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## Supporting Information

## Carbon Monoxide Release Properties and Molecular Structures of Thiophenolatomanganese(I) Carbonyl Complexes (Mn-based CORMs)

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Fig. S1: Molecular structure and numbering scheme of **1b**. The ellipsoids represent a probability of 40 %, hydrogen atoms are neglected for clarity reasons.



Fig. S2: Molecular structure of **1b**·**2b**. The ellipsoids represent a probability of 40 %, H atoms are omitted for clarity reasons (color code: C black, Mn blue, O red).



Fig. S3: Molecular structure and numbering scheme of centrosymmetric **1c**. The ellipsoids represent a probability of 40 %, hydrogen atoms are neglected for clarity reasons.



Fig. S4: Molecular structure and numbering scheme of centrosymmetric **1d**. The ellipsoids represent a probability of 40 %, hydrogen atoms are neglected for clarity reasons.



Fig. S5: Molecular structure and numbering scheme of centrosymmetric **1f**. The ellipsoids represent a probability of 40 %, hydrogen atoms are neglected for clarity reasons.



Fig. S6: Molecular structure and numbering scheme of centrosymmetric **1h**. The ellipsoids represent a probability of 40 %, hydrogen atoms are neglected for clarity reasons.



Fig. S7: Molecular structure and numbering scheme of **2b**. The ellipsoids represent a probability of 40 %, hydrogen atoms are neglected for clarity reasons.



Fig. S8: Molecular structure and numbering scheme of **2c**. The ellipsoids represent a probability of 40 %, hydrogen atoms are neglected for clarity reasons.



Fig. S9: Molecular structure and numbering scheme of  $2d \cdot CCl_4$ . The ellipsoids represent a probability of 40 %, hydrogen atoms are neglected for clarity reasons.



Fig. S10: Molecular structure and numbering scheme of centrosymmetric **4**. The ellipsoids represent a probability of 40 %, hydrogen atoms are neglected for clarity reasons.



Figure S11: IR spectra measured above CORM-Mn-S1 in the gas cuvette at different time points: addition of DMSO, 30 min before irradiation, and at the end of irradiation.



Figure S12: The ratio of CO molecules per CORM molecules against the time measured via IR spectroscopy in the gas phase above a CORM-Mn-S1 solution with DMSO. After 3 h 35 min the solution was irradiated with blue light. Exponential functions (red curves) representing first-order reactions are fitted to the reaction of CORM with DMSO and the light-induced decay of the CORM solution. Data points are means with confidential interval of 95%.



Results: CO ratios at different time points:

- time: 2 h CO ratio:  $2.42 \pm 0.06$
- time: 3.5 h CO ratio:  $2.495 \pm 0.084$
- time: 6.5 h CO ratio: 7.41 +- 0.31