# Self-healing Mechanism of Metallopolymers investigated by QM/MM Simulations and Raman Spectroscopy

Stephan Kupfer[1,2,§], Linda Zedler[1,2,§], Julien Guthmuller[3], Stefan Bode[4,5], Martin D. Hager[4,5], Ulrich S. Schubert[4,5], Jürgen Popp[1,2,6], Stefanie Gräfe[1,2], Benjamin Dietzek[1,2,6*]

[1]*Institute for Physical Chemistry, Friedrich Schiller University Jena, Helmholtzweg 4, 07743, Jena, Germany*

[2]*Abbe Center of Photonics, Friedrich Schiller University Jena*

[3]*Faculty of Applied Physics and Mathematics, Gdansk University of Technology, Narutowicza 11/12, 80233 Gdansk, Poland*

[4]*Laboratory for Organic and Macromolecular Chemistry, Friedrich Schiller University Jena, Humboldstr. 10, 07743, Jena, Germany*

[5]*Jena Center of Soft Matter, Friedrich Schiller University Jena, Philosophenweg 7, 07743, Jena, Germany*

[6]*Institute for Photonic Technology (IPHT) Jena, Albert-Einstein-Str. 9, 07745, Jena, Germany*

## Experimental Section

All used chemicals were purchased from Aldrich, ABCR and Hetcat. They were used without further purification. DMSO was dried with activated mol sieves. Elemental analyses were carried out on a Vario EL III (Elementar) elemental analyzer.

$^1$H and $^{13}$C NMR spectra were recorded on a Bruker AC 250 (250 MHz) at 298 K. Chemical shifts are reported in parts per million (ppm, $\delta$ scale) relative to the residual signal of the solvent. Coupling constants are given in Hz.

6-(2,2':6',2''-Terpyridin-4'-yloxy)-hexan-1-ol (**1**) was prepared according to literature.[1]

### Conversion of 1 with iron(II) sulfate

338 mg (0.97 mmol) of **1** were dissolved in 40 mL methanol. Subsequently, 135 mg iron(II) sulfate heptahydrate (0.49 mmol) were added and the color changed to dark violet. The reaction mixture was stirred for further 18 hours. Afterwards the solvent was evaporated and the residue was washed with 200 mL diethyl ether.

**$^1$H NMR** (250 MHz, $CD_3OD$): $\delta = 1.55 – 2.28$ (m, 8H), 3.65 (t, $J = 6$ Hz, 2H), 4.70 (t, $J = 6$ Hz, 2H), 7.19 (m, 4H), 7.95 (t, $J = 7.25$ Hz, 2H), 8.70 (m, 4H) ppm.
**$^{13}$C NMR** (62.5 MHz, $CD_3OD$): $\delta = 25.3$, 25.7, 28.7, 32.2, 61.5, 70.3, 111.2, 123.6, 127.1, 138.5, 152.7, 158.3, 160.8, 168.4 ppm.
Anal. calcd. for $C_{42}H_{46}N_6O_8SFe$: C 59.79, H 5.45, N 9.88, S 3.77; found: C 59.40, H 5.59, N 9.99, S 3.72

### Conversion of 1 with cadmium(II) bromide

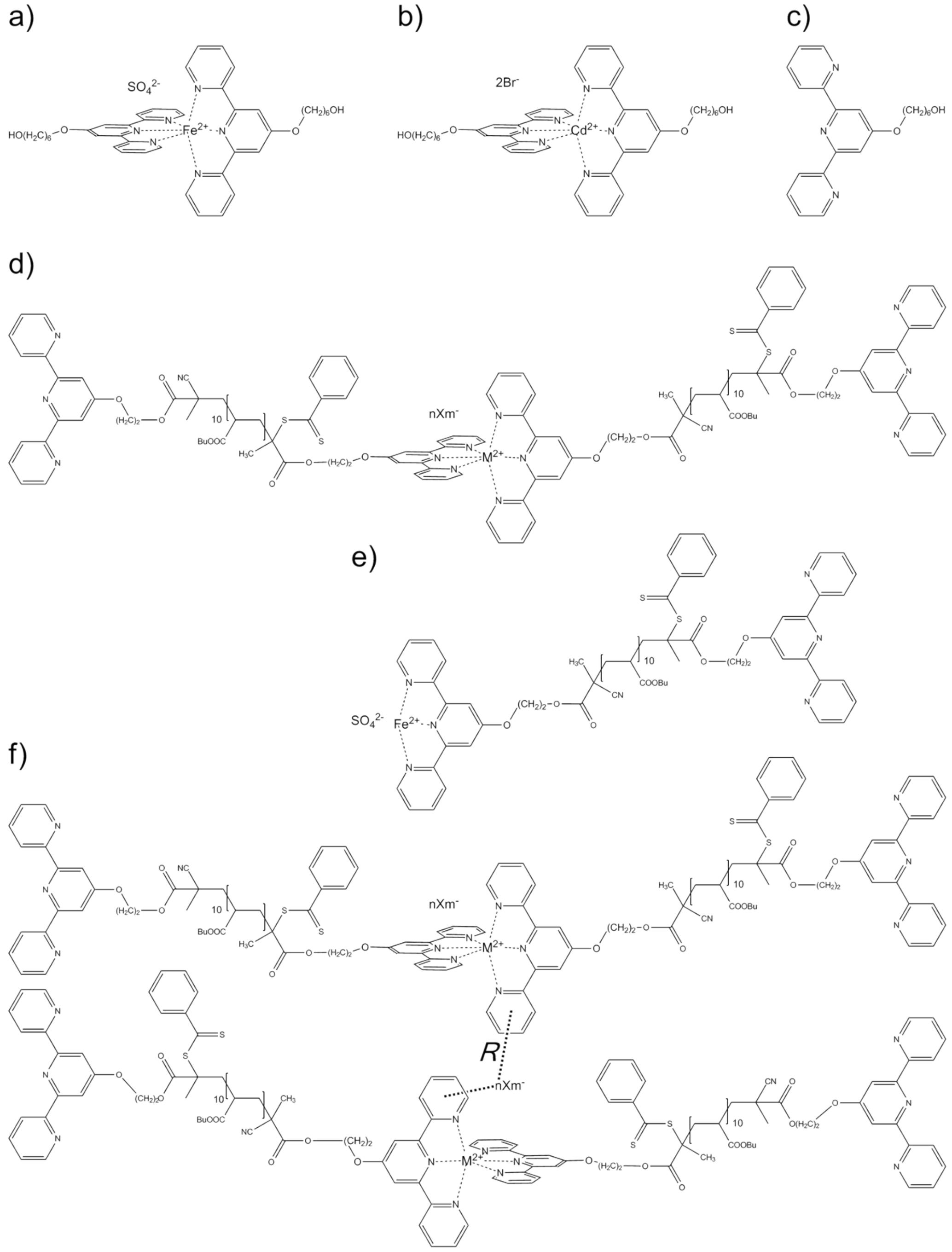
297 mg (0.85 mmol) of **1** were dissolved in 40 mL methanol. Subsequently, 147 mg cadmium(II) bromide tetrahydrate (0.43 mmol) were added and a precipitate formed. The reaction mixture was stirred for further 18 hours. Afterwards the product was obtained by filtration and was washed with 300 mL diethyl ether.

$^1$H NMR and $^{13}$C NMR were not measure due to the bad solubility of the product in all common solvents.
Anal. calcd. for $C_{42}H_{46}N_6O_4Br_2Cd$: C 51.95, H 4.77, N 8.65, Br 16.46; found: C 51.95, H 4.75, N 8.80, Br 16.86

## References

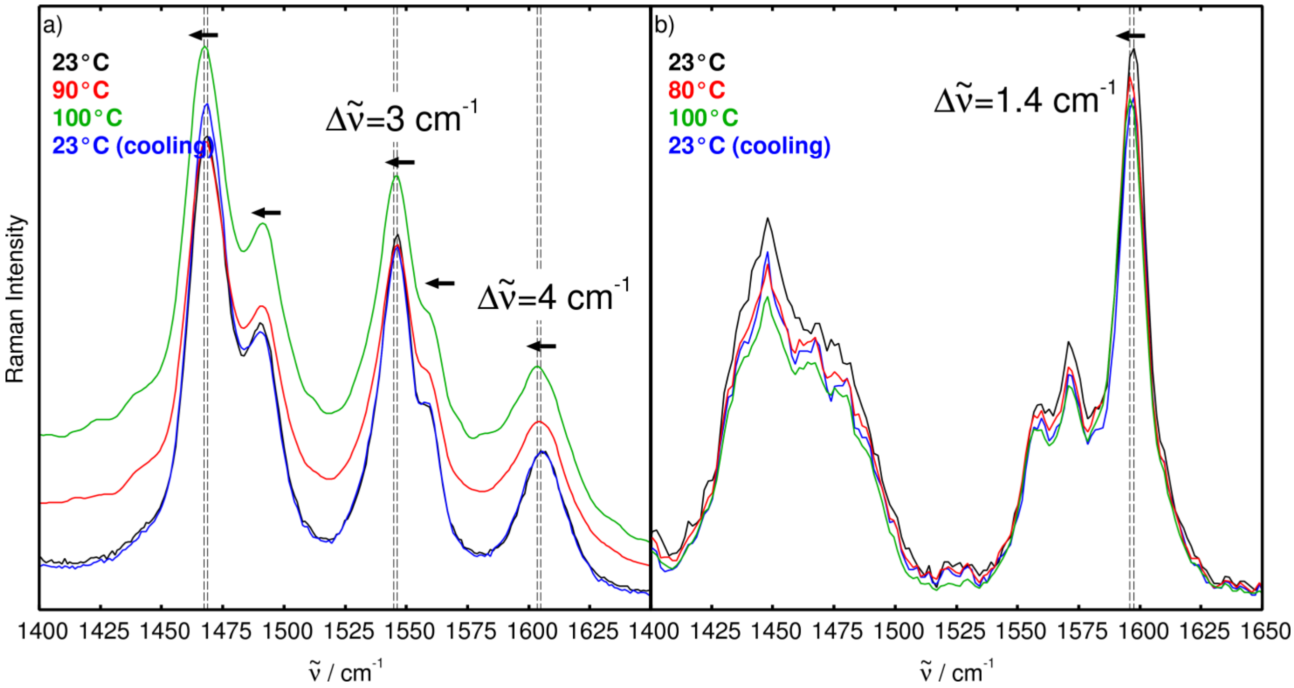
[1] U. S. Schubert, C. Eschbaumer, O. Hien, P. R. Andres, *Tetrahedron Lett.* **2001***, 42*, 4705–4707.

# Figure S1



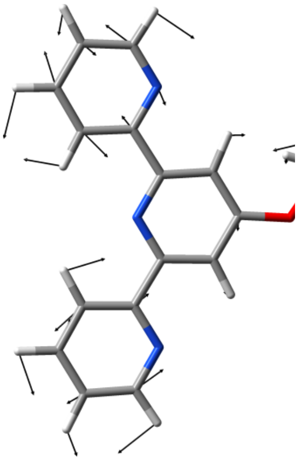
Schematic representation of the iron(II) terpyridine sulfate complex (a)), the cadmium(II) terpyridine bromide complex (b)), and the free terpyridine ligand (c)). d) depict the model systems used for the simulation of the Raman spectra of the iron(II) sulfate and the cadmium(II) bromide cross-linked metallopolymers, and e) the semi-decomplexed metallopolymer. The polymer model used in the calculation of the ionic clusters is illustrated in f); frozen coordinate $R$ is indicated.

## Figure S2



Temperature-dependent Raman spectra of the iron(II) sulfate (a)) and cadmium(II) bromide (b)) cross-linked metallopolymers in the spectral range between 1400 and 1650 cm$^{-1}$. Vertical dashed lines indicate the observed fully reversible bathochromic shifts of approximately 3 and 4 and 1.4 cm$^{-1}$.

# Figure S3



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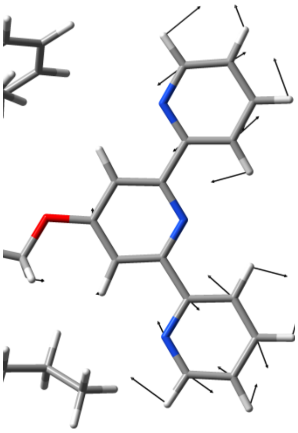

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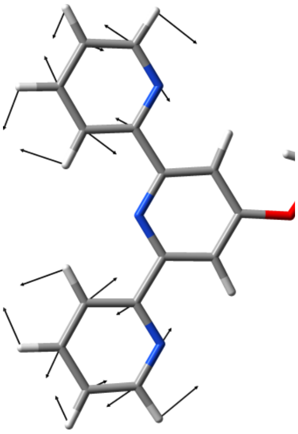

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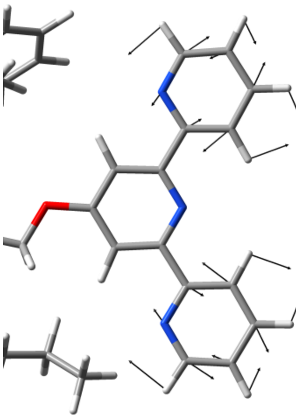

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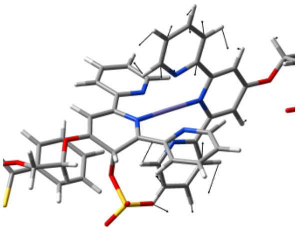

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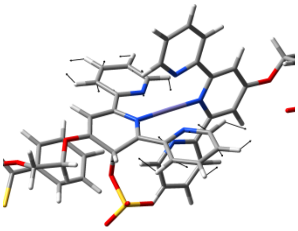

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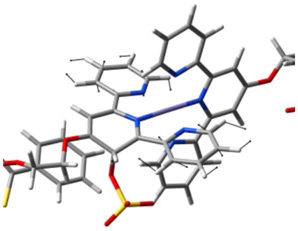

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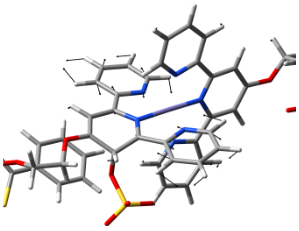

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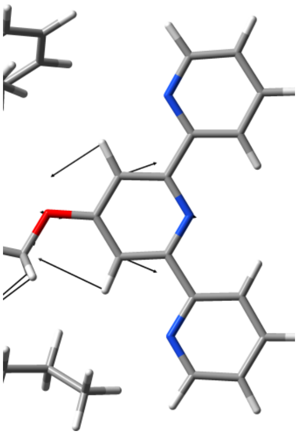

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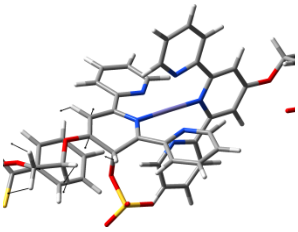

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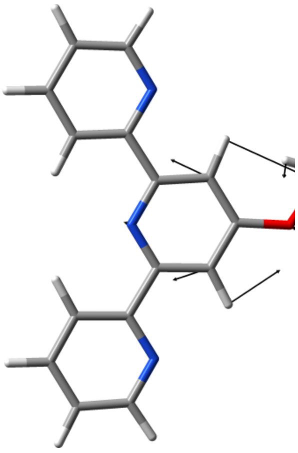

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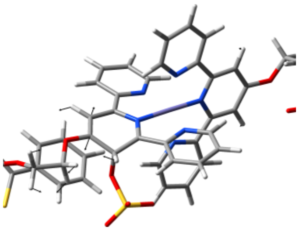

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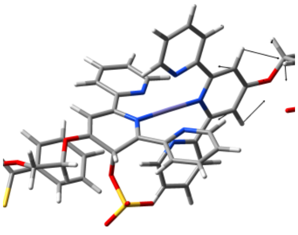
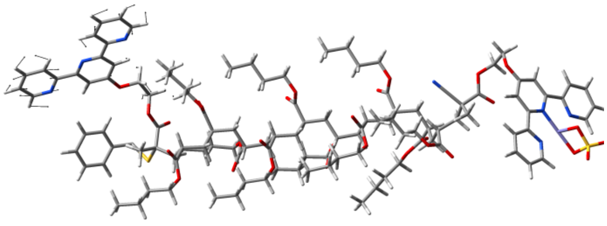


mode 1463

Intense vibrational modes of the iron(II) sulfate metallopolymer contributing to the experimental Raman bands at 1546, 1558, and 1606 $cm^{-1}$.

## Figure S4



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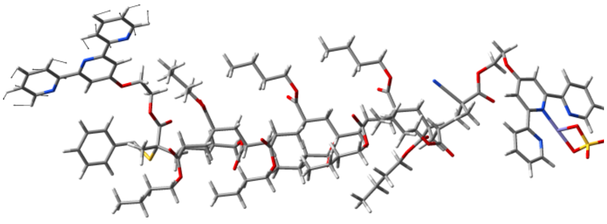

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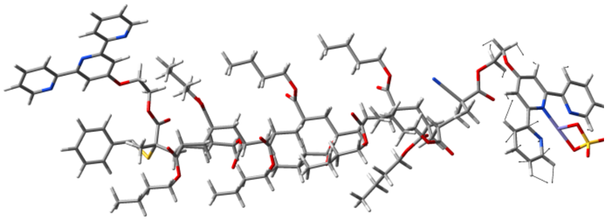

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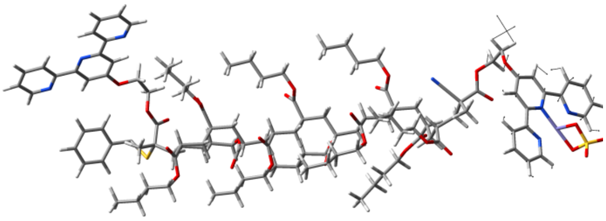

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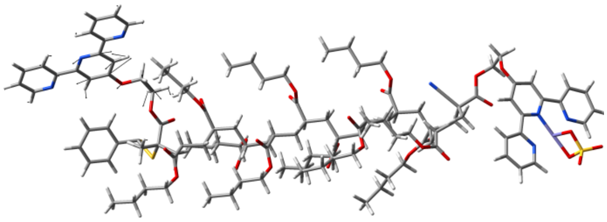

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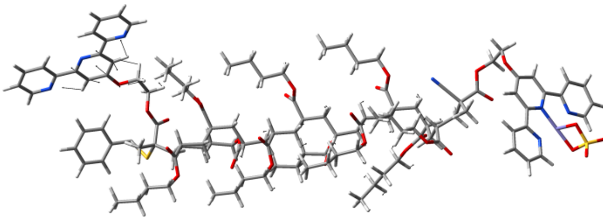

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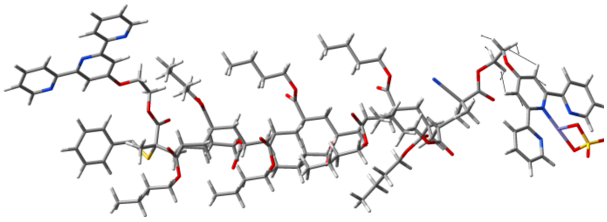


mode 739

Intense vibrational modes of the semi-decomplexed iron(II) sulfate metallopolymer.

# Table S5

iron(II) sulfate metallopolymer

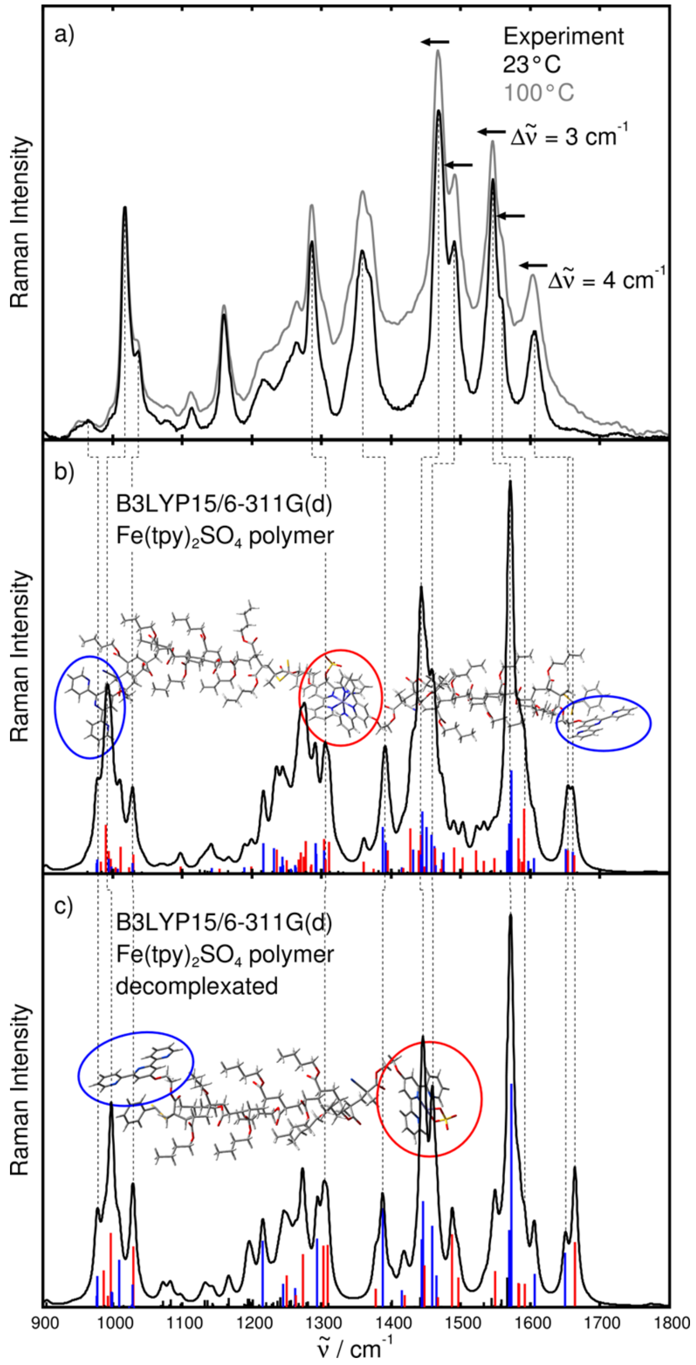
| | B3LYP(15)/6-31G(d) | | | B3LYP(15)/6-311G(d) | | | B3LYP/6-31G(d) | | |
|---|---|---|---|---|---|---|---|---|---|
| assignment | mode | $\tilde{\nu}/ cm^{-1}$ | $I$ / Å$^4 amu^{-1}$ | mode | $\tilde{\nu}/ cm^{-1}$ | $I$ / Å$^4 amu^{-1}$ | mode | $\tilde{\nu}/ cm^{-1}$ | $I$ / Å$^4 amu^{-1}$ |
| free tpy asym | 1415 | 1581.3 | 335 | 1415 | 1569.3 | 294 | 1417 | 1593.8 | 340 |
| free tpy asym | 1416 | 1581.7 | 309 | 1416 | 1569.6 | 212 | 1418 | 1594.2 | 312 |
| free tpy sym | 1417 | 1584.9 | 593 | 1417 | 1572.6 | 557 | 1421 | 1597.5 | 550 |
| free tpy sym | 1418 | 1585.0 | 605 | 1418 | 1572.8 | 610 | 1422 | 1597.6 | 572 |
| complex tpy asym | 1422 | 1593.5 | 94 | 1422 | 1583.2 | 210 | 1426 | 1606.1 | 114 |
| complex tpy asym | 1424 | 1594.5 | 200 | 1424 | 1583.8 | 87 | 1427 | 1607.8 | 217 |
| complex tpy sym | 1425 | 1595.3 | 42 | 1425 | 1587.9 | 70 | 1428 | 1608.1 | 43 |
| complex tpy sym | 1428 | 1602.3 | 394 | 1428 | 1591.1 | 385 | 1432 | 1615.0 | 458 |
| free tpy sym | 1450 | 1658.7 | 144 | 1445 | 1650.5 | 147 | 1460 | 1668.2 | 138 |
| complex tpy sym | 1452 | 1661.7 | 58 | 1447 | 1654.1 | 137 | 1462 | 1678.1 | 124 |
| free tpy sym | 1461 | 1668.7 | 123 | 1453 | 1660.8 | 129 | 1464 | 1679.8 | 111 |
| complex tpy sym | 1462 | 1669.7 | 65 | - | - | - | 1466 | 1681.1 | 39 |
| complex tpy sym | 1463 | 1670.6 | 113 | 1455 | 1662.9 | 107 | 1468 | 1683.8 | 36 |

iron(II) sulfate semi-decomplexed metallopolymer

| | B3LYP(15)/6-31G(d) | | | B3LYP(15)/6-311G(d) | | | B3LYP/6-31G(d) | | |
|---|---|---|---|---|---|---|---|---|---|
| assignment | mode | $\tilde{\nu}/ cm^{-1}$ | $I$ / Å$^4 amu^{-1}$ | mode | $\tilde{\nu}/ cm^{-1}$ | $I$ / Å$^4 amu^{-1}$ | mode | $\tilde{\nu}/ cm^{-1}$ | $I$ / Å$^4 amu^{-1}$ |
| free tpy asym | 716 | 1581.8 | 305 | 707 | 1570.0 | 209 | 717 | 1594.3 | 312 |
| free tpy sym | 717 | 1585.0 | 602 | 710 | 1572.8 | 606 | 718 | 1597.7 | 569 |
| complex tpy asym | 720 | 1592.9 | 57 | 718 | 1583.0 | 65 | 721 | 1605.9 | 86 |
| complex tpy sym | 721 | 1595.9 | 113 | 719 | 1584.0 | 63 | 723 | 1608.1 | 65 |
| free tpy sym | 733 | 1658.3 | 127 | 730 | 1650.2 | 147 | 738 | 1668.1 | 141 |
| complex tpy sym | 739 | 1671.7 | 185 | 736 | 1664.0 | 177 | 740 | 1681.8 | 124 |

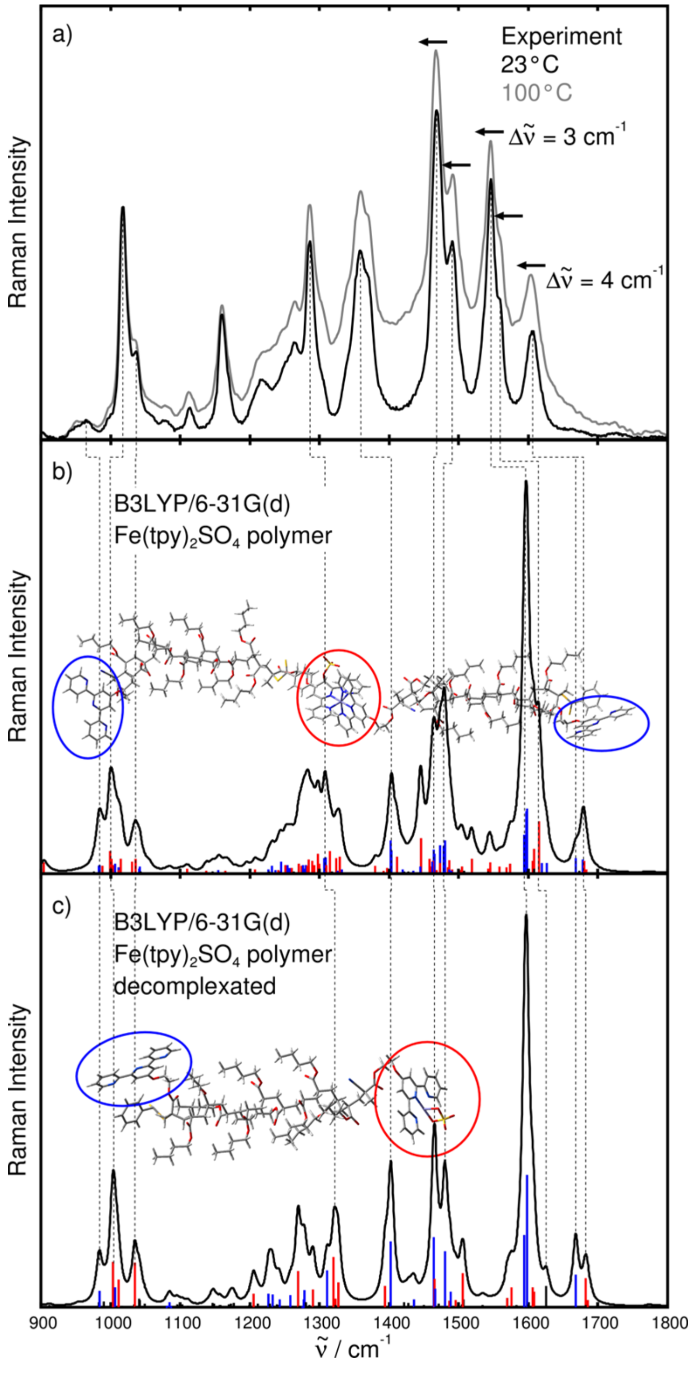
Assignment and comparison of the calculated vibrational frequencies (cm$^{-1}$) and relative Raman activities ( Å$^4 amu^{-1}$) for the iron(II) sulfate cross-linked metallopolymer as well as its semi-decomplexated form obtained at the B3LYP15/6-31G(d), B3LYP15/6-311G(d), and B3LYP/6-31G(d) levels of theory.

## Figure S6



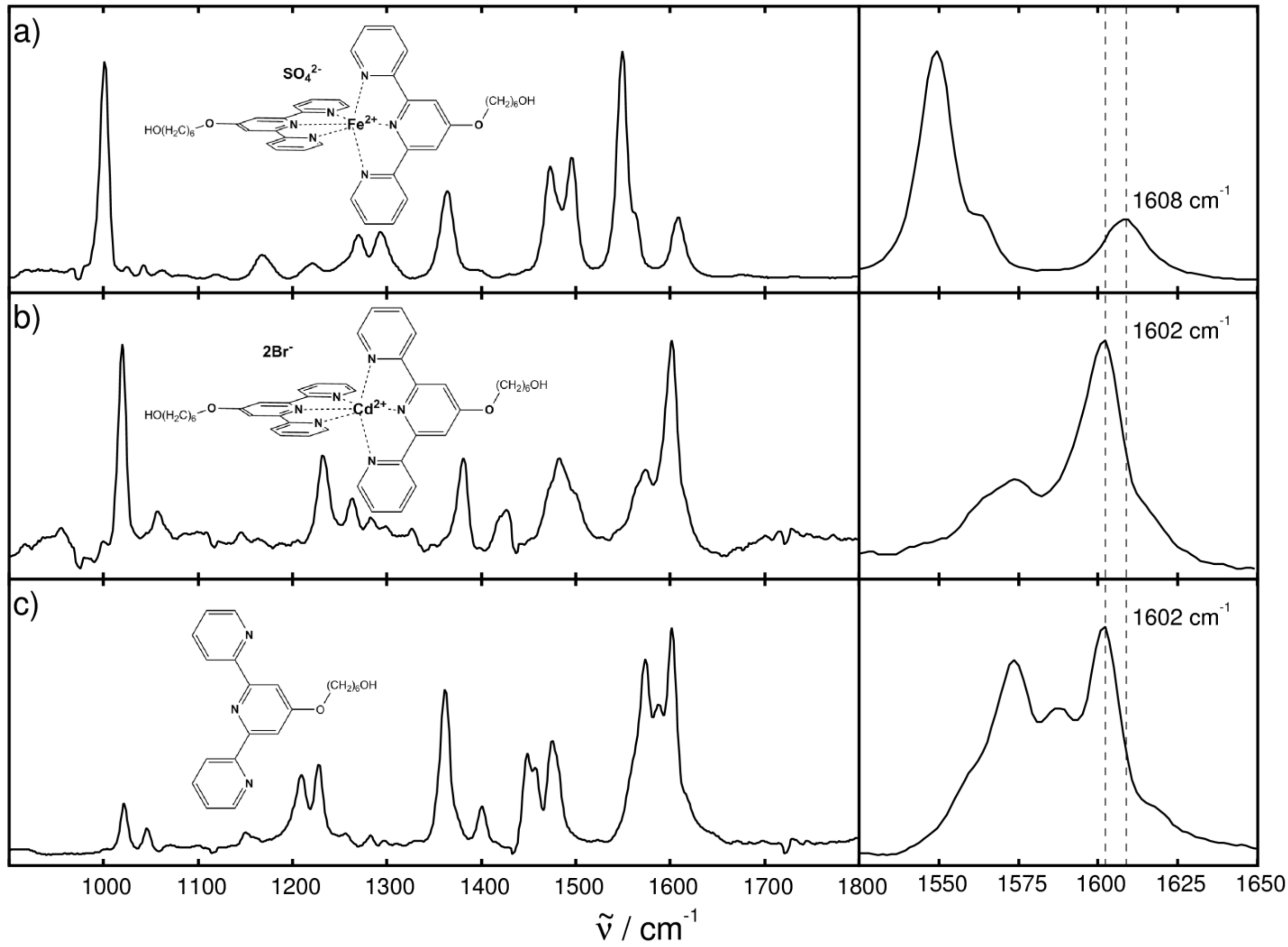
Raman spectra of the iron(II) sulfate metallopolymer. a) depicts temperature-dependent Raman spectra at 23 and 100 °C along with the thermally induced bathochromic shifts of the intensity pattern. b) and c) display calculated Raman spectra at the QM/MM level of theory using B3LYP(15) and the 6-311G(d) basis set and the universal force field for two polymer models. Vibrational modes centered at the *bis*terpyridine-iron(II) complex are shown in red and modes of the free terminal terpyridine moieties are shown in blue.

## Figure S7



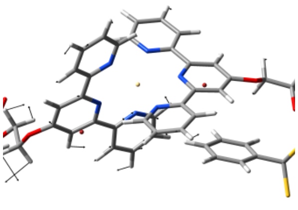
Raman spectra of the iron(II) sulfate metallopolymer. a) depicts temperature-dependent Raman spectra at 23 and 100 °C along with the thermally induced bathochromic shifts of the intensity pattern. b) and c) display calculated Raman spectra at the QM/MM level of theory using B3LYP and the 6-31G(d) basis set and the universal force field for two polymer models. Vibrational modes centered at the *bis*terpyridine-iron(II) complex are shown in red and modes of the free terminal terpyridine moieties are shown in blue.

# Figure S8



Raman spectra of the iron(II) sulfate a), cadmium(II) bromide b), and terpyridine c) monomers measured upon excitation at 568 nm. Raman frequencies for bands correlated to the observed bathochromic shifts of the metallopolymers are indicated.

# Figure S9



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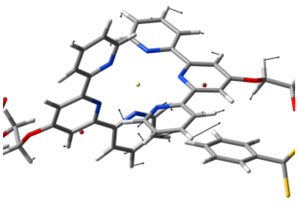

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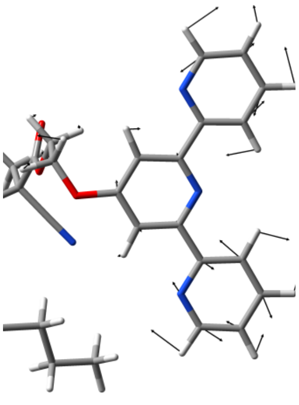

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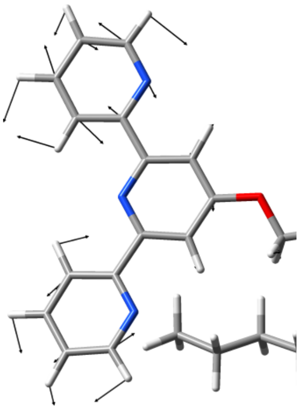

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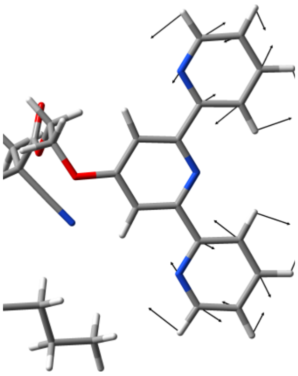

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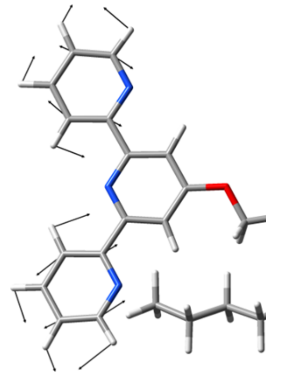

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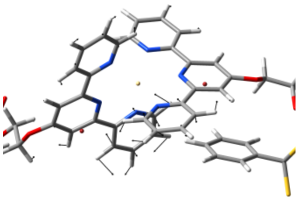

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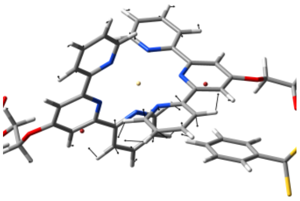

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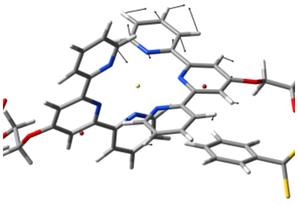

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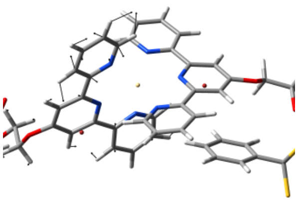

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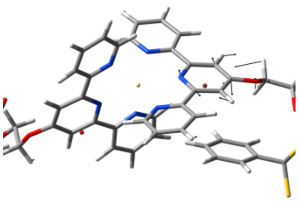

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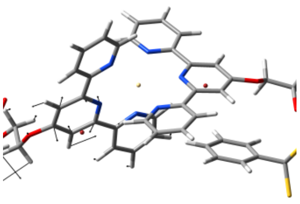

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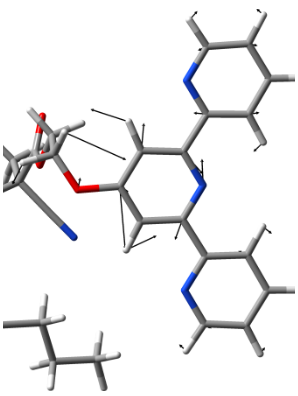

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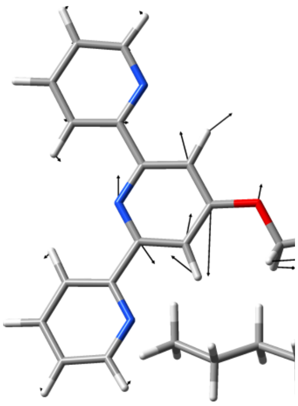

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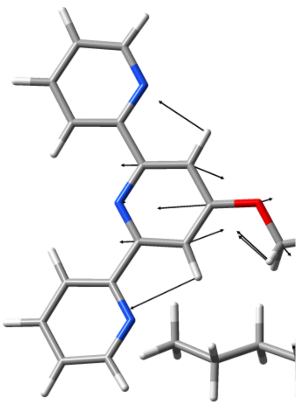

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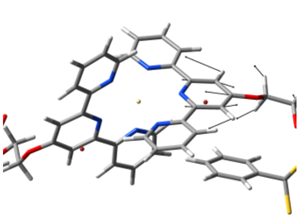

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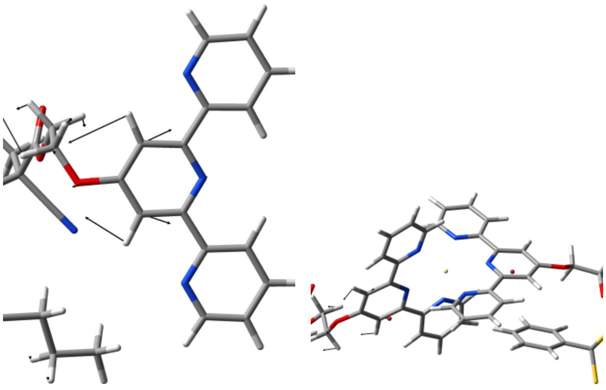


mode 1453 mode 1454

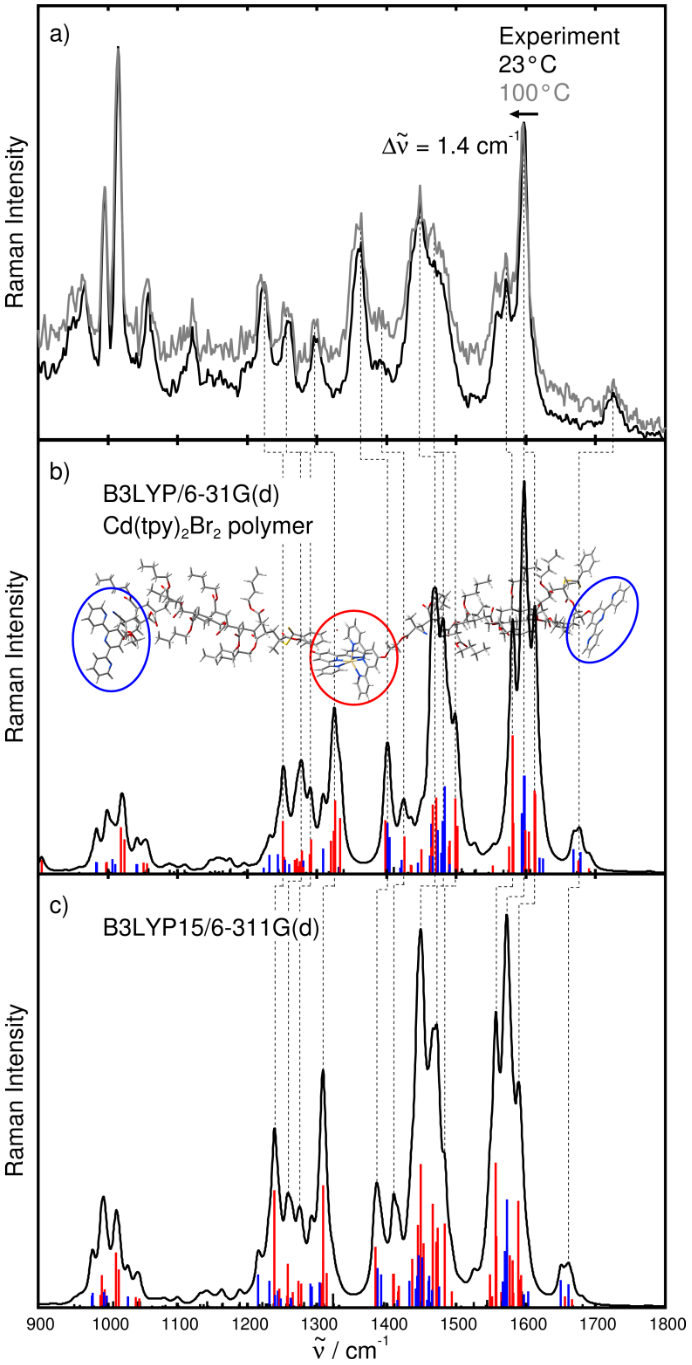
Intense vibrational modes of the cadmium(II) bromide metallopolymer contributing to the experimental Raman bands at 1597 and 1724 cm$^{-1}$.

# Table S10

| cadmium(II) bromide metallopolymer | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | B3LYP(15)/6-31G(d) | | | B3LYP(15)/6-311G(d) | | | B3LYP/6-31G(d) | | |
| assignment | mode | $\tilde{\nu}/ cm^{-1}$ | $I$ / Å$^4 amu^{-1}$ | mode | $\tilde{\nu}/ cm^{-1}$ | $I$ / Å$^4 amu^{-1}$ | mode | $\tilde{\nu}/ cm^{-1}$ | $I$ / Å$^4 amu^{-1}$ |
| complex tpy sym | 1381 | 1568.0 | 668 | 1370 | 1556.1 | 788 | 1402 | 1580.4 | 779 |
| complex tpy sym | 1384 | 1569.2 | 366 | 1373 | 1558.0 | 387 | 1403 | 1581.7 | 286 |
| free tpy asym | 1406 | 1581.3 | 333 | 1387 | 1569.2 | 308 | 1409 | 1593.8 | 341 |
| free tpy asym | 1407 | 1581.7 | 318 | 1389 | 1570.0 | 116 | 1411 | 1594.3 | 320 |
| free tpy sym | 1409 | 1584.9 | 593 | 1396 | 1572.6 | 341 | 1413 | 1597.5 | 555 |
| free tpy sym | 1410 | 1585.1 | 586 | 1398 | 1572.8 | 587 | 1414 | 1597.8 | 554 |
| complex tpy asym | 1411 | 1586.0 | 60 | 1408 | 1576.8 | 64 | 1415 | 1598.5 | 44 |
| complex tpy asym | 1412 | 1586.3 | 274 | 1409 | 1577.2 | 284 | 1416 | 1598.9 | 247 |
| complex tpy sym | 1414 | 1590.5 | 235 | 1412 | 1581.2 | 259 | 1418 | 1603.7 | 113 |
| complex tpy sym | 1415 | 1591.0 | 99 | 1413 | 1581.8 | 81 | 1419 | 1603.8 | 241 |
| complex tpy asym | 1420 | 1600.9 | 701 | 1415 | 1589.1 | 581 | 1421 | 1611.9 | 469 |
| complex tpy asym | 1421 | 1602.1 | 469 | 1418 | 1593.3 | 176 | 1424 | 1613.4 | 451 |
| free tpy asym | 1423 | 1608.7 | 96 | 1421 | 1597.5 | 73 | 1426 | 1419.2 | 93 |
| free tpy asym | 1426 | 1614.3 | 89 | 1423 | 1603.5 | 89 | 1427 | 1624.1 | 87 |
| free tpy sym | 1441 | 1658.1 | 143 | 1435 | 1649.9 | 149 | 1450 | 1667.9 | 140 |
| complex tpy sym | 1444 | 1663.6 | 62 | 1440 | 1656.4 | 63 | 1454 | 1674.9 | 74 |
| free tpy sym | 1453 | 1669.2 | 123 | 1444 | 1661.3 | 128 | 1455 | 1678.5 | 123 |
| complex tpy sym | 1454 | 1670.2 | 41 | 1449 | 1666.1 | 47 | 1465 | 1690.7 | 30 |

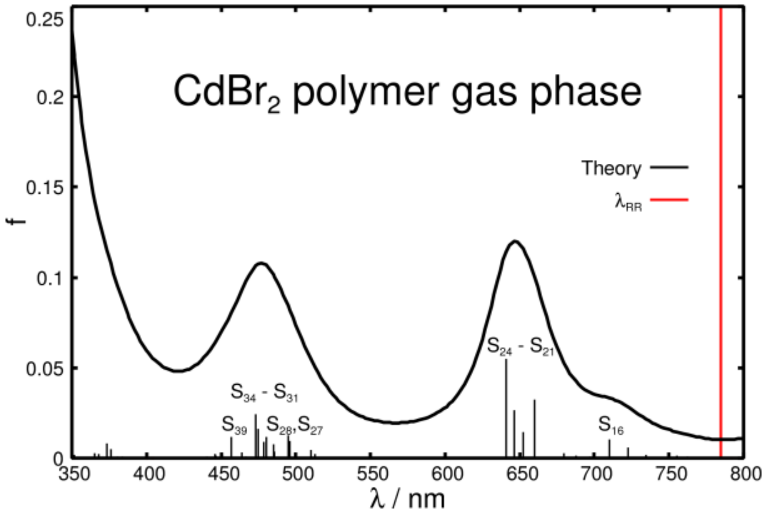
Assignment and comparison of the calculated vibrational frequencies (cm$^{-1}$) and relative Raman activities (Å$^4 amu^{-1}$) for the iron(II) sulfate cross-linked metallopolymer as well as its semi-decomplexated form obtained at the B3LYP15/6-31G(d), B3LYP15/6-311G(d), and B3LYP/6-31G(d) levels of theory.

## Figure S11



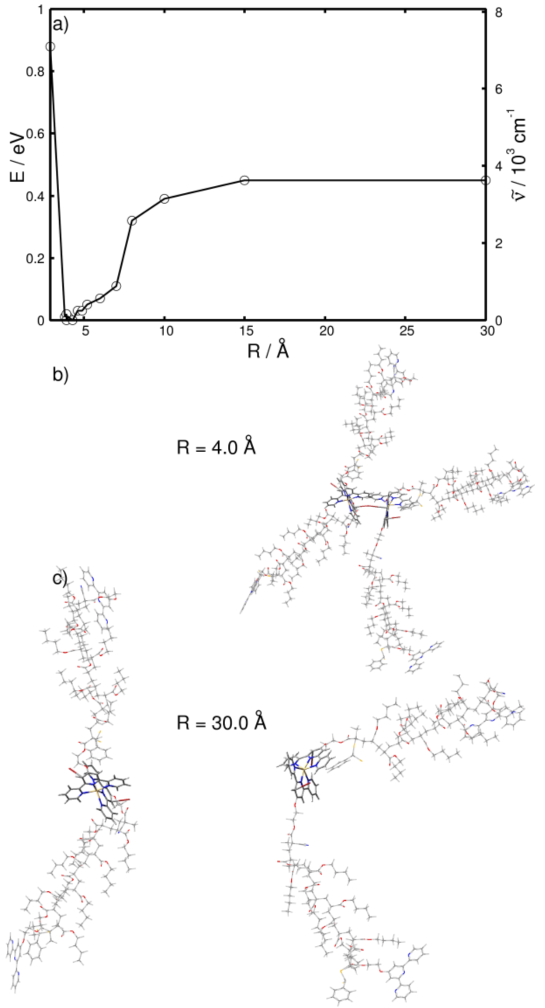
Raman spectra of the cadmium(II) bromide metallopolymer. a) depicts temperature-dependent Raman spectra at 23 and 100 °C along with the thermally induced bathochromic shifts of the intensity pattern. b) and c) display calculated Raman spectra at the QM/MM level of theory using B3LYP/6-31G(d) and B3LYP(15)/6-311G(d), respectively, and the universal force field the polymer models. Vibrational modes centered at the *bis*terpyridine-cadmium(II) complex are shown in red and modes of the free terminal terpyridine moieties are shown in blue.

## Figure S12



Simulated UV-vis spectrum of the cadmium(II) bromide metallopolymer in the gas phase performed at the QM/MM level of theory using TD-B3LYP(15) with the 6-31G(d) basis set and the UFF; the red line corresponds to excitation wavelength used in the Raman measurements.

## Figure S13



Calculation of the relaxed PES of the cadmium(II) bromide metallopolymer at the QM/MM level of theory using B3LYP(15) with the 6-31G(d) basis set and the universal force field with respect to the distance *R* describing the cleavage of the ionic cluster up to *R* = 30 Å. b) and c) depicts the global minimum of the PES (*R* = 4.0 Å) and the opened cluster at *R* = 30 Å in the orthogonal oriented conformation.