Supporting Information for

# Gallium(III) Tetraphenylporphyrinates Containing Hydrosulfide and Thiolate Ligands: Structural Models for Sulfur-Bound Iron(III) Hemes

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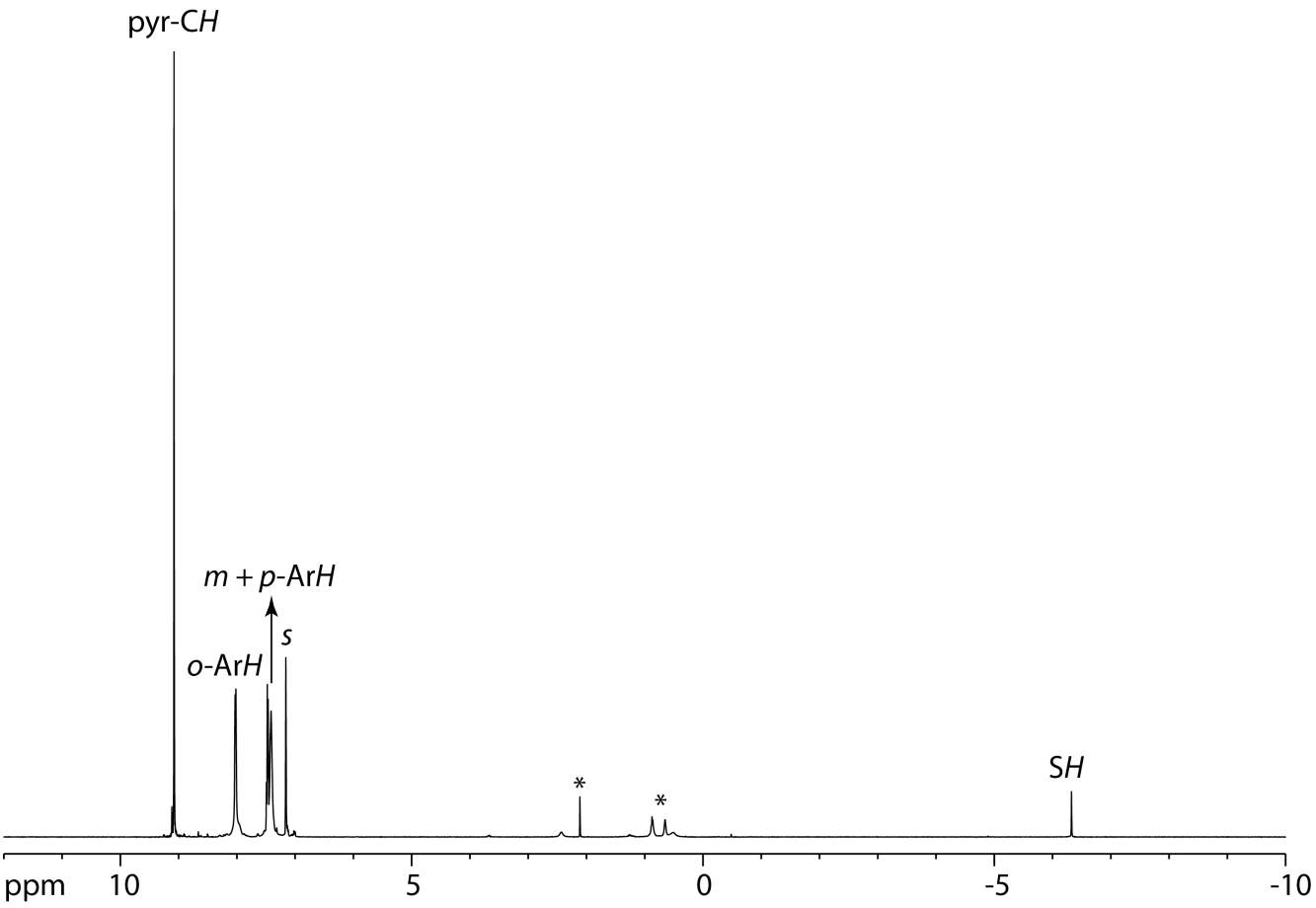


**Figure S1.** 500 MHz $^{1}$H NMR spectrum of [Ga(SH)(TPP)] in benzene-$d_6$ (*s*). Asterisks denote peaks due to residual toluene and pentane from recrystallization.

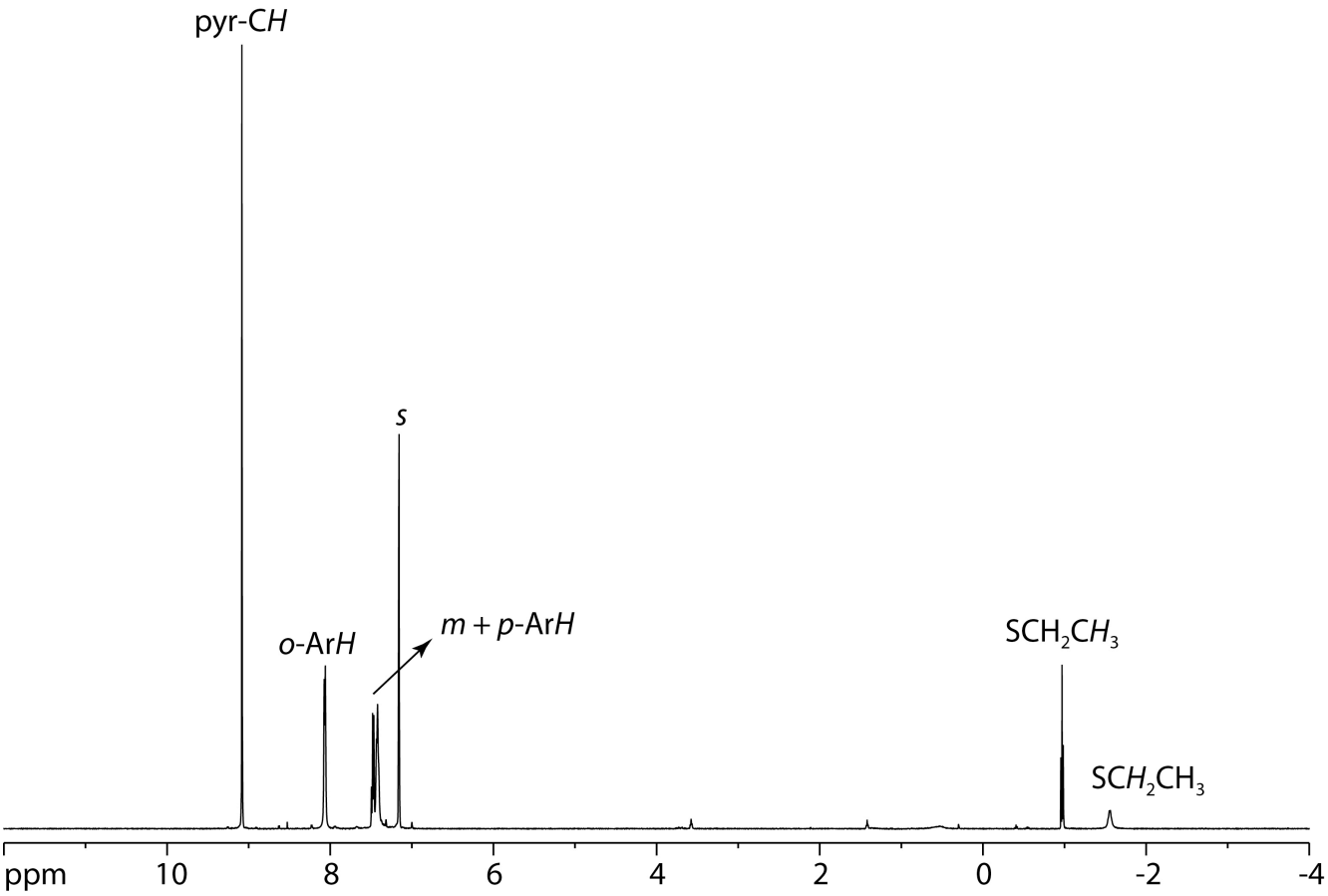


**Figure S2.** 500 MHz $^1$H NMR spectrum of [Ga(SEt)(TPP)] in benzene-$d_6$ (*s*).

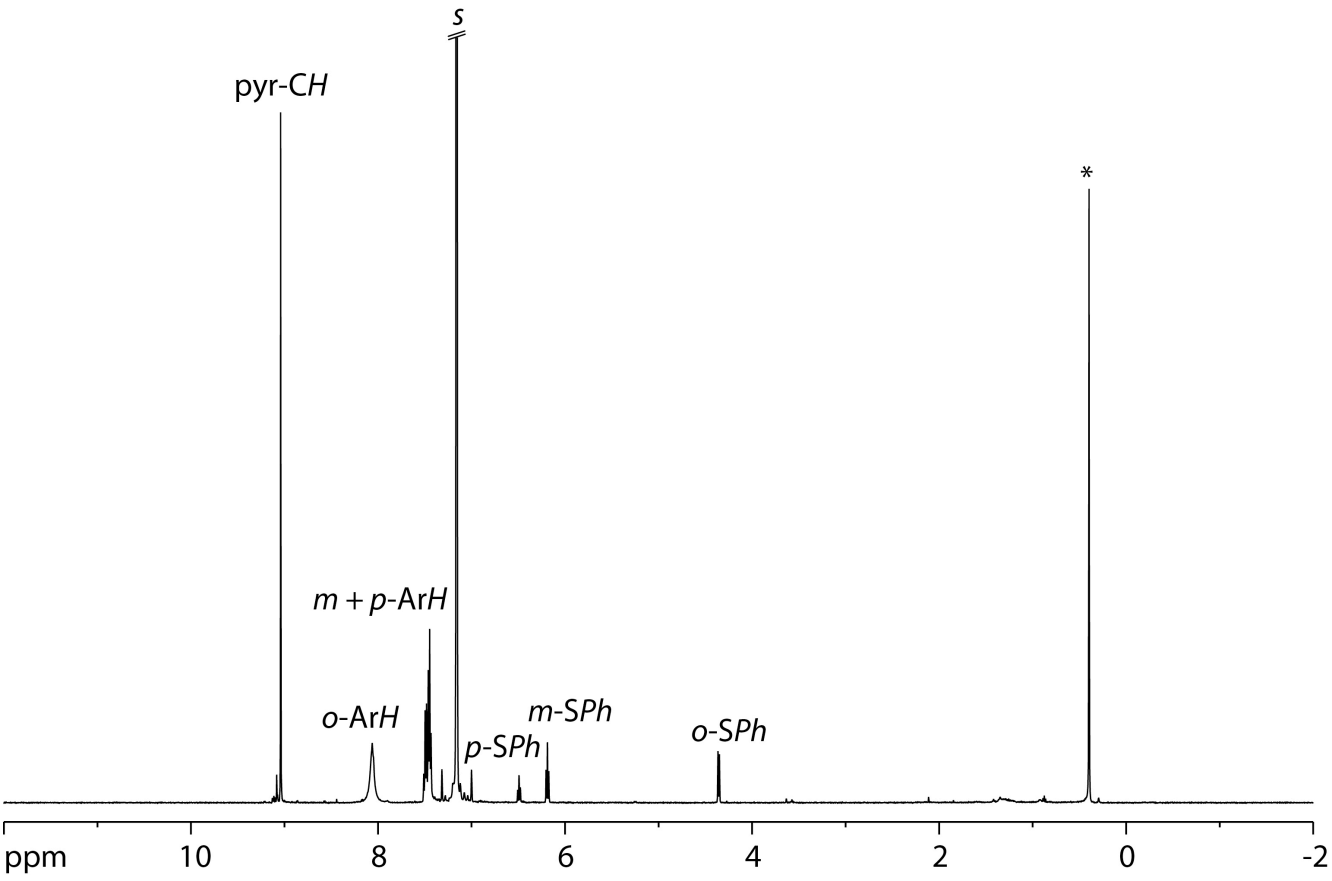


**Figure S3.** 500 MHz $^{1}$H NMR spectrum of [Ga(SPh)(TPP)] in benzene-$d_6$ (*s*). Asterisk denotes peak due to water from the NMR solvent.

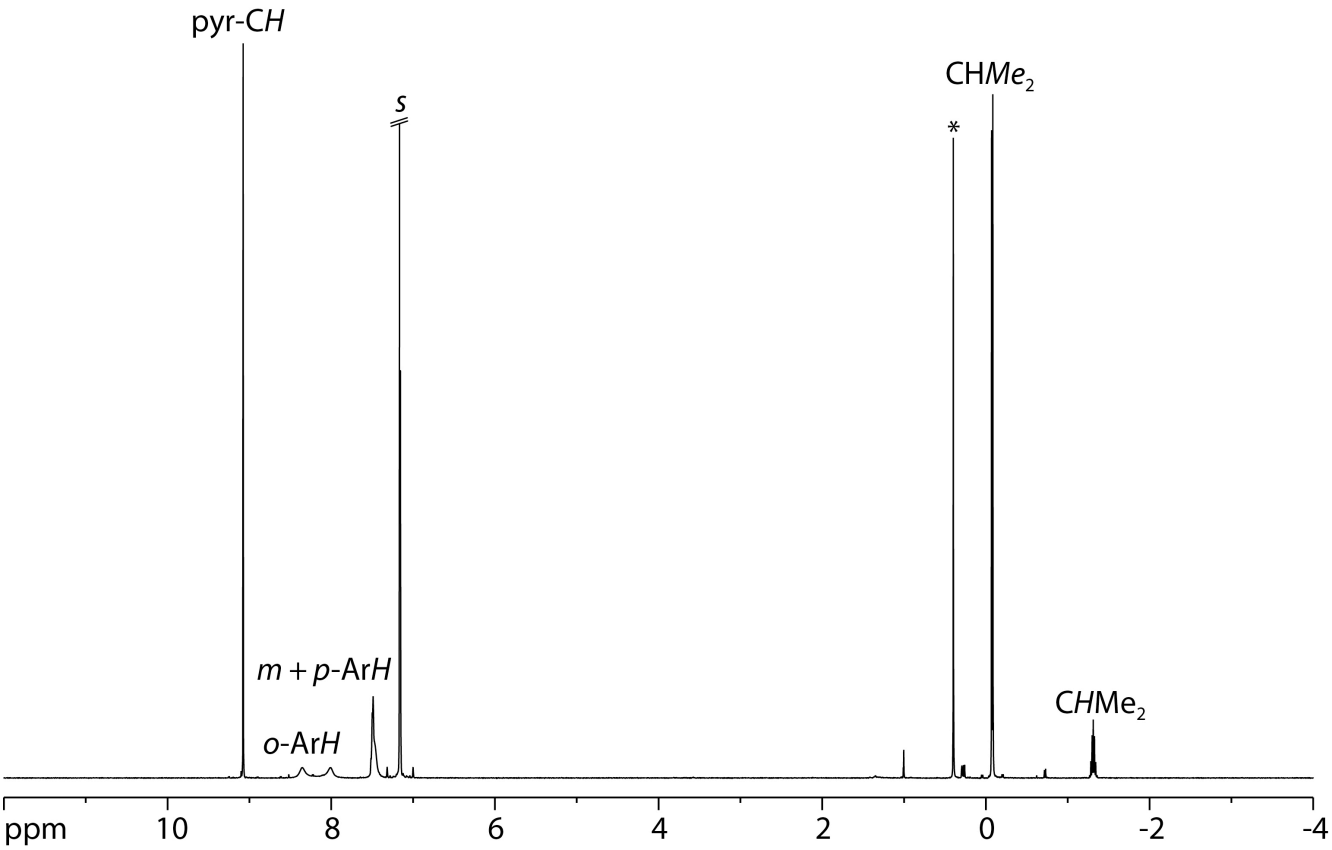


**Figure S4.** 500 MHz $^1$H NMR spectrum of [Ga(SSi$^i$Pr$_3$)(TPP)] in benzene-$d_6$ (*s*). Asterisk denotes peak due to water from the NMR solvent.

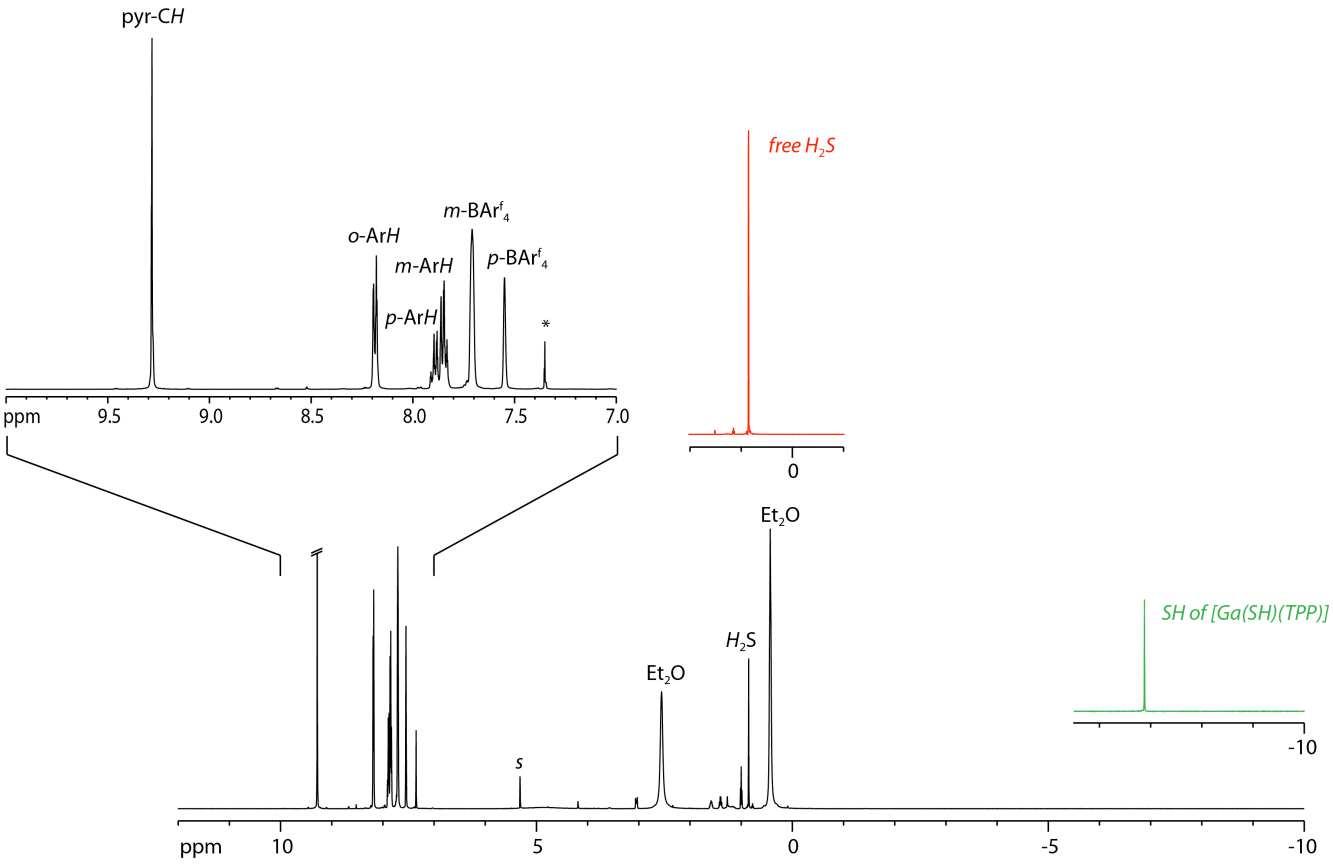


**Figure S5.** 500 MHz $^1$H NMR spectrum of the mixture obtained upon mixing [Ga(SH)(TPP)] with 1.5 equivalents of (H{$Et_2O$}$_2$)[B(3,5-{$CF_3$}$_2C_6H_3$)$_4$] ("HBAr$^f_4$") in dichloromethane-$d_2$ (*s*). Inset in black shows expansion of the aromatic region. Inset in red displays the spectrum of free $H_2S_{(g)}$ recorded in dichloromethane-$d_2$. Inset in green displays the upfield region of the spectrum for [Ga(SH)(TPP)] in dichloromethane-$d_2$ prior to addition of HBAr$^f_4$. Asterisk denotes small amount of benzene from purification.

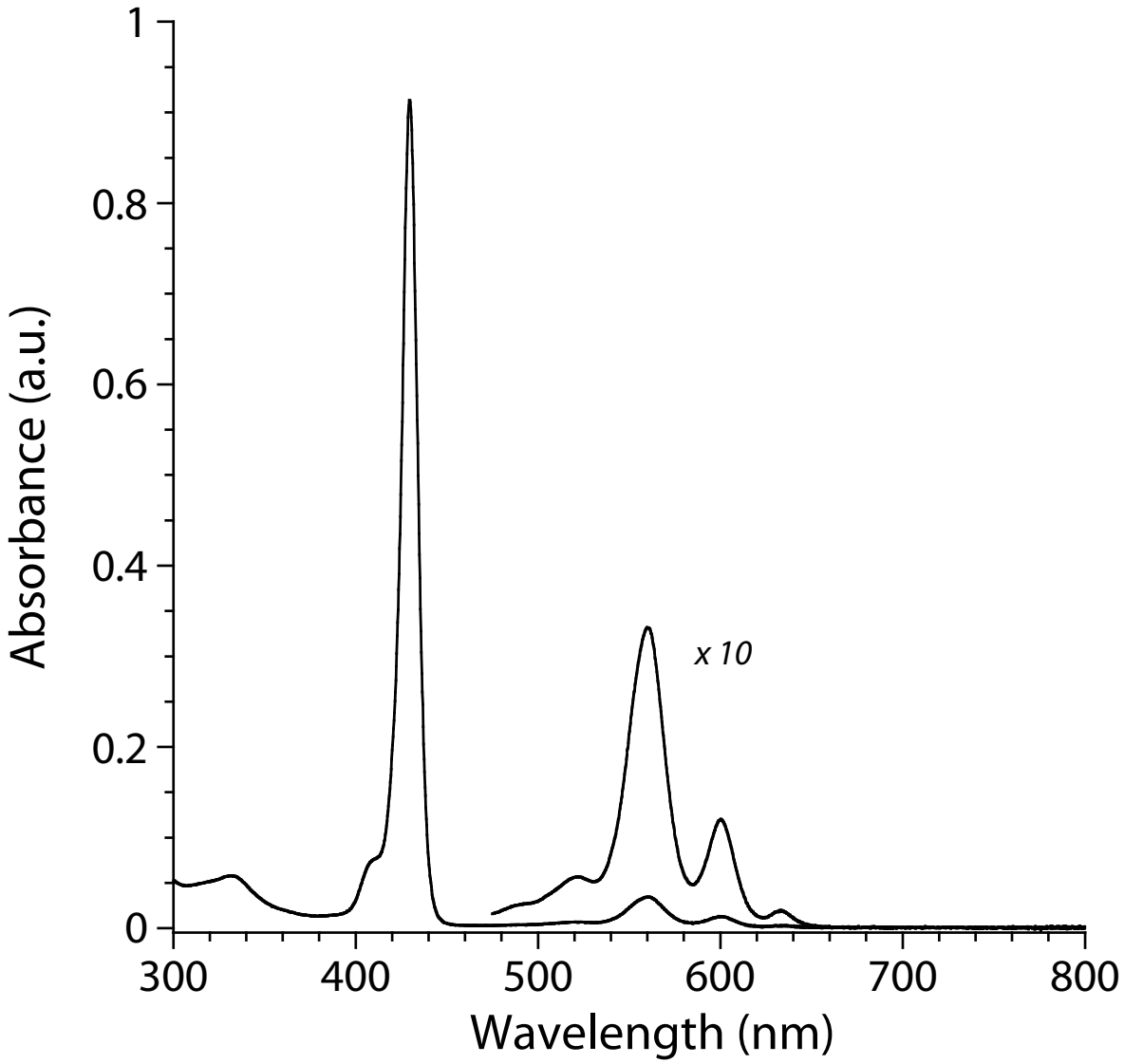


**Figure S6.** Electronic absorbance spectrum of [Ga(SH)(TPP)] in toluene.

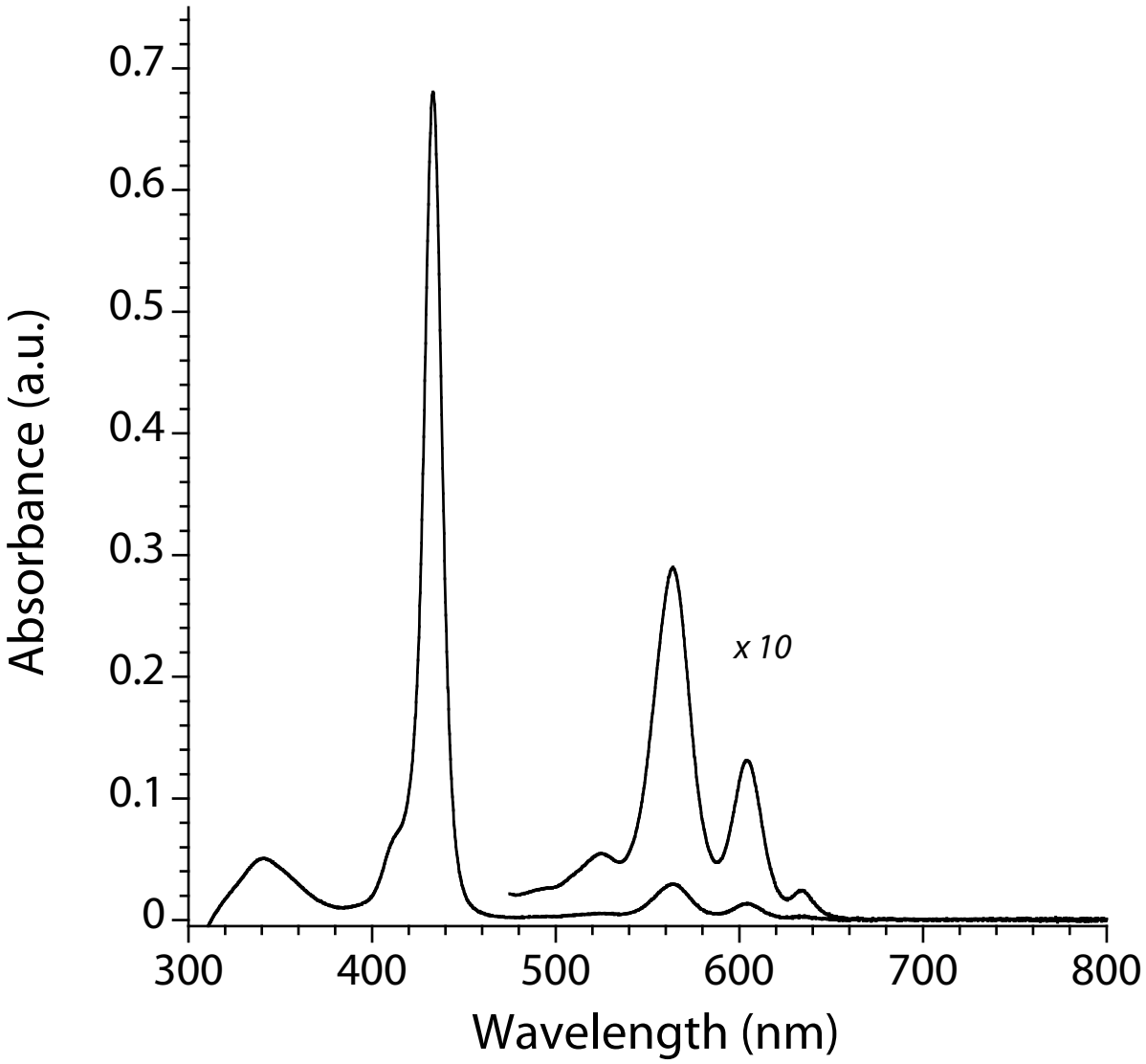


**Figure S7.** Electronic absorbance spectrum of [Ga(SEt)(TPP)] in toluene.

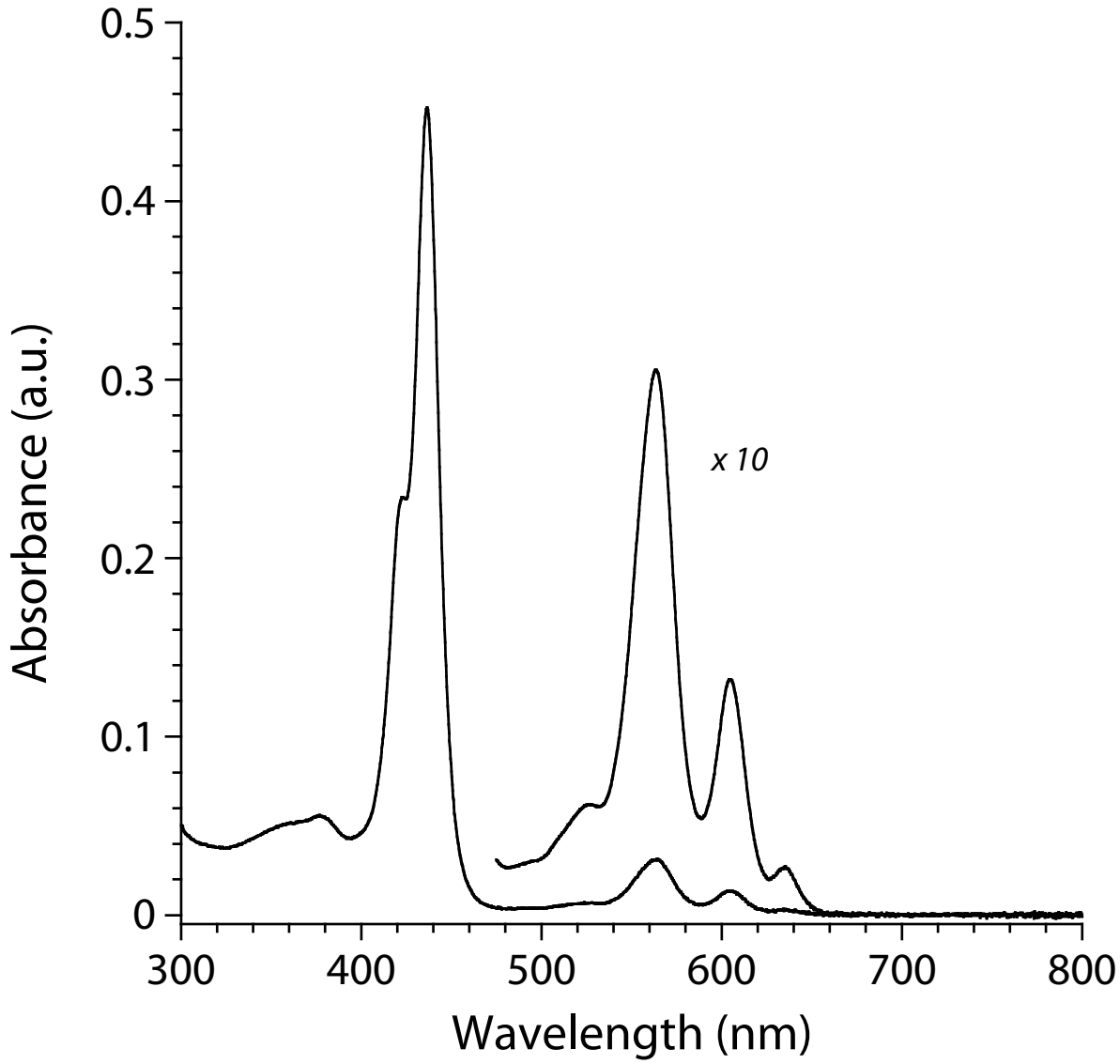


**Figure S8.** Electronic absorbance spectrum of [Ga(SPh)(TPP)] in toluene.

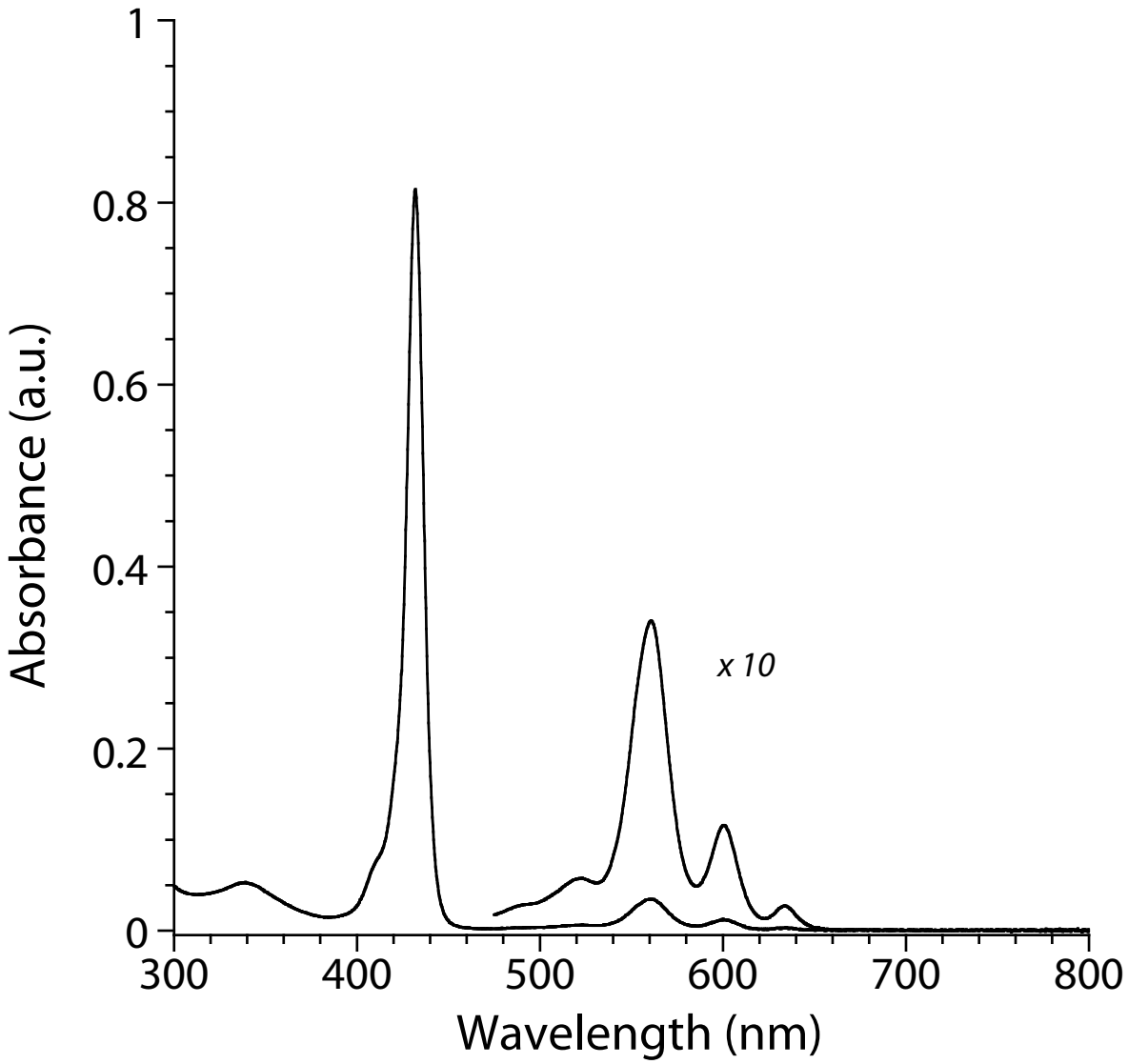


**Figure S9.** Electronic absorbance spectrum of [Ga(SSi$^{i}$Pr$_3$)(TPP)] in toluene.

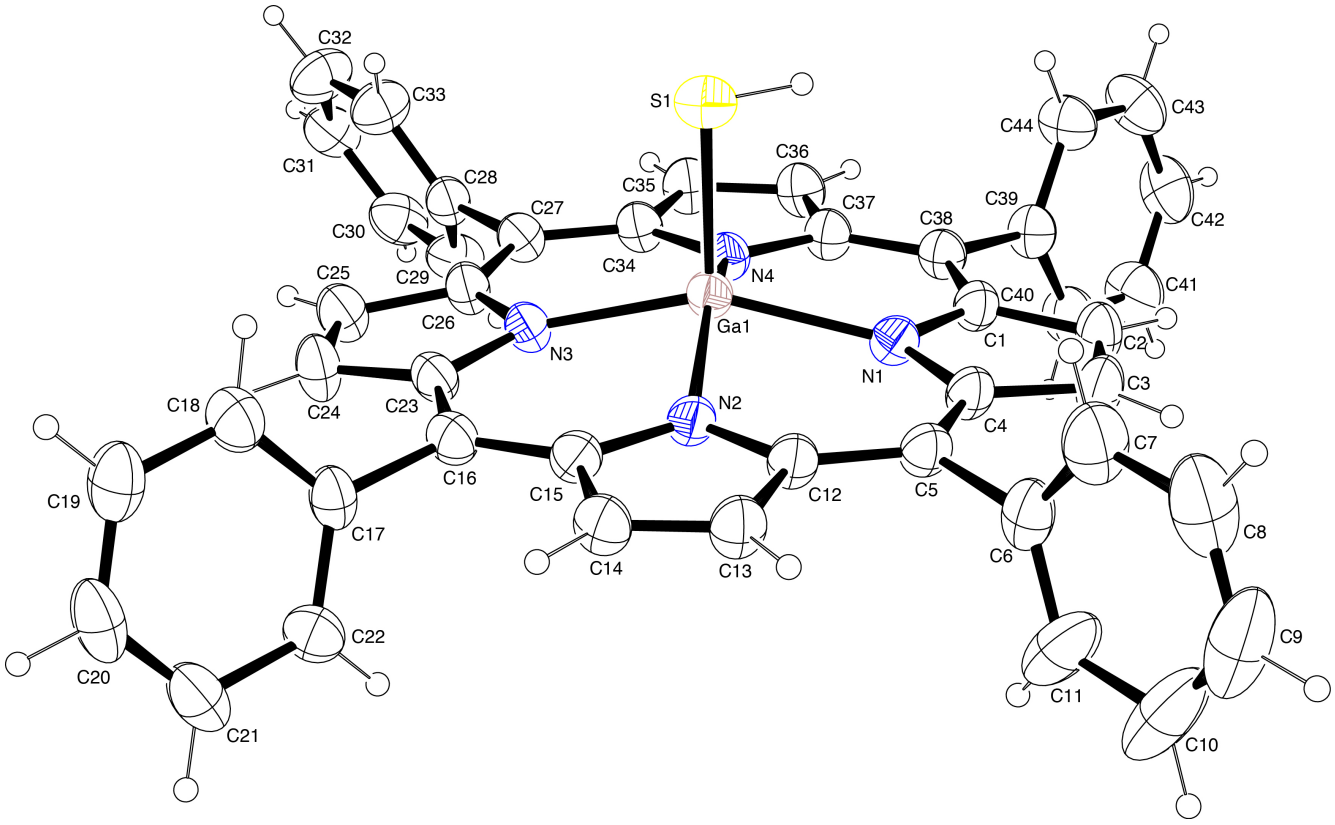


**Figure S10.** Thermal ellipsoid drawing (30%) of [Ga(SH)(TPP)].

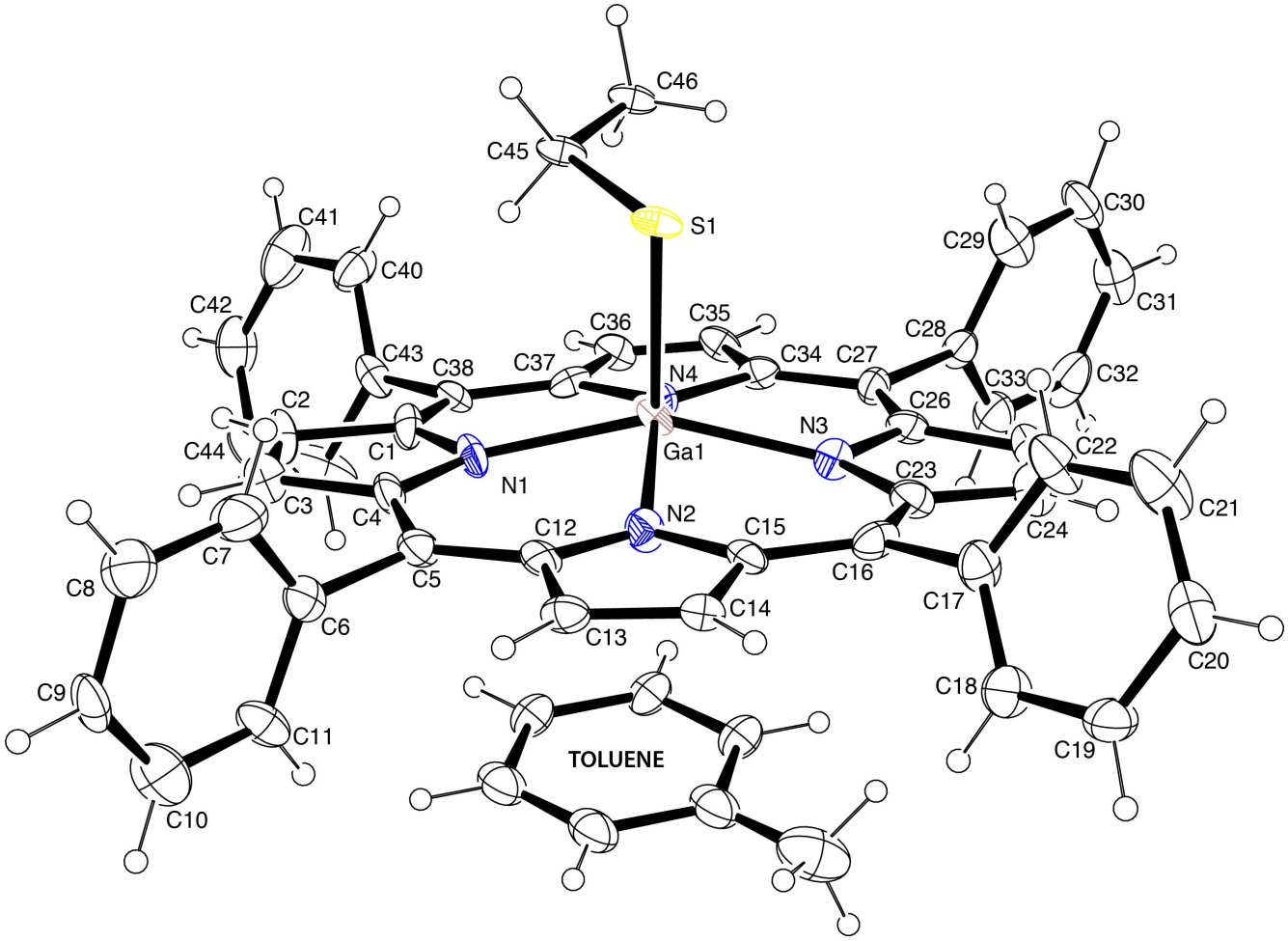


**Figure S11.** Thermal ellipsoid drawing (50%) of [Ga(SEt)(TPP)]·toluene. Minor components of the disorder omitted for clarity.

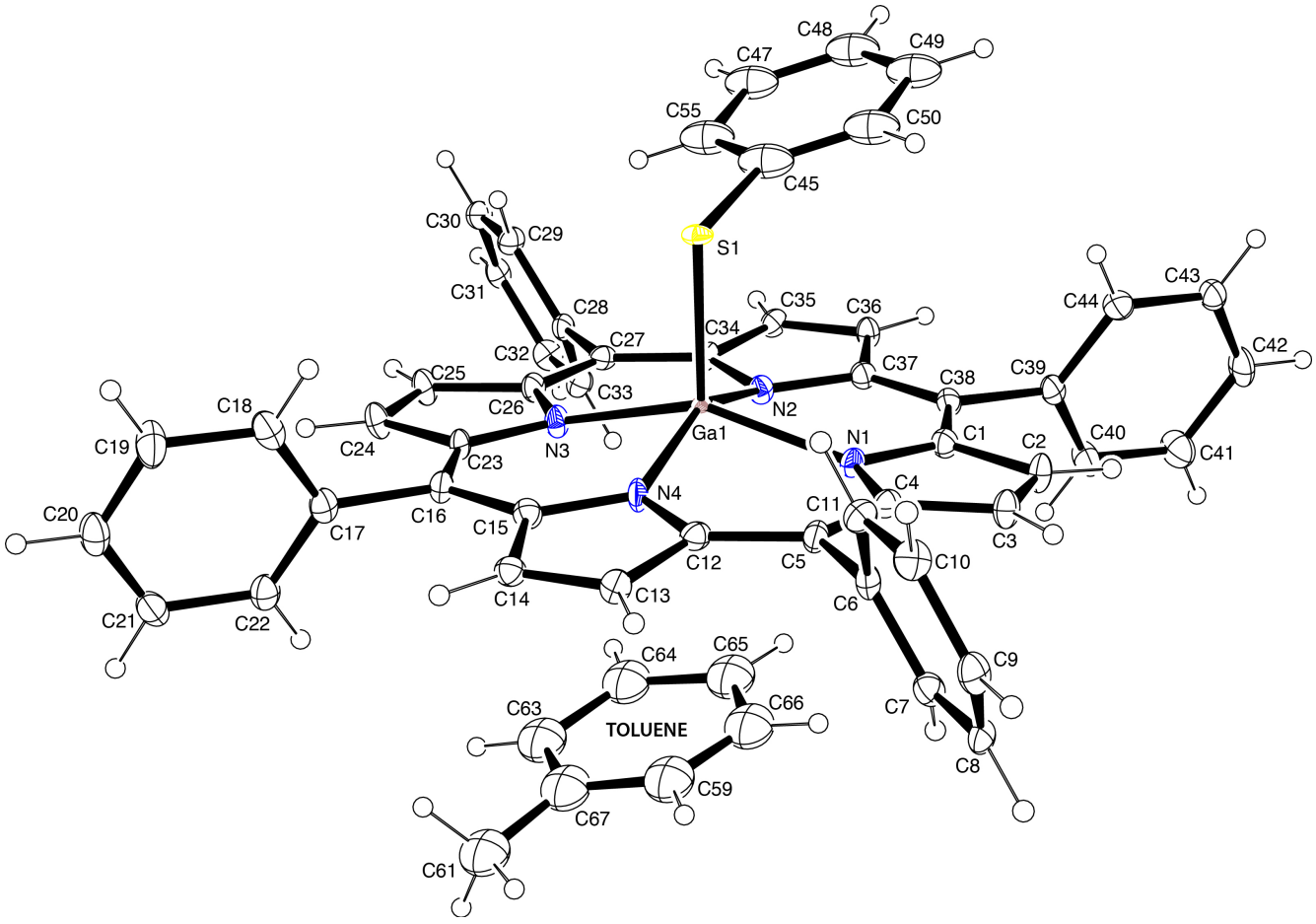


**Figure S12.** Thermal ellipsoid drawing (50%) of [Ga(SPh)(TPP)]·toluene. Minor components of the disorder omitted for clarity.

**Table S1.** Crystallographic data and refinement parameters for [Ga(SR)(TPP)].[§]

| **Compound** | [Ga(SH)(TPP)] | [Ga(SEt)(TPP)] | [Ga(SPh)(TPP)] |
|---|---|---|---|
| Empirical formula | $C_{44}H_{29}GaN_4S$ | $C_{46}H_{33}GaN_4S \cdot C_7H_8$ | $C_{50}H_{33}GaN_4S \cdot C_7H_8$ |
| Formula weight (g/mol) | 715.49 | 1112.14 | 883.75 |
| Temperature (K) | 293(2) | 98(2) | 98(2) |
| Crystal system, space group | Monoclinic, $P2_1/n$ | Monoclinic, $Pc$[a] | Triclinic, $P1$[b] |
| Unit cell dimensions (Å) | $a$ = 10.253(4)<br>$b$ = 16.179(7)<br>$c$ = 21.076(9)<br>$\beta$ = 90.460(11) | $a$ = 10.9029(19)<br>$b$ = 15.445(3)<br>$c$ = 12.296(2)<br>$\beta$ = 102.636(7) | $a$ = 10.4828(19)<br>$b$ = 11.1917(18)<br>$c$ = 11.492(2)<br>$\alpha$ = 109.728(8)<br>$\beta$ = 104.749(7)<br>$\gamma$ = 109.738(8) |
| Volume (Å$^3$) | 3496(3) | 2020.5(6) | 1086.3(3) |
| Z | 4 | 2 | 1 |
| Calculated density (g/cm$^3$) | 1.359 | 1.327 | 1.351 |
| Absorption coefficient (mm$^{-1}$) | 0.885 | 0.774 | 0.726 |
| F(000) | 1472 | 837 | 458 |
| Crystal size (mm) | 0.2 × 0.2 × 0.2 | 0.2 × 0.2 × 0.2 | 0.4 × 0.3 × 0.2 |
| Θ range | 2.202 to 25.050º | 3.116 to 24.550º | 3.050 to 25.048º |
| Limiting indices | $-12 \le h \le 7$,<br>$-19 \le k \le 9$,<br>$-22 \le l \le 25$ | $-11 \le h \le 12$,<br>$-18 \le k \le 17$,<br>$-14 \le l \le 13$ | $-12 \le h \le 12$,<br>$-13 \le k \le 13$,<br>$-13 \le l \le 13$ |
| Reflections collected / unique | 11910 / 6114<br>[$R_{int}$ = 0.0792] | 10559 / 5129<br>[$R_{int}$ = 0.0748] | 6839 / 5491<br>[$R_{int}$ = 0.0327] |
| Completeness to Θ | 98.9% | 99.6% | 99.8% |
| Absorption correction | multi-scan ABSCOR | multi-scan ABSCOR | multi-scan ABSCOR |
| Min. and max transmission | 0.506 and 1.000 | 0.311 and 0.910 | 0.797 and 1.000 |
| Data / restraints / parameters | 6114 / 0 / 454 | 5129 / 2 / 493 | 5491 / 3 / 529 |
| Goodness-of-fit on $F^2$ | 1.047 | 0.968 | 1.003 |
| Final R indices<br>[$I > 2\sigma(I)$] | $R_1$ = 0.0656,<br>$wR_2$ = 0.1323 | $R_1$ = 0.0951,<br>$wR_2$ = 0.2203 | $R_1$ = 0.0521,<br>$wR_2$ = 0.1277 |
| R indices (all data) | $R_1$ = 0.1050,<br>$wR_2$ = 0.1568 | $R_1$ = 0.0990,<br>$wR_2$ = 0.2233 | $R_1$ = 0.0538,<br>$wR_2$ = 0.1296 |
| Largest diff. peak and hole (e·Å$^{-3}$) | 0.416 and −0.395 | 0.702 and −0.784 | 0.795 and −0.774 |

[§]Refinement method was full-matrix least-squares on $F^2$; wavelength = 0.71073 Å. $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

[a]This molecule crystallizes in space group $P2_1/c$. However, due to disorder between the ethanethiolate and toluene molecules (70/30%) in the crystal lattice, the structure refined better in space group $Pc$.

[b]There is a positional disorder (65/35%) between benzenethiolate and a toluene molecule. Several attempts to transform the space group from $P1$ to $P\bar{1}$ resulted in an overall poor refinement of the structure. The structure refined the best in space group $P1$, however, the correct space group should be $P\bar{1}$.