2\text{Y}_2]^{2-}$ clusters (X, Y = Cl, Br, I) – Alternative preparations, structural analogies and spectroscopic properties in solution and solid state

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Supplementary Figures

(Figures S1 – S29)

- Figure S1. Negative ESI MS of $(\text{Et}_4\text{N})_2[\text{Fe}_4\text{S}_4\text{Cl}_4]$ obtained from reaction with $[\text{CoCl}_4]^{2-}$ in MeCN.
- Figure S2. Negative ESI MS of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{I}_4]$ in THF.
- Figure S3. Negative ESI MS of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Cl}_2\text{I}_2]$ in THF; conversion with I_2 and chloride.
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- Figure S7. Negative UHR ESI MS of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_4]$ in acetone and simulated patterns of molecular ions of fragmentation and oxidation products as well as adducts ($[\text{Fe}_4\text{S}_4\text{Br}_3]^-$, $[\text{Fe}_4\text{S}_4\text{Br}_3\text{O}_2]^-$, $[\text{Fe}_4\text{S}_4\text{Br}_4]$, $[\text{Fe}_4\text{S}_4\text{Br}_3\text{Li}]^-$, $[\text{Fe}_4\text{S}_4\text{Br}_3\text{Na}]^-$).
- Figure S8. Negative UHR ESI MS of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_4]$ in acetone (red: measurement after dissolving; green: measurement after one day).
- Figure S9. Negative UHR ESI MS of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{Cl}_2]$ in acetone and simulated patterns of molecular ions.
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- Figure S11. Negative UHR ESI MS of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{Cl}_2]$ in acetone (red: measurement after dissolving; green: measurement after 24 h).
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- Figure S13. Negative UHR ESI MS of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{I}_2]$ in acetone and simulated patterns of molecular ions; $[\text{Fe}_4\text{S}_4\text{Br}_{3-n}\text{I}_n]^-$ and $[\text{Fe}_4\text{S}_4\text{Br}_{3-n}\text{I}_n\text{O}_2]^-$ fragmentation series.
- Figure S14. Negative UHR ESI MS of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{I}_2]$ in acetone (red: measurement after dissolving; green: measurement after 24 h).
- Figure S15. Negative UHR ESI MS of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Cl}_2\text{I}_2]$ in acetone (above, measured spectra; below, simulated molecular peaks; detailed view of $[\text{Fe}_4\text{S}_4\text{Cl}_2\text{I}_2]^{2-}$ with its simulation is given on the right side).
- Figure S16. Decay ion series of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Cl}_2\text{I}_2]$ in acetone (above, measured spectra; below, simulated molecular peaks).
- Figure S17. Negative UHR ESI MS of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Cl}_2\text{I}_2]$ in acetone (red: measurement after dissolving; green: measurement after 24 h).
- Figure S18. UV-vis-NIR spectra of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{I}_4]$ in acetonitrile.
- Figure S19. UV-vis-NIR spectra of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Cl}_4]$ in acetonitrile.
- Figure S20. UV-vis-NIR spectra of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_4]$ in acetonitrile.
- Figure S21. UV-vis-NIR spectra of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{Cl}_2]$ in acetonitrile.
- Figure S22. UV-vis-NIR spectra of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Cl}_2\text{I}_2]$ in acetonitrile.

- Figure S23. UV-vis-NIR spectra of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{I}_2]$ in acetonitrile.
- Figure S24. Synchrotron XRPD of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{I}_4]$ at ambient temperature (above: experimental data, with $\lambda = 0.207203 \text{ \AA}$; below calculated pattern¹).
- Figure S25. Synchrotron XRPD of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_4]$ at ambient temperature (above: experimental data, with $\lambda = 0.207203 \text{ \AA}$; below calculated pattern²).
- Figure S26. Synchrotron XRPD of $(\text{Ph}_4\text{P})_2[\text{Fe}_4\text{S}_4\text{Br}_4]$ at ambient temperature (above: experimental data, with $\lambda = 0.551155 \text{ \AA}$; below calculated pattern).
- Figure S27. XRPD of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{Cl}_2]$; experiment with $\lambda = 0.207203 \text{ \AA}$ synchrotron radiation (DESY, beam line P02.1, storage ring Petra III); calculated pattern based single crystal structure data.¹
- Figure S28. XRPD von $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{I}_2]$; experiment with $\lambda = 0.207203 \text{ \AA}$ synchrotron radiation (DESY, beam line P02.1, storage ring Petra III); calculated pattern based single crystal structure data.¹
- Figure S29. XRPD of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Cl}_2\text{I}_2]$; experiment with $\lambda = 0.207203 \text{ \AA}$ synchrotron radiation (DESY, beam line P02.1, storage ring Petra III); calculated pattern based single crystal structure data.¹

ESI mass spectrometry

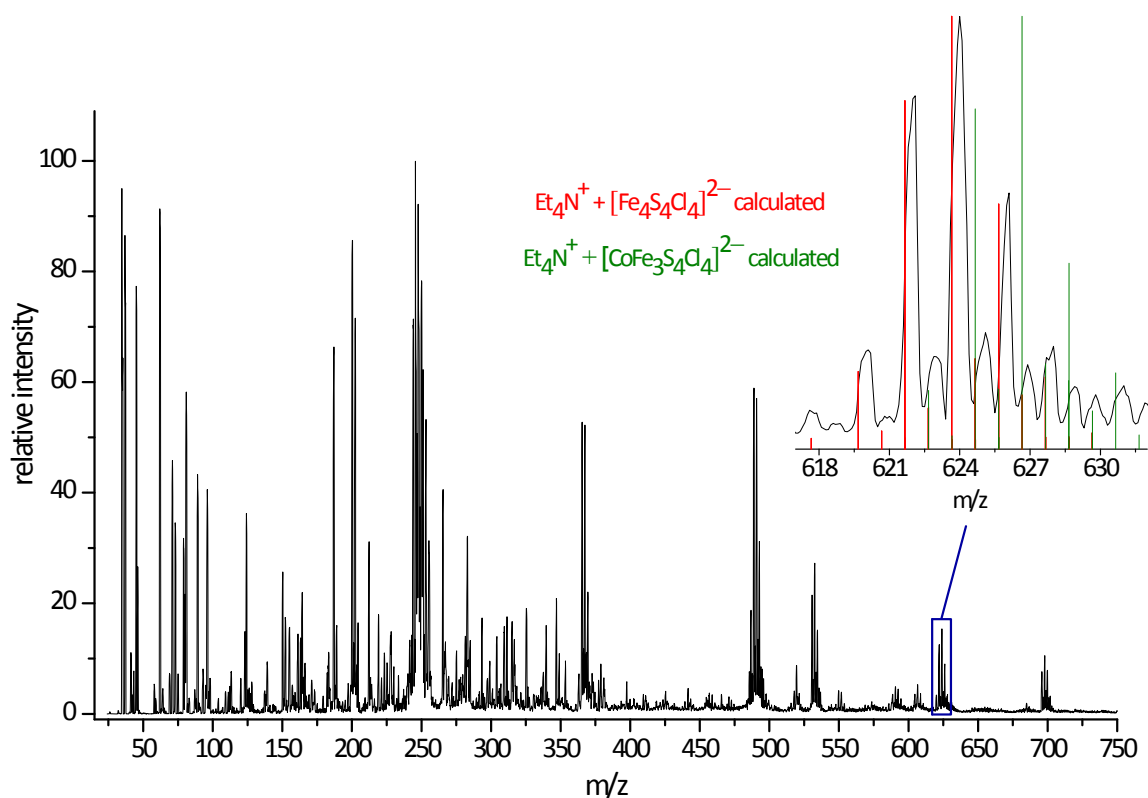


Figure S1: Negative ESI MS of $(\text{Et}_4\text{N})_2[\text{Fe}_4\text{S}_4\text{Cl}_4]$ obtained from reaction with $[\text{CoCl}_4]^{2-}$ in MeCN.

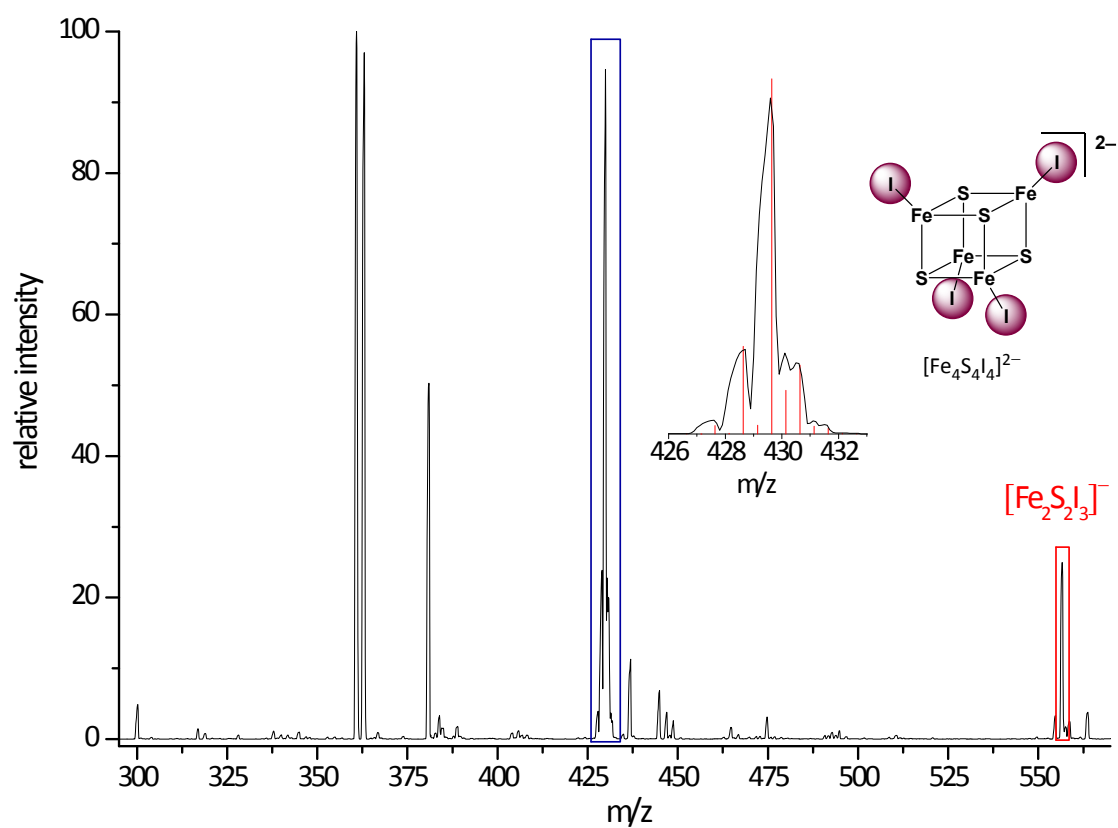


Figure S2: Negative ESI MS of (BTMA)₂[Fe₄S₄I₄] in THF.

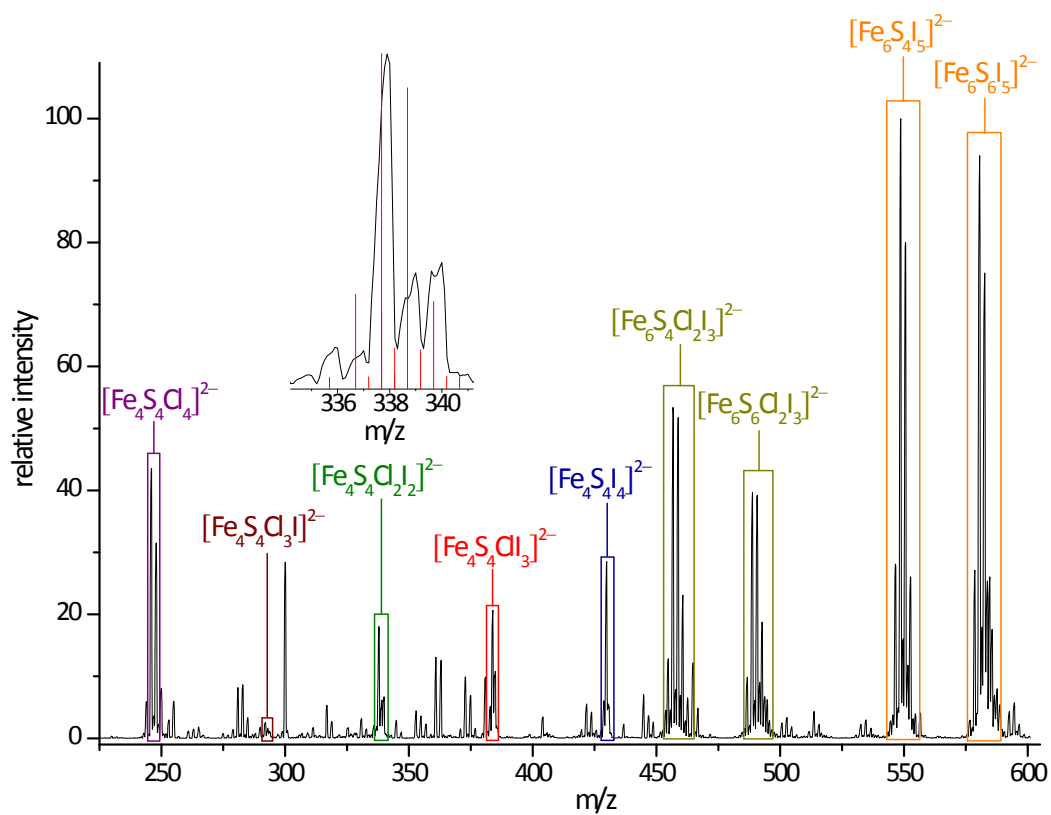


Figure S3: Negative ESI MS of (BTMA)₂[Fe₄S₄Cl₂I₂] in THF; conversion with iodine and chloride.

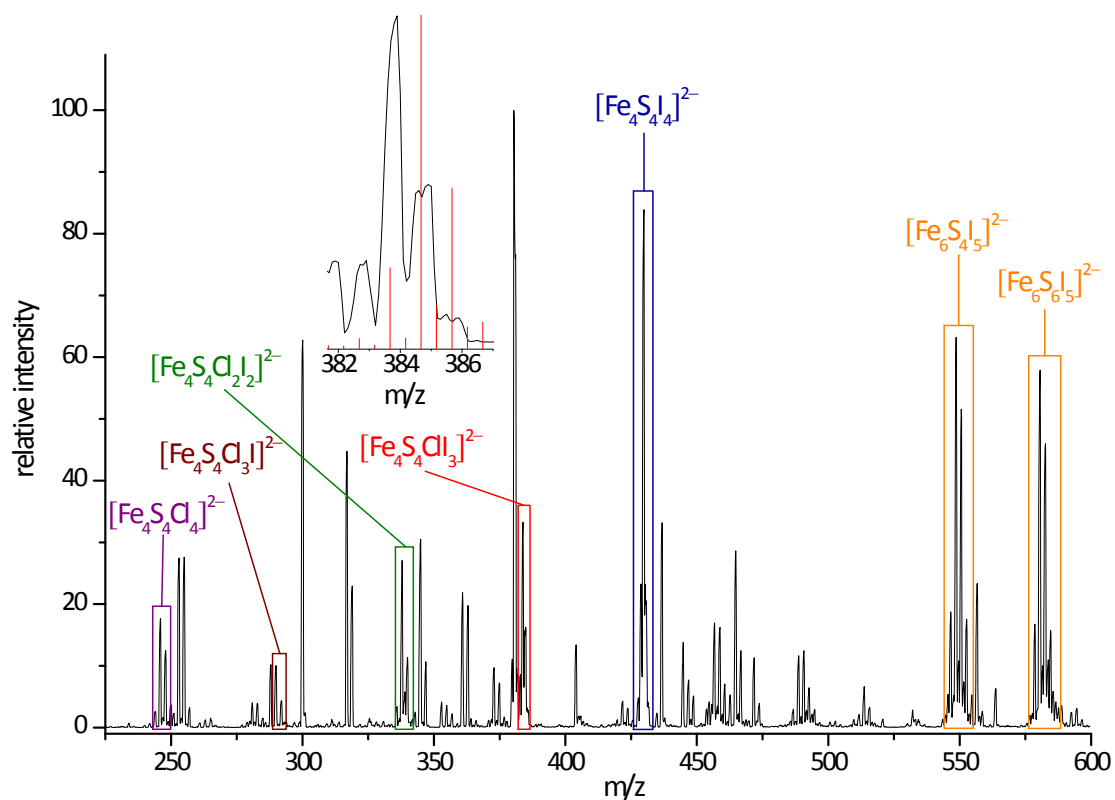


Figure S4: Negative ESI MS of (BTMA₂[Fe₄S₄Cl₃]) in THF; conversion with iodine monochloride and iodide.

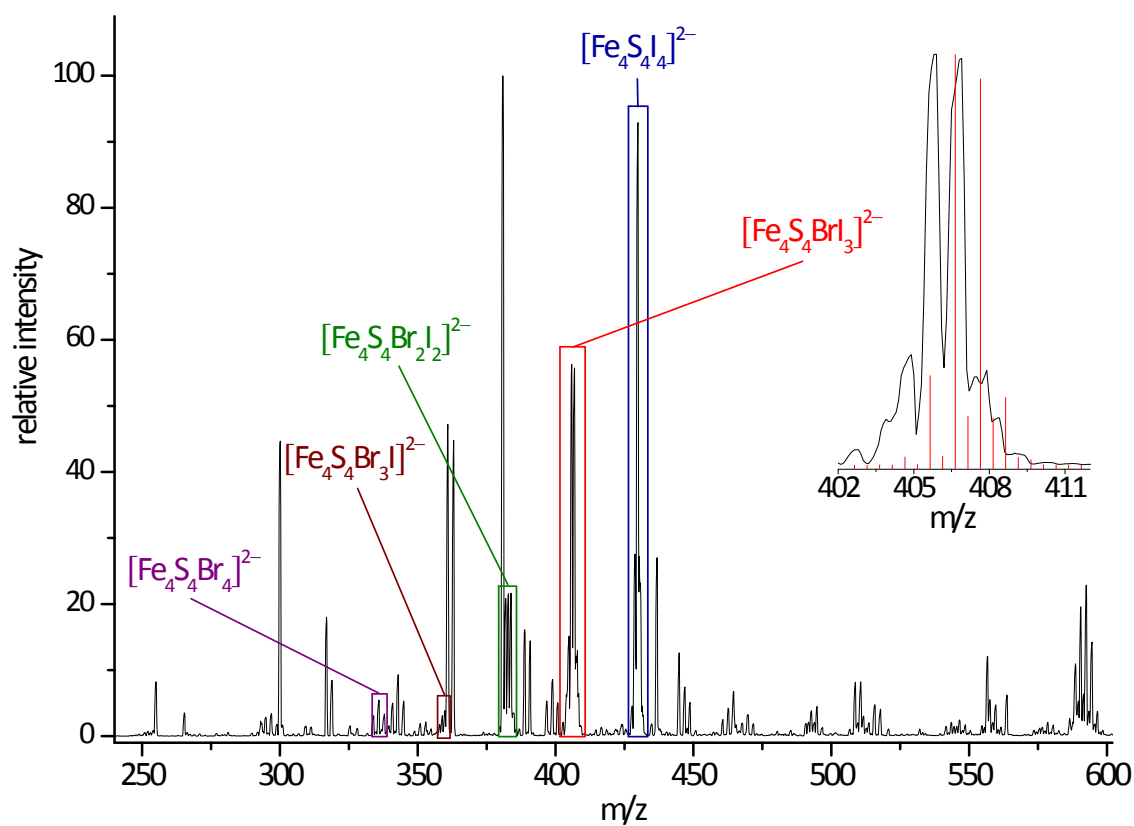


Figure S5: Negative ESI MS of (BTMA₂[Fe₄S₄BrI₃]) in THF; conversion with iodine monobromide and iodide.

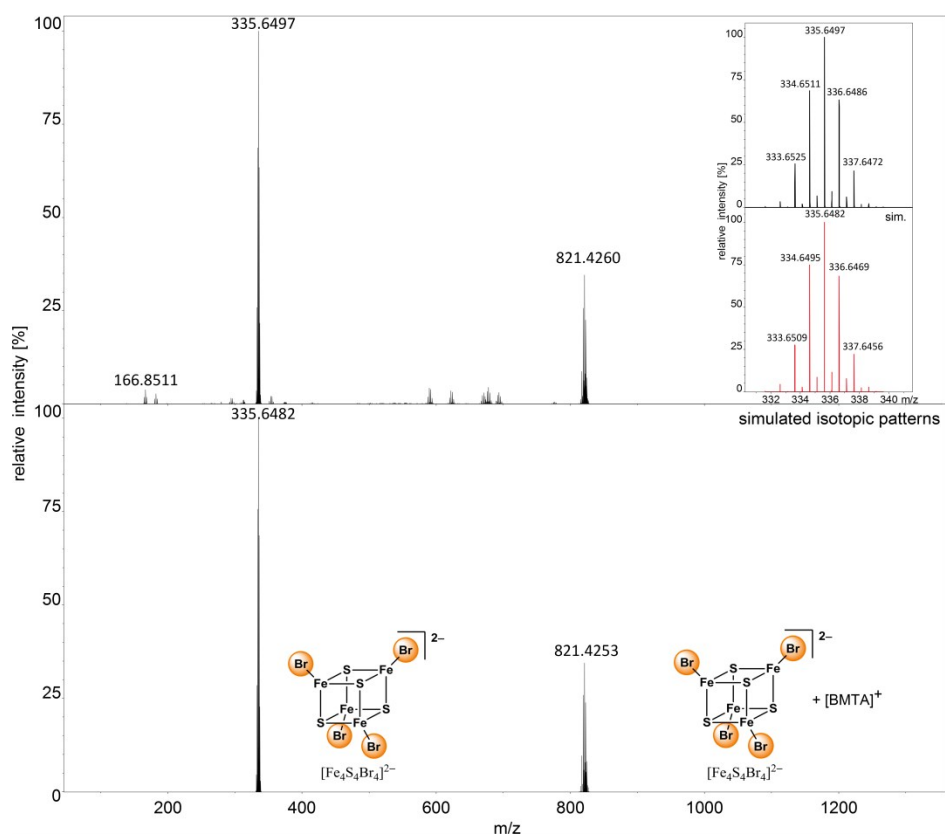


Figure S6: Negative UHR ESI MS of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_4]$ in acetone (above, measured spectra; below, simulated molecular peaks; detailed view of $[\text{Fe}_4\text{S}_4\text{Br}_4]^{2-}$ with its simulation is given on the right side).

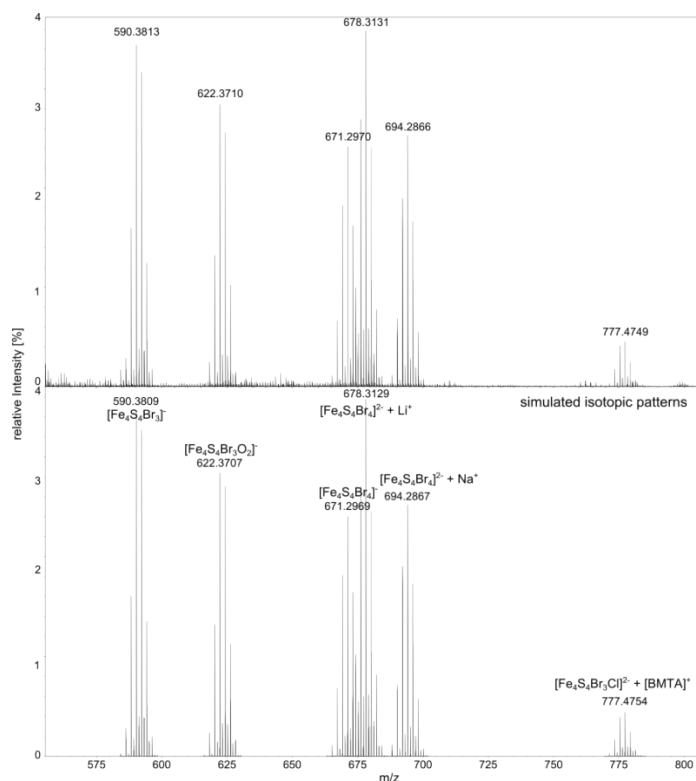


Figure S7: Negative UHR ESI MS of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_4]$ in acetone and simulated patterns of molecular ions of fragmentation and oxidation products as well as adducts ($[\text{Fe}_4\text{S}_4\text{Br}_3]^-$, $[\text{Fe}_4\text{S}_4\text{Br}_3\text{O}_2]^-$, $[\text{Fe}_4\text{S}_4\text{Br}_4]^{2-}$, $[\text{Fe}_4\text{S}_4\text{Br}_3\text{Li}]^-$, $[\text{Fe}_4\text{S}_4\text{Br}_3\text{Na}]^-$).

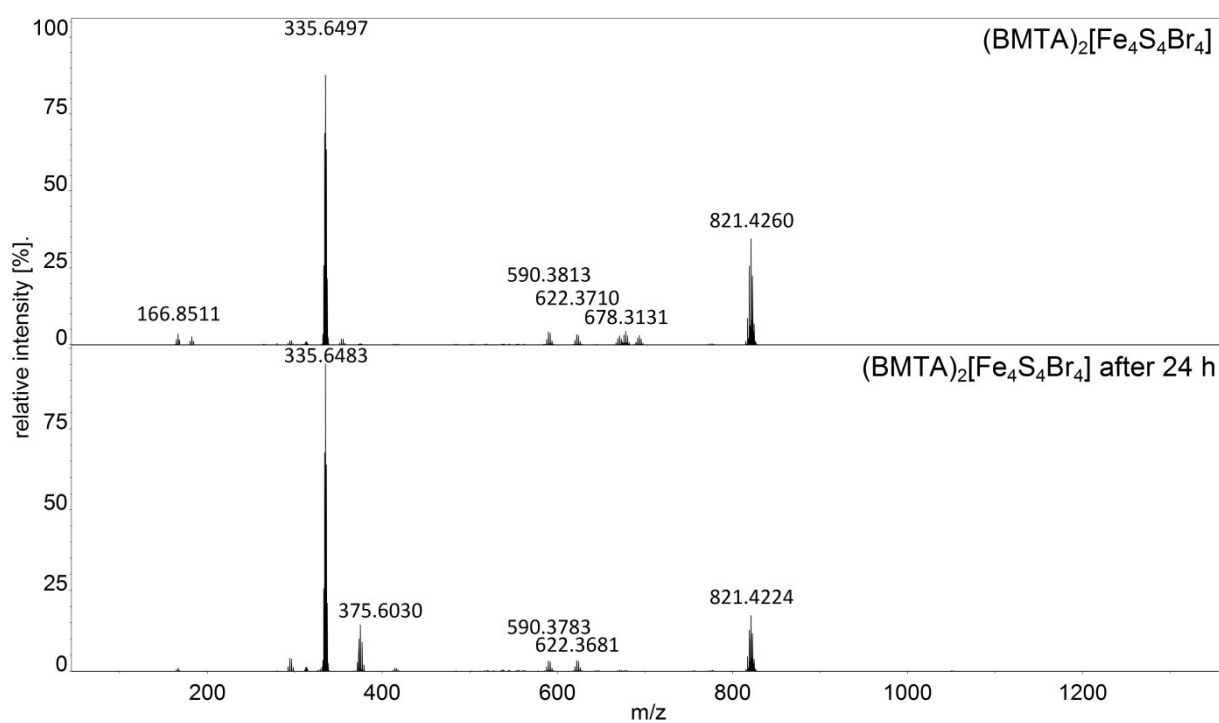


Figure S8: Negative UHR ESI MS of $(\text{BMTA})_2[\text{Fe}_4\text{S}_4\text{Br}_4]$ in acetone (above: measurement after dissolving; below: measurement after 24 h).

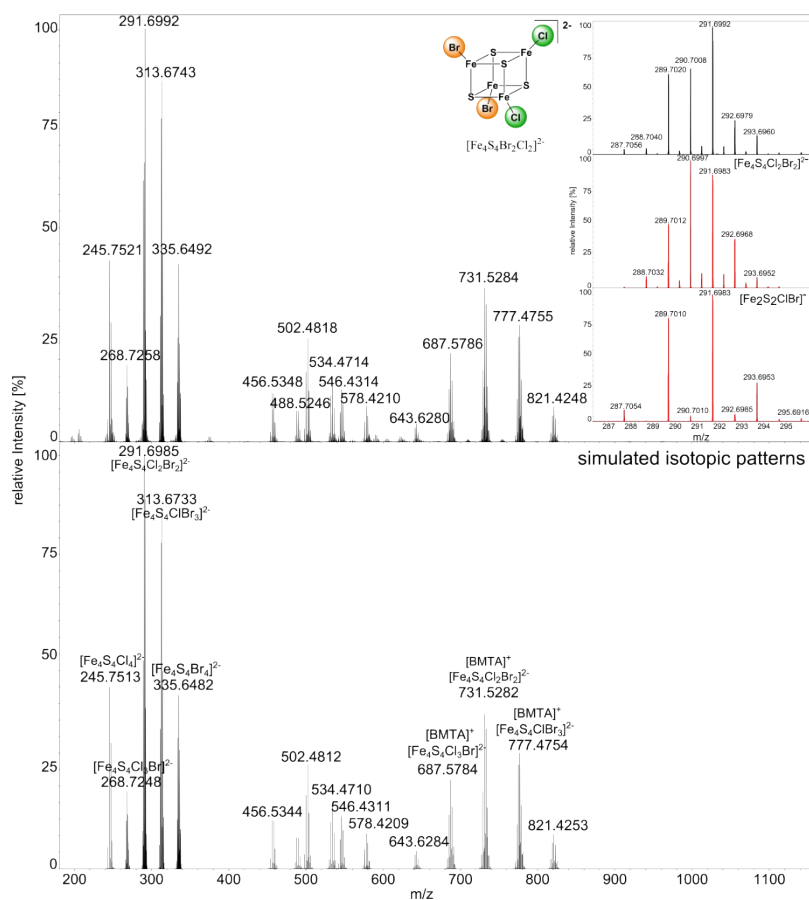


Figure S9: Negative UHR ESI MS of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{Cl}_2]$ in acetone and simulated patterns of molecular ions.

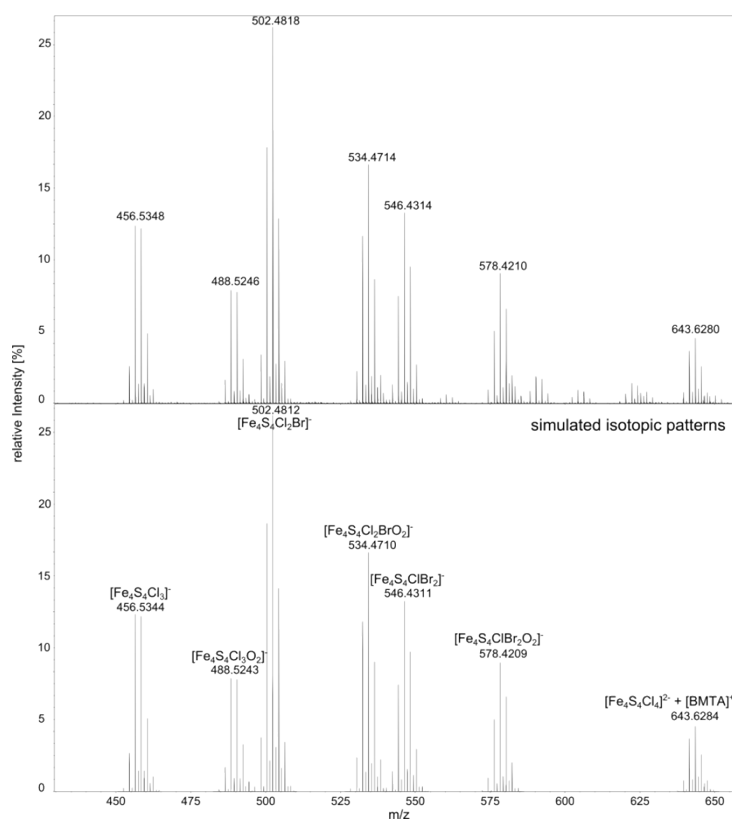


Figure S10: Negative UHR ESI MS of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{Cl}_2]$ in acetone and simulated patterns of molecular ions; $[\text{Fe}_4\text{S}_4\text{Br}_{3-n}\text{Cl}_n]^-$ and $[\text{Fe}_4\text{S}_4\text{Br}_{3-n}\text{Cl}_n\text{O}_2]^-$ fragmentation series.

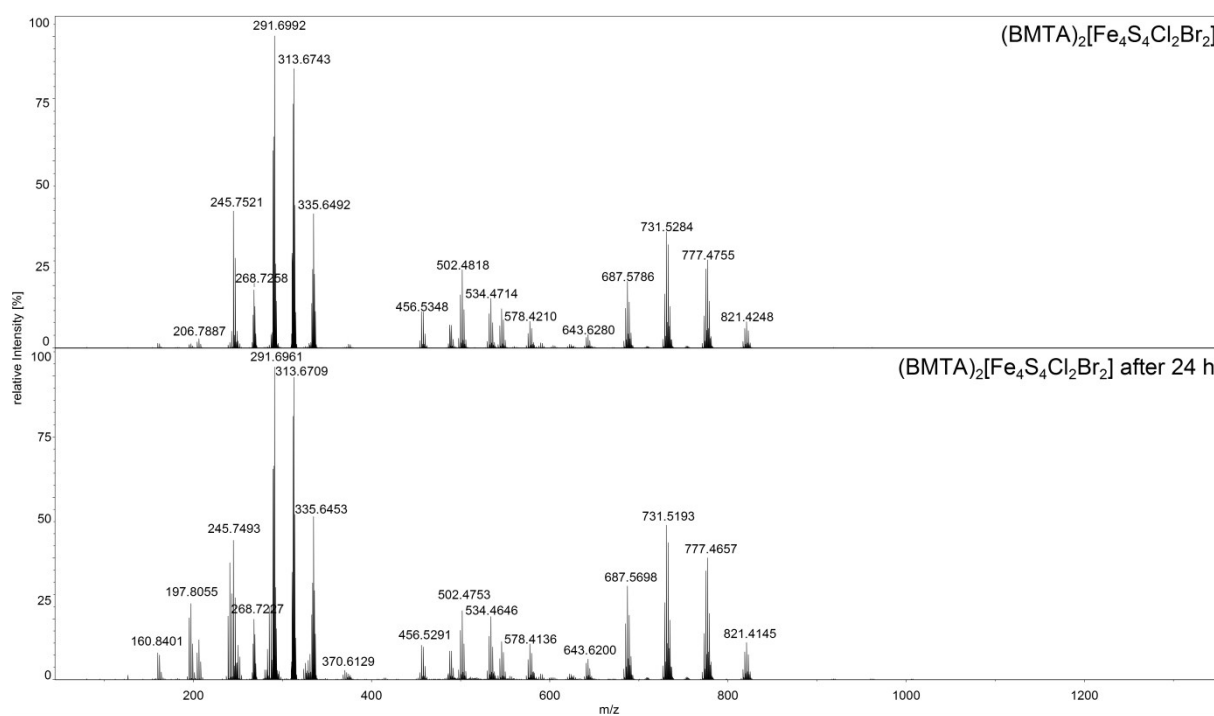


Figure S11: Negative UHR ESI MS of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{Cl}_2]$ in acetone (top: measurement after dissolving; bottom: measurement after 24 h).

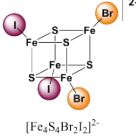


Figure 1 displays two simulated isotopic patterns for the complexes $[\text{Fe}_4\text{S}_4\text{Br}_2]^+$ (top) and $[\text{Fe}_4\text{S}_4\text{Br}_2\text{O}]^+$ (bottom). The x-axis represents the mass-to-charge ratio (m/z) from 560 to 740, and the y-axis represents the relative intensity in percent (%).

The top panel shows the simulated isotopic pattern for $[\text{Fe}_4\text{S}_4\text{Br}_2]^+$. The major peaks are labeled with their m/z values: 590.3805, 622.3701, 638.3662, 670.3558, 684.3543, and 716.3439. The pattern is characterized by a series of peaks with varying intensities, reflecting the isotopic distribution of the elements in the complex.

The bottom panel shows the simulated isotopic pattern for $[\text{Fe}_4\text{S}_4\text{Br}_2\text{O}]^+$. The major peaks are labeled with their m/z values: 590.3809, 622.3707, 638.3667, 670.3566, 684.3553, and 716.3451. This pattern is similar to the one for $[\text{Fe}_4\text{S}_4\text{Br}_2]^+$ but shifted due to the presence of an additional oxygen atom.

Figure S13: Negative UHR ESI MS of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{I}_2]$ in acetone and simulated patterns of molecular ions; $[\text{Fe}_4\text{S}_4\text{Br}_{3-n}\text{I}_n]^-$ and $[\text{Fe}_4\text{S}_4\text{Br}_{3-n}\text{I}_n\text{O}_2]^-$ fragmentation series.

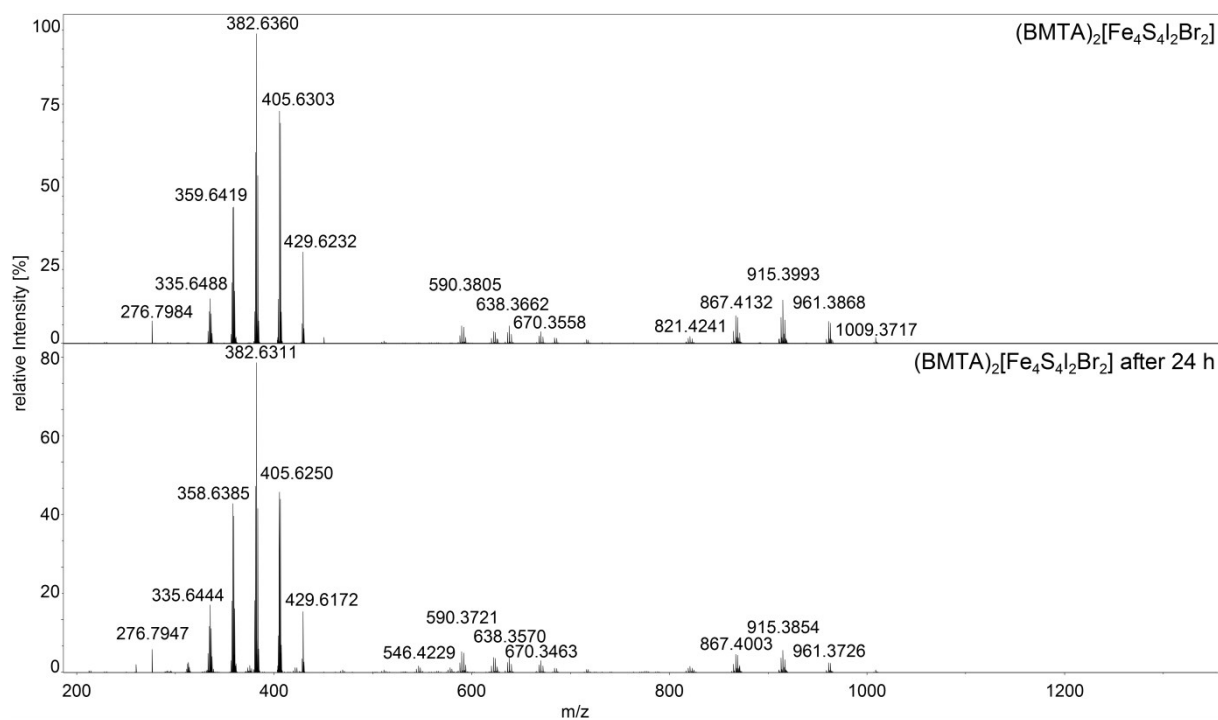


Figure S14: Negative UHR ESI MS of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{I}_2]$ in acetone (red: measurement after dissolving; green: measurement after 24 h).

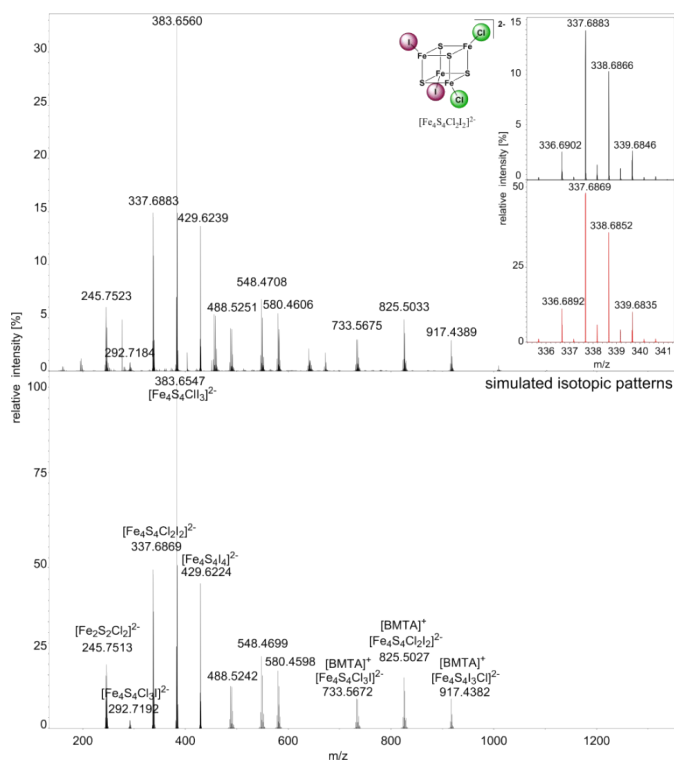


Figure S15: Neg. UHR ESI MS of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Cl}_2\text{I}_2]$ in acetone (above, measured spectra; below, simulated molecular peaks; detailed view of $[\text{Fe}_4\text{S}_4\text{Cl}_2\text{I}_2]^{2-}$ with its simulation is given on the right side).

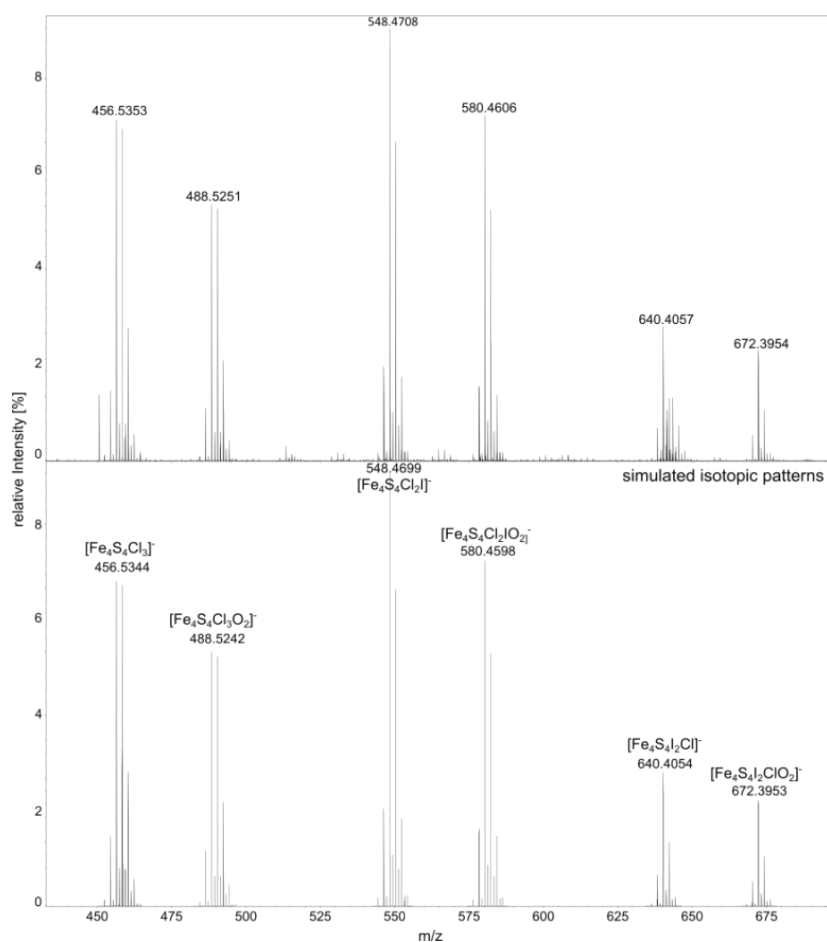


Figure S16: Decay ion series of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Cl}_2\text{I}_2]$ in acetone (above, measured spectra; below, simulated molecular peaks).

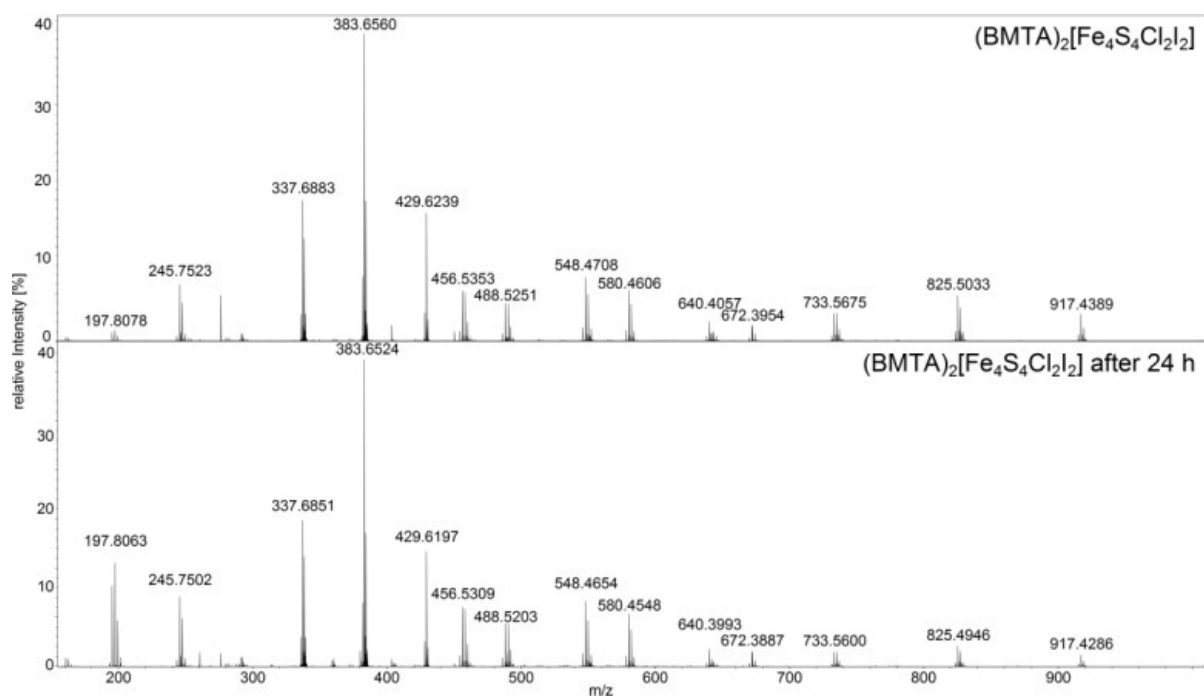


Figure S17: Neg. UHR ESI MS of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Cl}_2\text{I}_2]$ in acetone (red: measurement after dissolving; green: measurement after 24 h).

UV-vis-NIR absorption spectroscopy

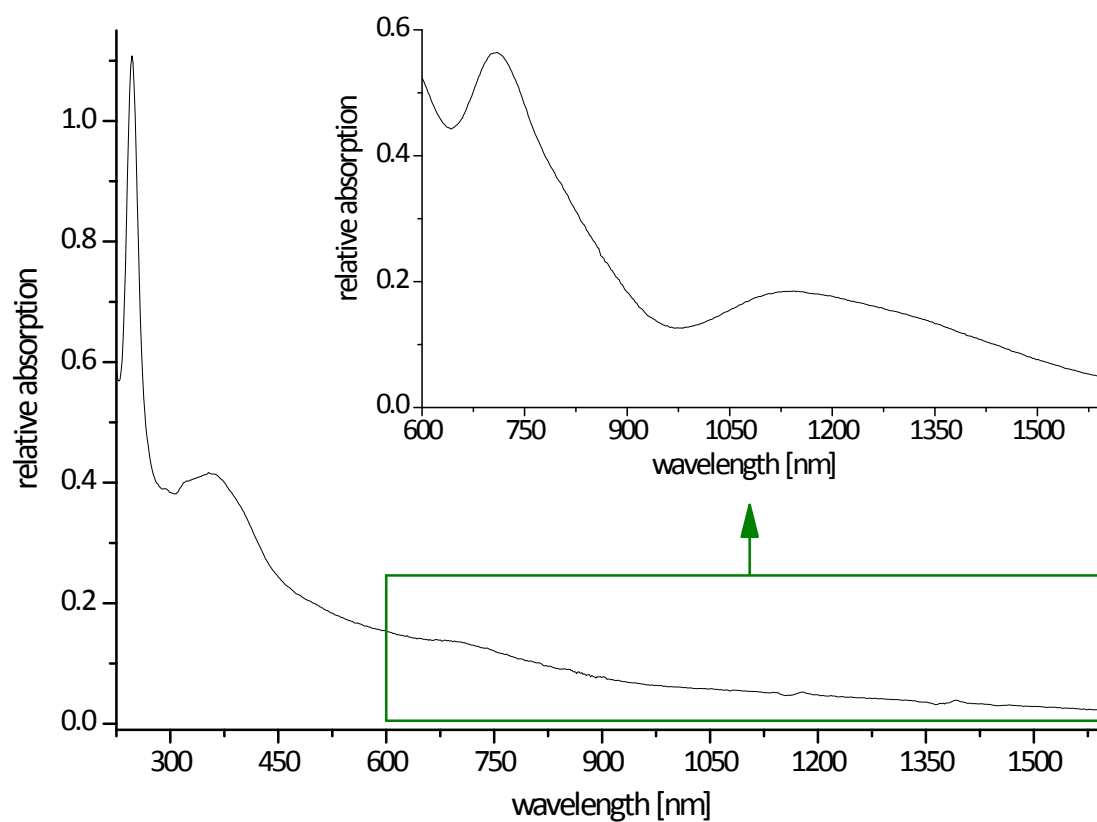


Figure S18: UV-vis-NIR spectra of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{I}_4]$ in acetonitrile.

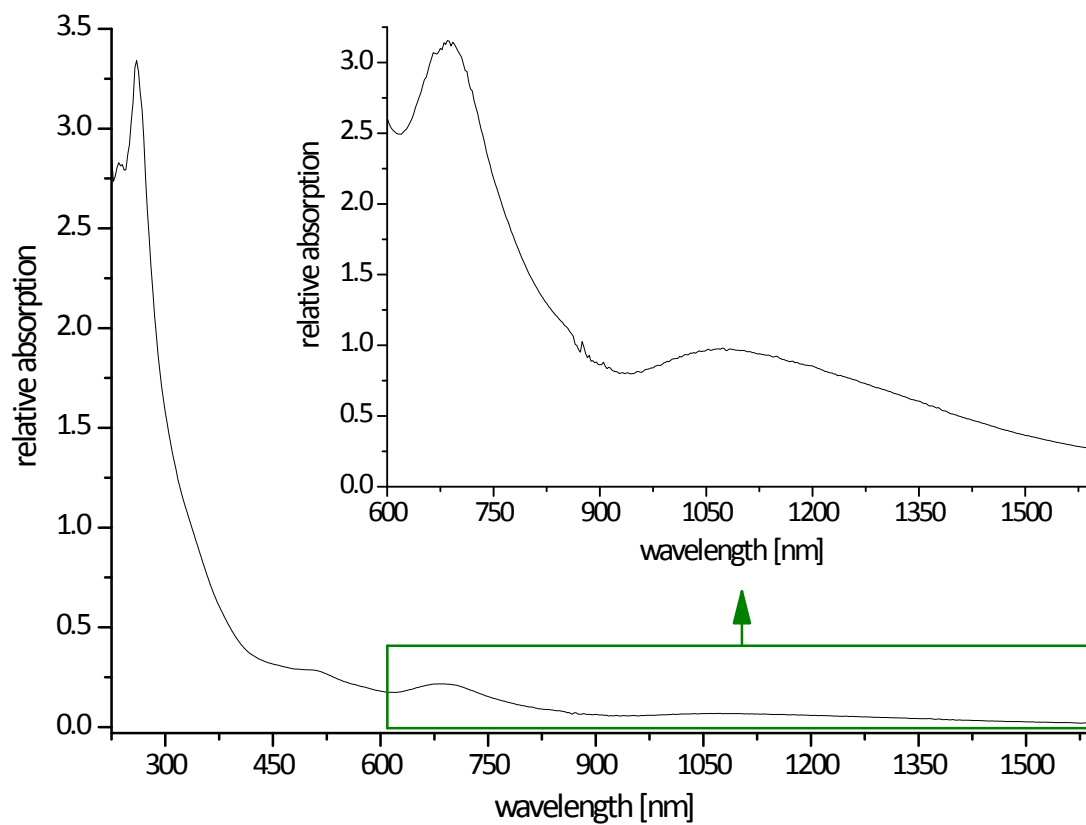


Figure S19: UV-vis-NIR absorption for reaction control during synthesis of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Cl}_4]$ in acetonitrile.

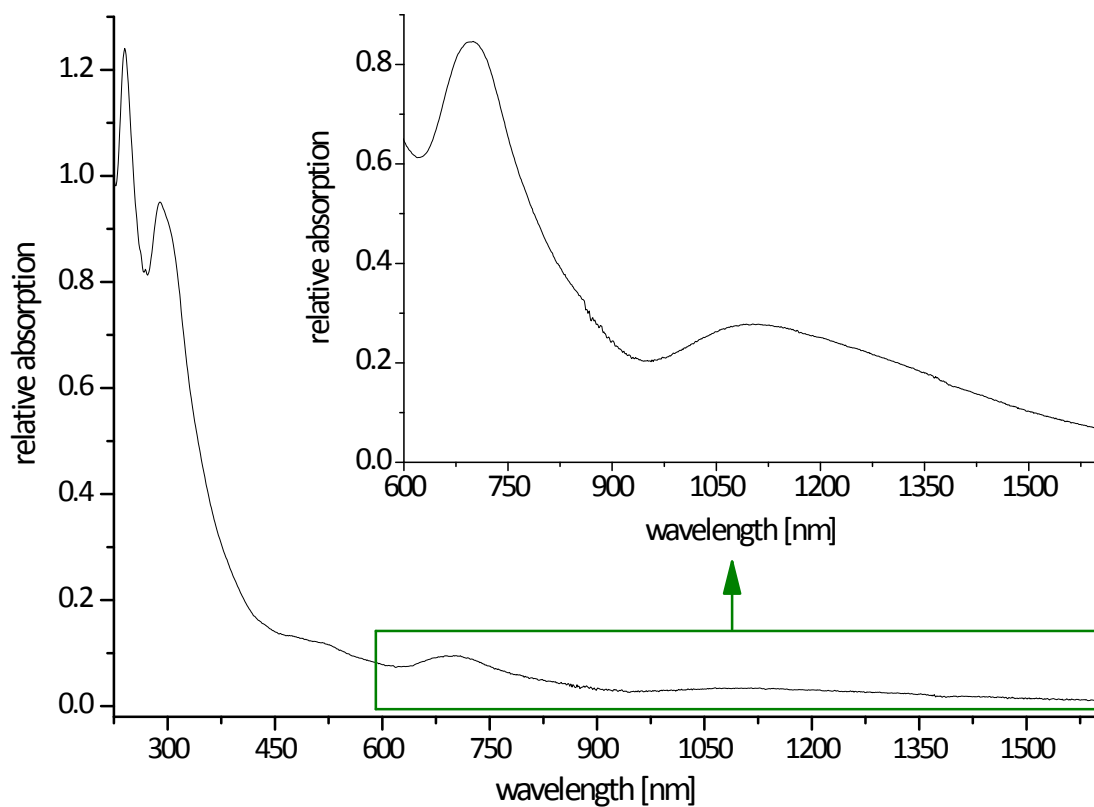


Figure S20: UV-vis-NIR spectra of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_4]$ in acetonitrile.

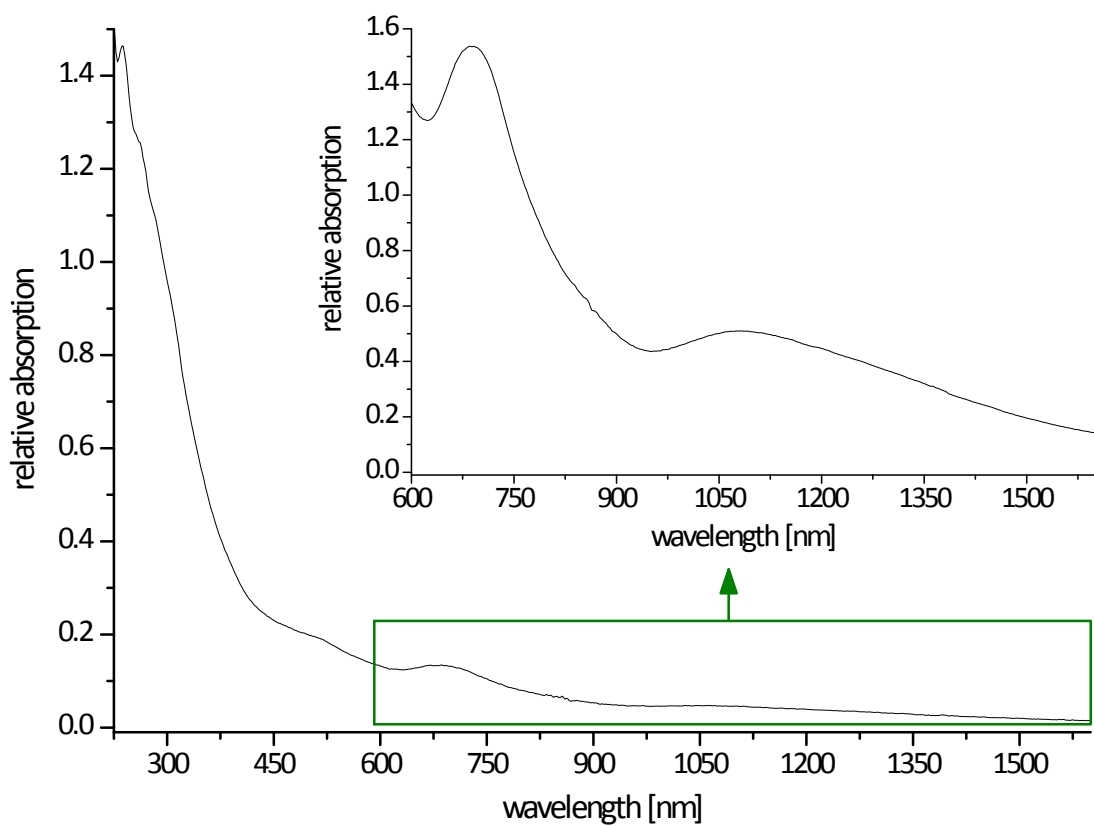


Figure S21: UV-vis-NIR spectra of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{Cl}_2]$ in acetonitrile.

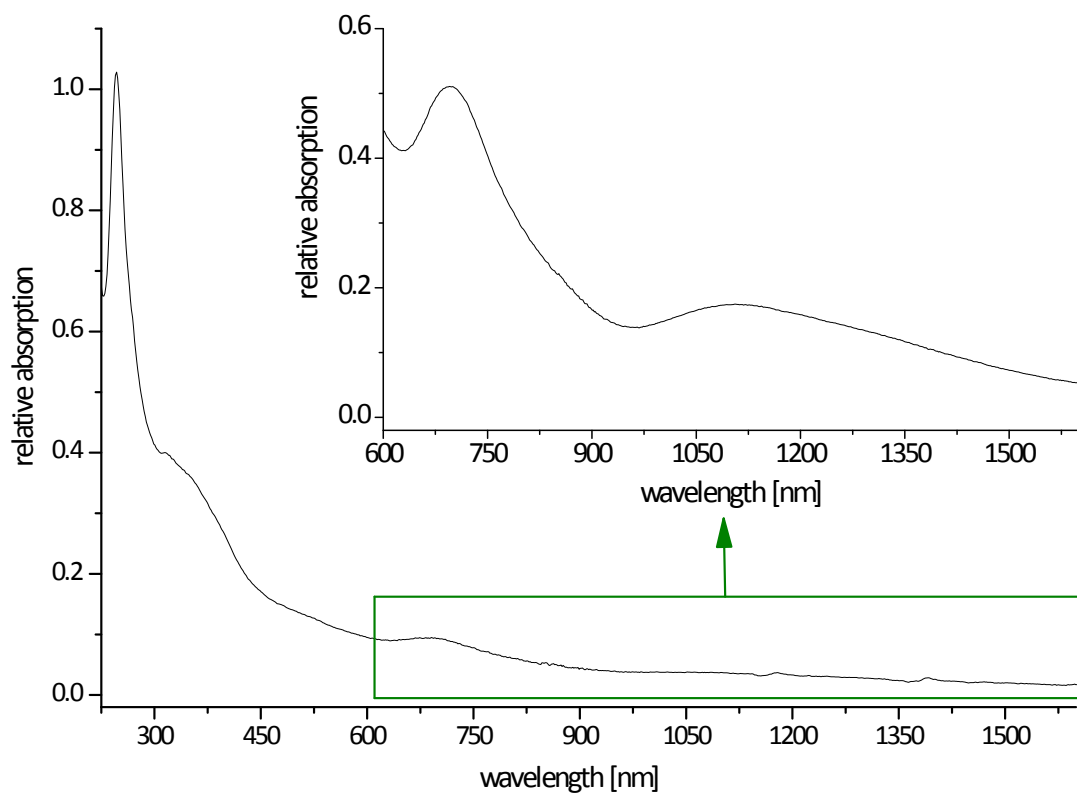


Figure S22: UV-vis-NIR spectra of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Cl}_2\text{I}_2]$ in acetonitrile.

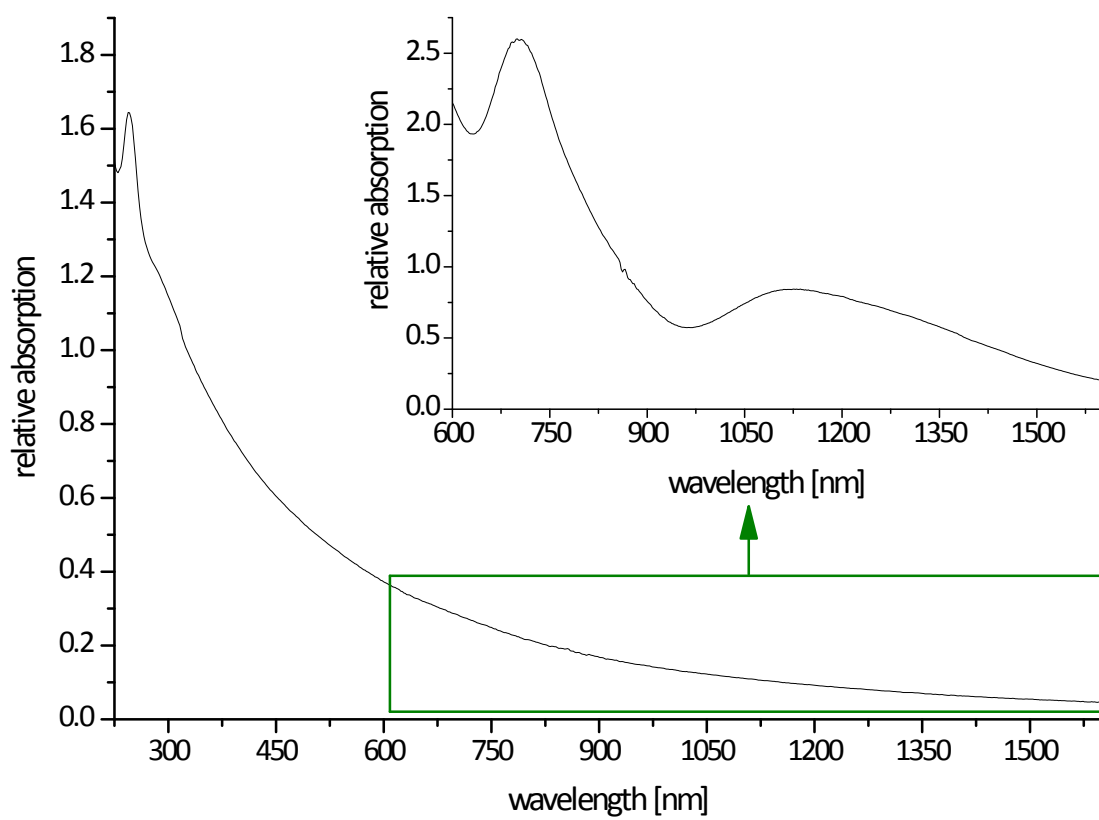


Figure S23: UV-vis-NIR spectra of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{I}_2]$ in acetonitrile.

Synchrotron X-ray powder diffraction

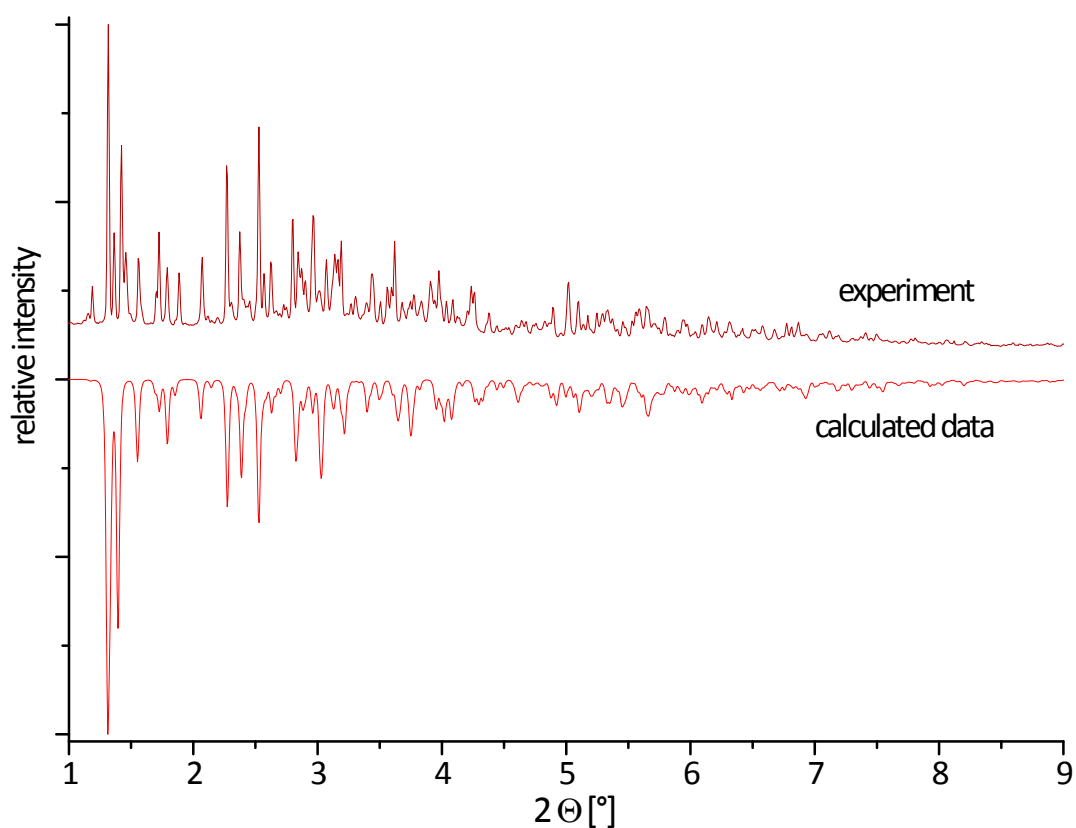


Figure S24: Synchrotron XRPD of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{I}_4]$ at ambient temperature (above: experimental data, with $\lambda = 0.207203 \text{ \AA}$; below calculated pattern¹).

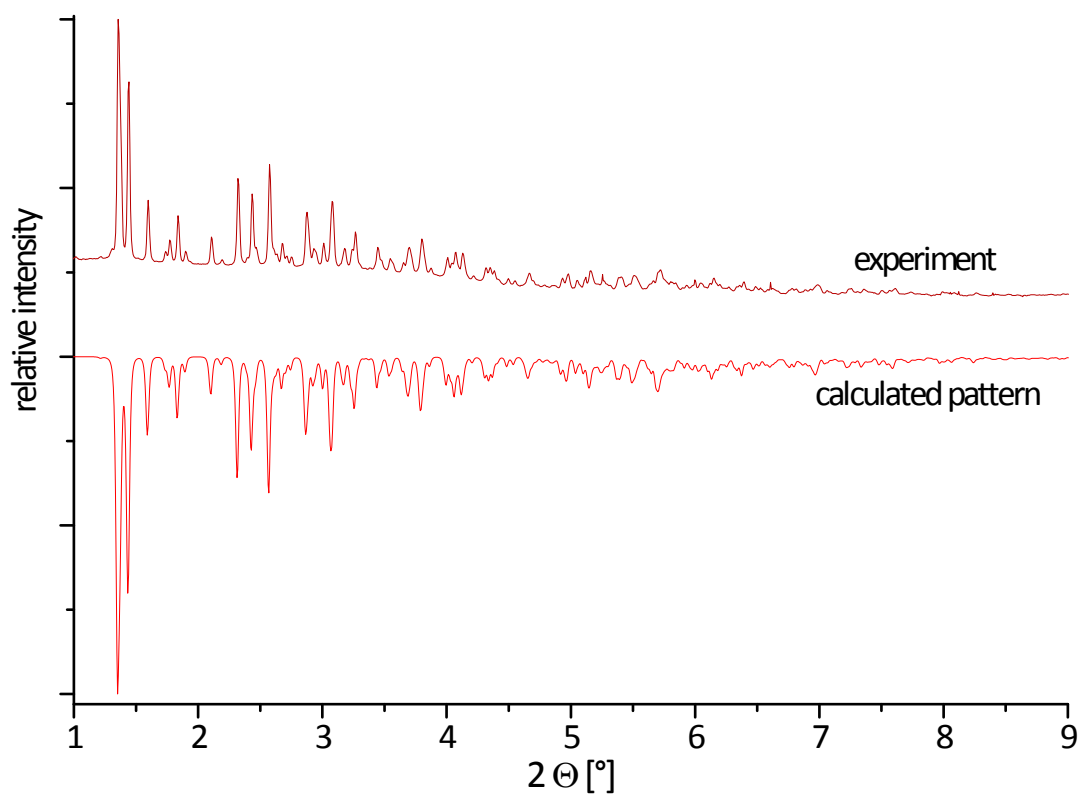


Figure S25: Synchrotron XRPD of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_4]$ at ambient temperature (above: experimental data, with $\lambda = 0.207203 \text{ \AA}$; below calculated pattern²).

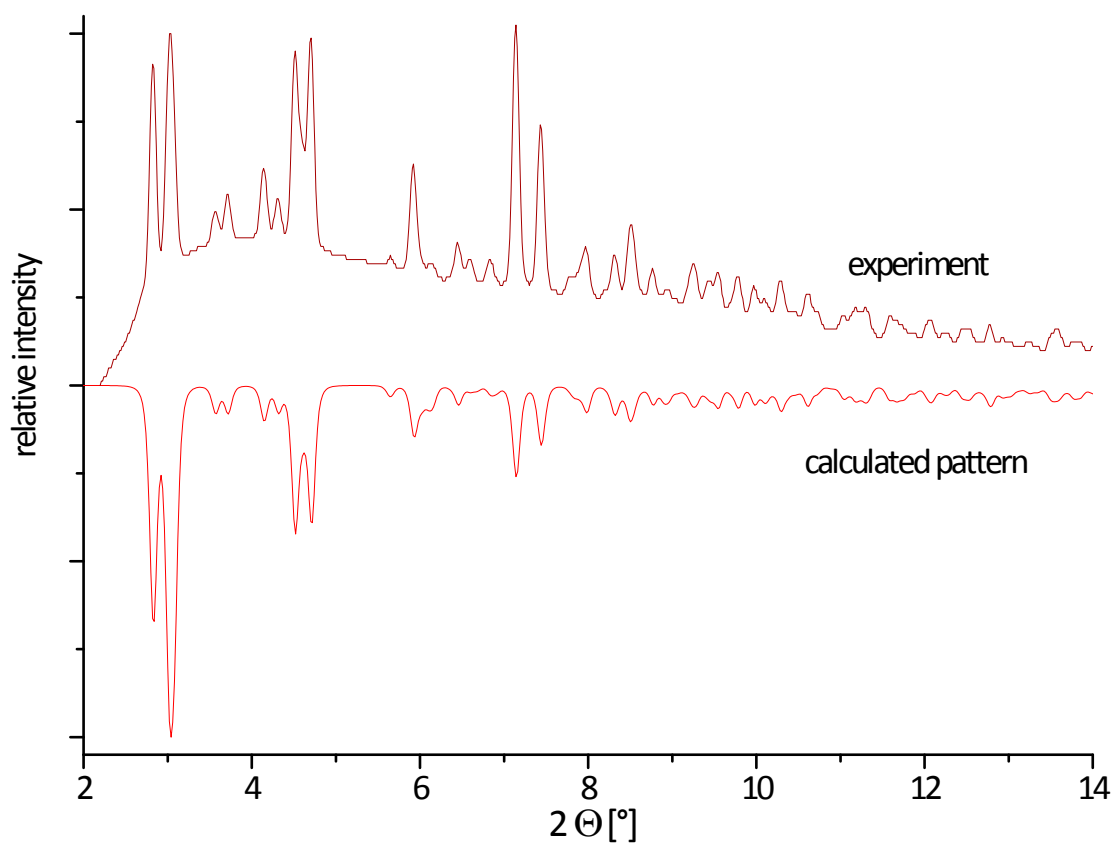


Figure S26: Synchrotron XRPD of $(\text{Ph}_4\text{P})_2[\text{Fe}_4\text{S}_4\text{Br}_4]$ at ambient temperature (above: experimental data, with $\lambda = 0.551155 \text{ \AA}$; below calculated pattern³).

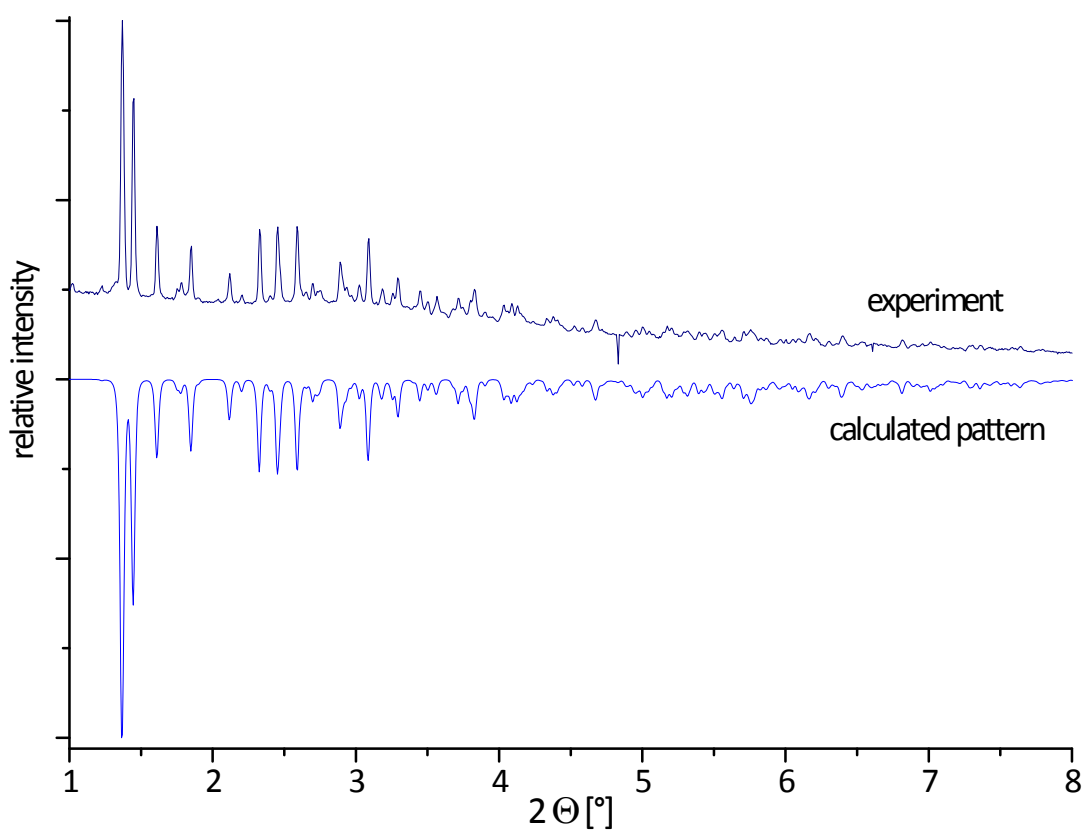


Figure S27: XRPD of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{Cl}_2]$; experiment with $\lambda = 0.207203 \text{ \AA}$ synchrotron radiation (DESY, beam line P02.1, storage ring Petra III); calculated pattern based single crystal structure data.¹

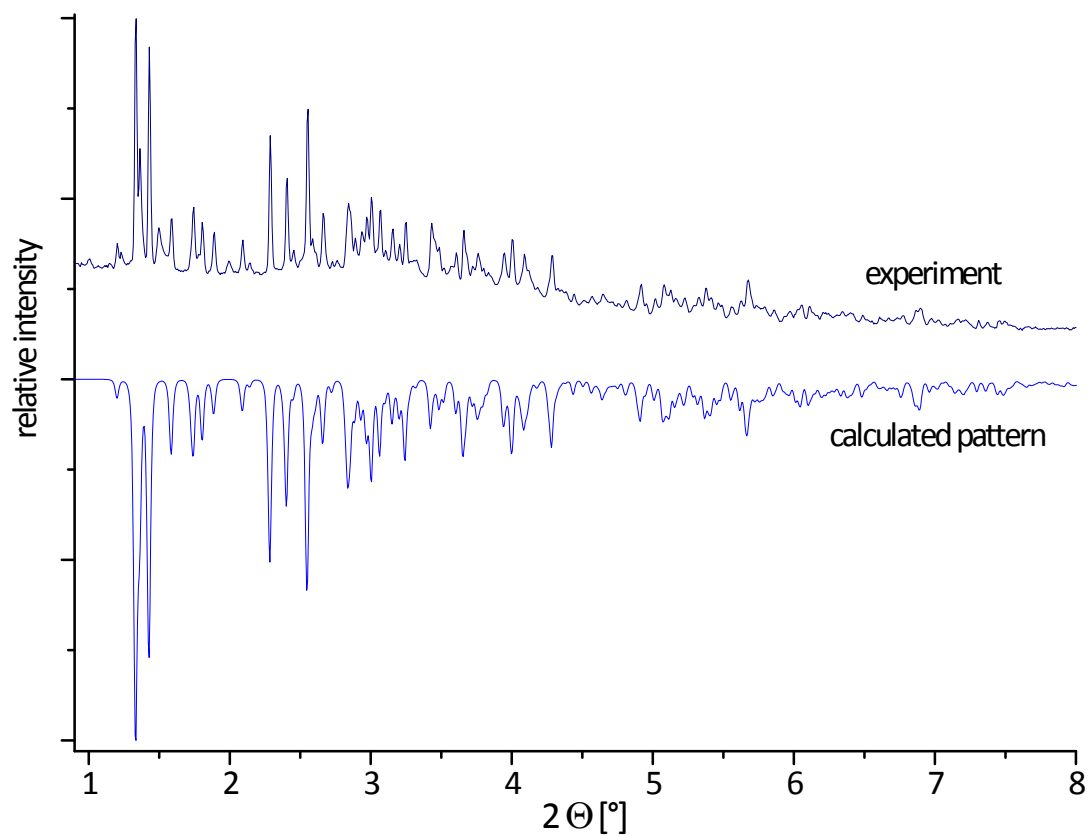


Figure S28: XRPD von $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Br}_2\text{I}_2]$; experiment with $\lambda = 0.207203 \text{ \AA}$ synchrotron radiation (DESY, beam line P02.1, storage ring Petra III); calculated pattern based single crystal structure data.¹

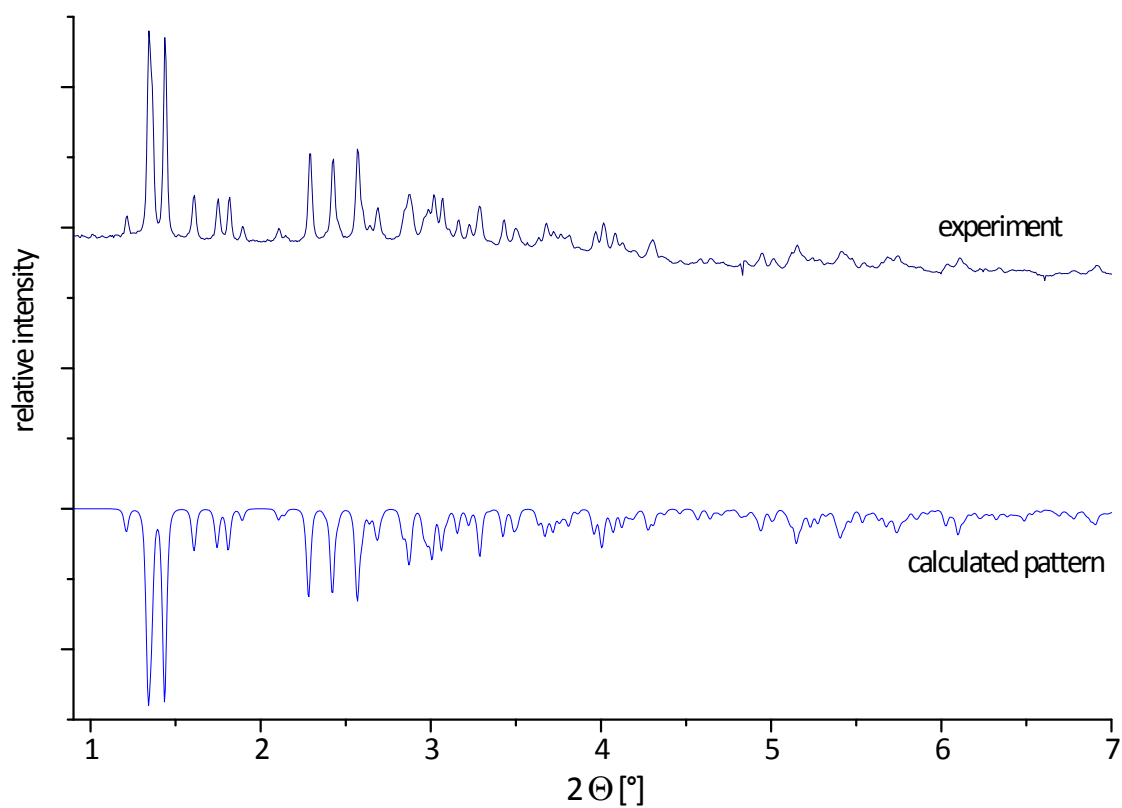


Figure S29: XRPD of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{Cl}_2\text{I}_2]$; experiment with $\lambda = 0.207203 \text{ \AA}$ synchrotron radiation (DESY, beam line P02.1, storage ring Petra III); calculated pattern based single crystal structure data.¹

Literature

1. W. Saak and S. Pohl, *Z. Naturforsch.*, 1985, **40b**, 1105-1112.
2. A. O. Schüren, L. Carrella, E. Rothe, B. M. Ridgway, V. K. Gramm, F. Doctorovich, E. Rentschler, V. Schünemann, and A. Klein, *manuscript in preparation*, 2016.
3. A. Müller, N. H. Schladerbeck, E. Krickemeyer, H. Bögge, K. Schmitz, E. Bill, and A. X. Trautwein, *Z. Anorg. Allg. Chem.*, 1989, **570**, 7-36.