

SUPPORTING INFORMATION ACCOMPANYING:

Gallium-containing conducting metallopolymers which display chemically tunable reactivity for the growth of Ga₂S₃ semiconducting nanoparticles

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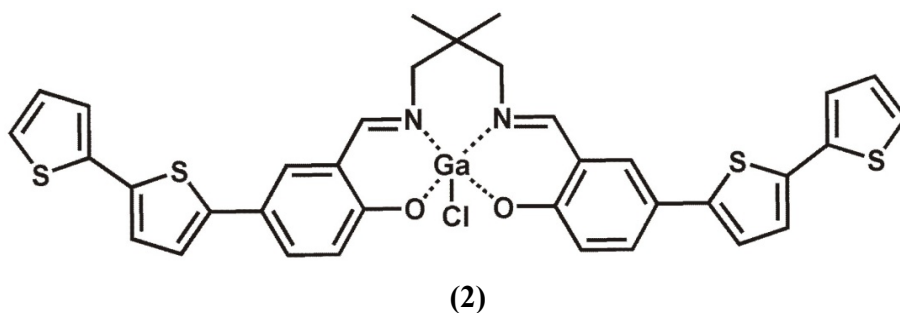
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General Methods

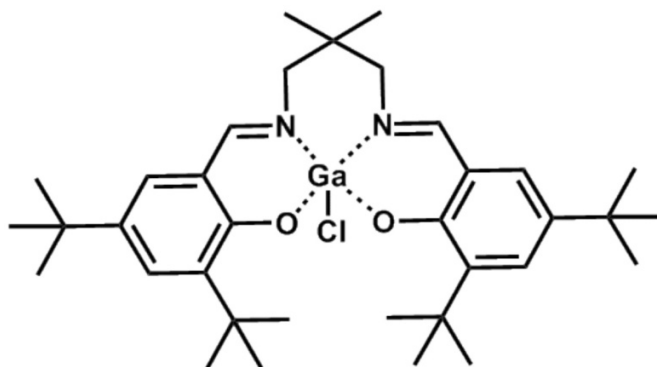
The ligands **1**¹ and **3**² were synthesized by following previously published synthetic routes. All solvents were dried using an Innovative Technology, Pure Solv solvent purifier with a double purifying column. All reactions were performed using standard Schlenk techniques. NMR spectra were recorded on a Mercury 400 MHz spectrometer (¹H, 400 MHz) and/or a Varian 300 Unity Plus spectrometer (¹H, 300 MHz). ¹H NMR signals are reported relative to residual solvent peaks. All NMR peaks are reported in ppm and coupling constants are reported in Hz. Elemental analyses were performed by QTI, Whitehouse, NJ (www.qtionline.com). Chemical ionization (CI) mass spectra were collected on a Micromass Autospec Ultima mass spectrometer. Infrared spectra were recorded using a Nicolet IR 200 FTIR spectrophotometer. X-ray photoelectron spectroscopy (XPS) was carried out on a PHI 5700 XPS system equipped with a dual Mg X-ray source and monochromatic Al X-ray source complete with depth profile and angle-resolved capabilities.

Synthesis of **2**, **4**, **5**, and **6**.



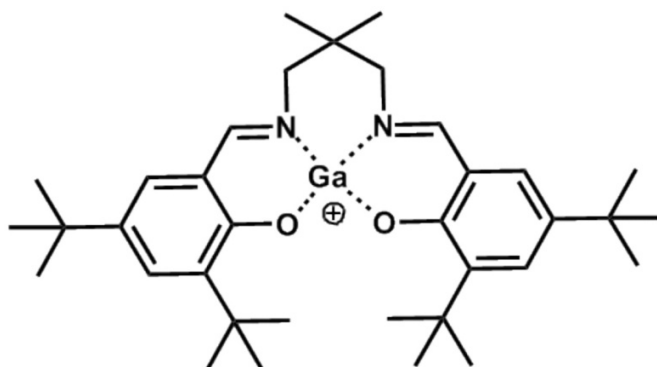
(2) A solution of the **1** (0.250 g, 0.32 mmol) in THF (20 mL) was added to a slurry of NaH (0.019 g, 0.78 mmol) in THF. The mixture was stirred at room temperature for 12 h. Filtration through Celite gave a clear yellow solution, which was then added slowly to a solution of GaCl₃ (0.069 g, 0.32 mmol) in THF (10 mL). After stirring overnight, the mixture was once more filtered through Celite and all volatiles were removed under reduced pressure to afford the crude material as a yellow powder (0.230 g, 0.30 mmol, 97%). Recrystallization from CH₂Cl₂ / *n*-hexane by slow diffusion resulted in a crop of orange block crystals which were suitable for X-ray diffraction studies. dec. 268-271 °C. ¹H NMR (CDCl₃): 8.28 (s, 2H), 7.69 (d, *J* = 2.1, 2H), 7.53 (d, *J* = 2.1, 2H), 7.28 (m, 2H), 7.23 (m, 2H), 7.17 (m, 4H), 7.06-7.09 (m, 4H), 4.06 (d, *J* = 12.9, 2H), 3.40 (d, *J* = 12.9, 2H), 1.22 (s, 3H), 1.09 (s, 3H). ¹³C {¹H} NMR is not reported due to

solubility. UV-Vis (λ_{\max} (ϵ), CH_2Cl_2): 354 nm ($74,200 \text{ cm}^{-1}\text{M}^{-1}$). MS (Cl^+ m/z): 741 [M^+], HRMS (Cl^+ CH_4) calcd. for $\text{C}_{35}\text{H}_{28}\text{GaN}_2\text{O}_2\text{S}_4\text{Cl}$ 741.0056, found 741.0054. Elemental analysis calculated (found): C, 56.65 (56.13); H, 3.80 (3.76); N 3.78 (3.56).



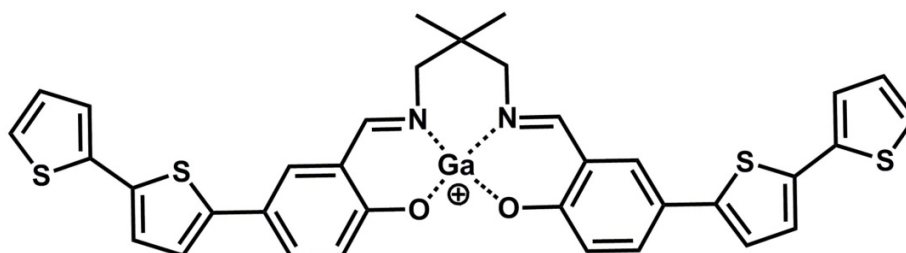
(4)

(4) To a solution of **3** (1.00 g, 1.87 mmol) in THF (50 mL) was added a suspension of KH (0.150 g, 3.74 mmol) in THF (50 mL) at room temperature. The reaction mixture was allowed to stir for 12 h, then transferred into a solution of GaCl_3 in THF. This reaction was stirred for 12 h at room temperature, the solvent was then removed to give a pale yellow powder (1.04 g, 90%). dec. 274-277 °C. ^1H NMR (CDCl_3): 8.17 (s, 2H), 7.51 (d, $J = 2.7$, 2H), 6.98 (d, $J = 2.4$, 2H), 3.66 (d, $J = 12.6$, 2H), 3.35 (d, $J = 12.3$, 2H), 1.50 (s, 18H), 1.28 (s, 18H), 1.08 (s, 3H), 1.03 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2): 170, 163, 139, 136, 129, 127, 114, 65, 34, 33, 32, 28, 27, 23. UV-Vis (λ_{\max} (ϵ), CH_2Cl_2): 289 nm ($20,500 \text{ cm}^{-1}\text{M}^{-1}$). MS (Cl^+ m/z): 637 [$\text{M}+\text{H}$]. HRMS (Cl^+ CH_4): calcd. For $\text{C}_{35}\text{H}_{52}\text{GaN}_2\text{O}_2\text{Cl}$: 636.2973. Found: 636.2976. Elemental analysis calculated (found): C, 62.70(62.91); H, 8.69(8.06); N, 3.18(4.37).



(5)

(5) To a solution of **4** (1.00 g, 1.87 mmol) in DCM:ACN (1:1) was added one portion of $\text{KB}(\text{ArF})_4$. The reaction mixture was stirred at room temperature for 12 hr, then filtered. The solution was removed in vacuo to give a yellow solid (0.94 g, 80%). ^1H NMR (CDCl_3): 8.54 (s, 2H), 7.66 (d, $J = 2.4$, 2H), 7.42 (d, $J = 2.4$, 2H), 3.76 (s, 4H), 1.47 (s, 18H), 1.36 (s, 18H), 1.24 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2): 170, 157, 143, 137, 132, 131, 129, 116, 64, 36, 34, 30, 29, 23. MS (Cl^+ , CH_4): m/z 602 (M+H). HRMS (CI) m/z calculated for $\text{C}_{35}\text{H}_{52}\text{O}_2\text{S}_2\text{N}_2\text{Ga}$ 601.3285, found 601.3283. Elemental analysis calculated (found): C, 52.91(52.33); H, 4.08(4.12); N, 2.99(2.10).



(6)

(6) In an amber vial inside a glove box, **2** (0.20 g, 0.27 mmol) was dissolved in the minimum amount of methylene chloride and acetonitrile (25 mL, 1:1). To this solution was added $\text{KB}(\text{ArF})_4$ (0.194 g, 0.27 mmol) and the resulting mixture was stirred overnight, filtered through Celite and all volatiles removed under reduced pressure, giving the product as a red powder (0.233 g, 0.048 mmol, 96%). ^1H NMR (CDCl_3): 8.45 (s, 2H), 8.01 (d, $J = 8.1$, 2H), 7.74 (s, 2H), 7.05-7.31 (m, 8H), 7.07 (m, 4H), 3.87 (s, 4H), 1.22 (s, 3H), 1.40 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR is not

reported due to solubility. MS (Cl^+ m/z) (%): 705 (MH^+). HRMS (Cl^+ CH_4) calcd. for $\text{C}_{35}\text{H}_{28}\text{GaN}_2\text{O}_2\text{S}_4$ 705.0289, found 705.0284. Elemental analysis calculated (found): C, 45.68 (45.16); H, 2.31 (2.43); N 1.69 (1.59).

Ga₂S₃ Nanoparticle Growth

The electropolymerized thin films were treated with a saturated solution of H_2S in DCM for two minutes then rinsed thoroughly with dry DCM. The film was then treated with a solution of $\text{Ga}(\text{NO}_3)_3$ in MeOH (2.02×10^{-3} M) for two minutes followed by rinsing with DCM. The film is once again treated with a solution of H_2S in DCM followed by rinsing once more with DCM. This process constitutes one iteration of the growth process that was repeated up to four times.

Transmission Electron Microscopy

TEM experiments were carried out on JEOL 2010F microscope. Films were grown electrochemically onto carbon coated gold grids purchased from Electron Microscopy Sciences. Films were made by electropolymerization of **2** and **6** by cycling between -0.5 V and 1.5 V ten times. Films were kept in an air free environment and nanoparticles were grown directly onto the grid. After rinsing the film with DCM, the films were observed under the microscope. Analysis of the nanoparticles was done using Gatan Digital Micrograph software. Size distribution data is reported for 100-115 particles per size.

Crystal Structure Determination

Data were collected on a Nonius Kappa CCD diffractometer with graphite monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073$ Å) at 153 K. Absorption corrections were applied using GAUSSIAN. The structures were solved by direct methods and refined anisotropically using full-matrix least-squares methods with the SHELX 97 program package.³ The coordinates of the non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included in the calculation isotropically but not refined. Neutral atom scattering factors were taken from Cromer and Waber.⁴ The crystallographic data and structure refinement for complex **2** are listed in Table S1. Selected bond lengths and angles for **2** are given in Table S2. The crystallographic data and structure refinement for complex **4** are listed in Table S3. Selected bond lengths and angles for **4** are given in Table S4.

Electrochemistry

Electrochemical polymerizations were all done under a nitrogen atmosphere in a dry-box using a GPES system from Eco. Chemie B. V.. The electrolyte used was 0.1 M tetrabutylammonium hexafluorophosphate [(*n*-Bu)₄N][PF₆] (TBAPF₆) which was purified through recrystallization three times from hot ethanol then dried for 3 days at 100 °C under active vacuum.

Electrochemical experiments were carried out in a three-electrode cell with a Ag/AgNO₃ non-aqueous reference electrode, a Pt button working electrode (1.6 mm diameter), and a Pt wire coil counter electrode. To calibrate the reference electrode, Ferrocene was used as an external reference to which potentials were corrected. Films were electropolymerized with a 2×10^{-4} M monomer solution by cycling between -0.5 V and 1.5 V at $\nu = 100 \text{ mV s}^{-1}$.

Film Thickness

Film thickness was determined using a Veeco Dektak Profilometer. Films were prepared on ITO coated glass that was first treated by successive sonication in deionized water, ethanol, acetone, and methylene chloride. Electropolymerization was done as previously described for 20 cycles at a scan rate of 100 mV/s. Thickness measurements are reported as an average of twelve measurements taken on two films.

| | # of scans | Thickness (t) |
|---------------|------------|---------------|
| Poly-2 | 20 | 1703 ± 41 nm |
| Poly-6 | 20 | 934 ± 23 nm |

Table S1. Crystal data and structure refinement of **2**.

| | | |
|-----------------------------------|---|-----------------|
| Empirical formula | C ₃₇ H ₃₂ Cl ₅ Ga N ₂ O ₂ S ₄ | |
| Formula weight | 911.86 | |
| Temperature | 153(2) K | |
| Wavelength | 0.71069 Å | |
| Crystal system | Triclinic | |
| Space group | p-1 | |
| Unit cell dimensions | a = 9.418(5) Å | α = 92.035(5)°. |
| | b = 13.039(5) Å | β = 97.726(5)°. |
| | c = 17.289(5) Å | γ = 97.726(5)°. |
| Volume | 2081.6(15) Å ³ | |
| Z | 2 | |
| Density (calculated) | 1.455 Mg/m ³ | |
| Absorption coefficient | 1.217 mm ⁻¹ | |
| F(000) | 928 | |
| Crystal size | 0.20 x 0.15 x 0.08 mm ³ | |
| Theta range for data collection | 1.92 to 27.50°. | |
| Index ranges | -11 ≤ h ≤ 12, -16 ≤ k ≤ 15, -22 ≤ l ≤ 21 | |
| Reflections collected | 12554 | |
| Independent reflections | 8199 [R(int) = 0.0288] | |
| Completeness to theta = 27.50° | 85.7 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.907 and 0.803 | |
| Refinement method | Full-matrix least-squares on F ² | |
| Data / restraints / parameters | 8199 / 0 / 469 | |
| Goodness-of-fit on F ² | 1.020 | |
| Final R indices [I > 2σ(I)] | R1 = 0.0480, wR2 = 0.1145 | |
| R indices (all data) | R1 = 0.0762, wR2 = 0.1326 | |
| Largest diff. peak and hole | 0.649 and -0.818 e.Å ⁻³ | |

Table S2. Selected bond lengths (Å) and angles (deg) of **2**.

| Bond distances (Å) | | | |
|---------------------------|------------|------------------|------------|
| N(1)-Ga(1) | 2.031(3) | | |
| N(2)-Ga(1) | 1.994(3) | | |
| O(1)-Ga(1) | 1.841(2) | | |
| O(2)-Ga(1) | 1.937(2) | | |
| Cl(1)-Ga(1) | 2.4436(13) | | |
| Bond angles (°) | | | |
| C(6)-N(1)-Ga(1) | 126.3(2) | O(2)-Ga(1)-N(2) | 80.41(10) |
| C(2)-N(1)-Ga(1) | 114.1(2) | O(1)-Ga(1)-N(1) | 90.64(11) |
| C(13)-N(2)-Ga(1) | 127.4(2) | O(2)-Ga(1)-N(1) | 170.40(11) |
| C(3)-N(2)-Ga(1) | 115.0(3) | N(2)-Ga(1)-N(1) | 92.80(11) |
| C(8)-O(1)-Ga(1) | 130.7(2) | O(1)-Ga(1)-Cl(1) | 118.78(9) |
| C(15)-O(2)-Ga(1) | 126.7(2) | O(2)-Ga(1)-Cl(1) | 104.35(8) |
| O(1)-Ga(1)-O(2) | 87.65(10) | N(2)-Ga(1)-Cl(1) | 116.92(9) |
| O(1)-Ga(1)-N(2) | 124.27(12) | N(1)-Ga(1)-Cl(1) | 84.74(9) |

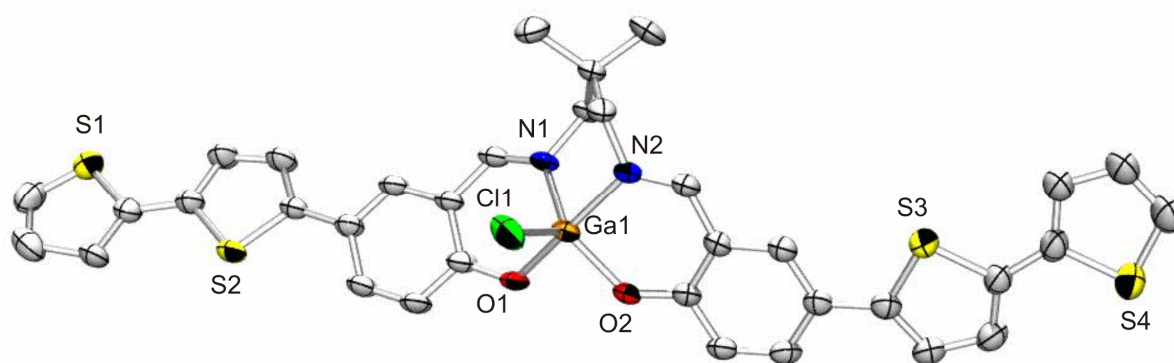


Figure S1. A view of the molecular structure of **2**. H atoms and solvent molecules have been omitted for clarity and thermal ellipsoids drawn at the 50% probability level.

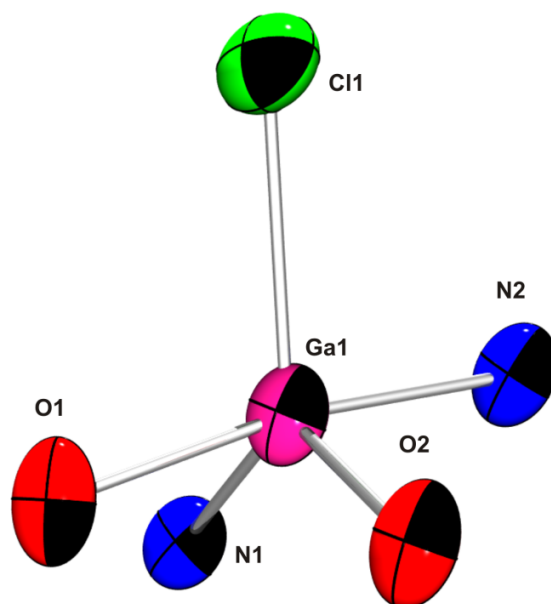


Figure S2. View of the coordination around the Ga center in **2**.

Table S3. Crystal data and structure refinement for 4.

| | | |
|-----------------------------------|---|----------|
| Empirical formula | C ₃₅ H ₅₂ Cl Ga N ₂ O ₂ | |
| Formula weight | 637.96 | |
| Temperature | 153(2) K | |
| Wavelength | 0.71069 Å | |
| Crystal system | Orthorhombic | |
| Space group | P b c a | |
| Unit cell dimensions | a = 12.1280(2) Å | a = 90°. |
| | b = 22.6490(3) Å | b = 90°. |
| | c = 25.8340(5) Å | g = 90°. |
| Volume | 7096.3(2) Å ³ | |
| Z | 8 | |
| Density (calculated) | 1.194 Mg/m ³ | |
| Absorption coefficient | 0.881 mm ⁻¹ | |
| F(000) | 2720 | |
| Crystal size | 0.21 x 0.18 x 0.18 mm ³ | |
| Theta range for data collection | 2.30 to 27.46°. | |
| Index ranges | -15<=h<=15, -29<=k<=29, -33<=l<=33 | |
| Reflections collected | 15270 | |
| Independent reflections | 8090 [R(int) = 0.0466] | |
| Completeness to theta = 27.46° | 99.6 % | |
| Max. and min. transmission | 0.8575 and 0.8366 | |
| Refinement method | Full-matrix least-squares on F ² | |
| Data / restraints / parameters | 8090 / 246 / 384 | |
| Goodness-of-fit on F ² | 0.740 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0437, wR2 = 0.1051 | |
| R indices (all data) | R1 = 0.0864, wR2 = 0.1396 | |
| Largest diff. peak and hole | 0.587 and -0.728 e.Å ⁻³ | |

Table S4. Bond lengths [\AA] and angles [$^\circ$] for **4**.

| | |
|------------------|------------|
| C(21)-N(2) | 1.295(4) |
| C(27)-O(2) | 1.321(3) |
| N(1)-Ga(1) | 2.063(2) |
| N(2)-Ga(1) | 2.001(2) |
| O(1)-Ga(1) | 1.844(2) |
| O(2)-Ga(1) | 1.9103(18) |
| Cl(1)-Ga(1) | 2.2135(8) |
| | |
| C(6)-N(1)-C(4) | 120.4(2) |
| C(6)-N(1)-Ga(1) | 125.14(18) |
| C(4)-N(1)-Ga(1) | 114.41(18) |
| C(21)-N(2)-C(5) | 119.0(2) |
| C(21)-N(2)-Ga(1) | 121.38(18) |
| C(5)-N(2)-Ga(1) | 119.61(18) |
| C(12)-O(1)-Ga(1) | 132.85(18) |
| C(27)-O(2)-Ga(1) | 122.21(16) |
| O(1)-Ga(1)-O(2) | 86.92(8) |
| O(1)-Ga(1)-N(2) | 126.36(10) |
| O(2)-Ga(1)-N(2) | 88.95(8) |
| O(1)-Ga(1)-N(1) | 89.41(9) |
| O(2)-Ga(1)-N(1) | 169.67(9) |
| N(2)-Ga(1)-N(1) | 85.46(9) |
| O(1)-Ga(1)-Cl(1) | 120.75(7) |
| O(2)-Ga(1)-Cl(1) | 96.16(6) |
| N(2)-Ga(1)-Cl(1) | 112.87(7) |
| N(1)-Ga(1)-Cl(1) | 94.01(7) |

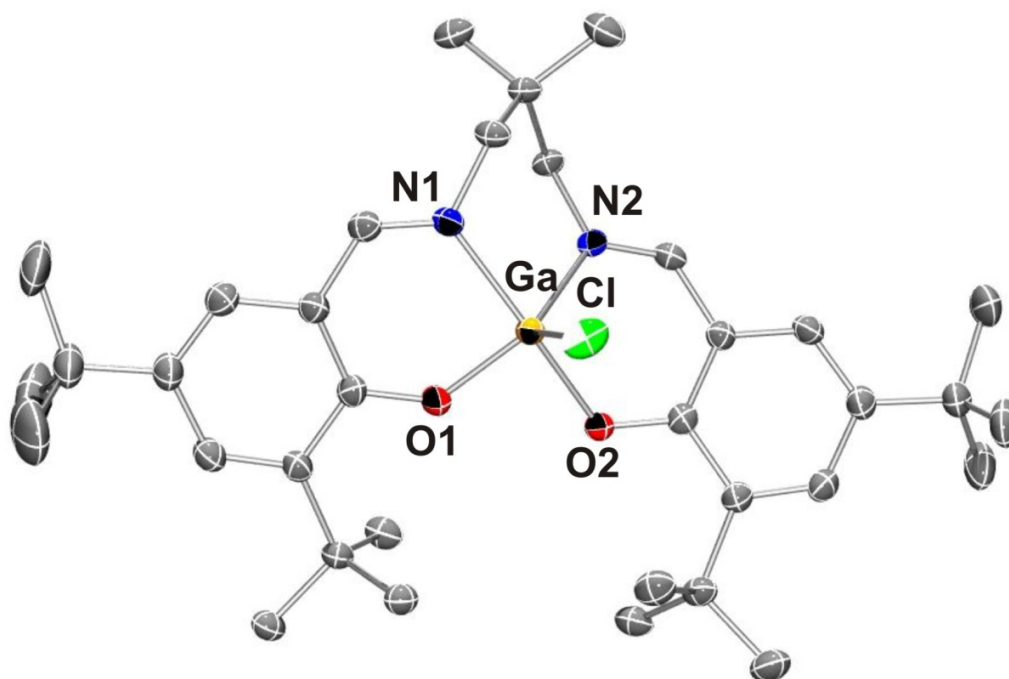


Figure S3. A view of the molecular structure of **4**. H atoms have been omitted for clarity and thermal ellipsoids drawn at the 50% probability level.

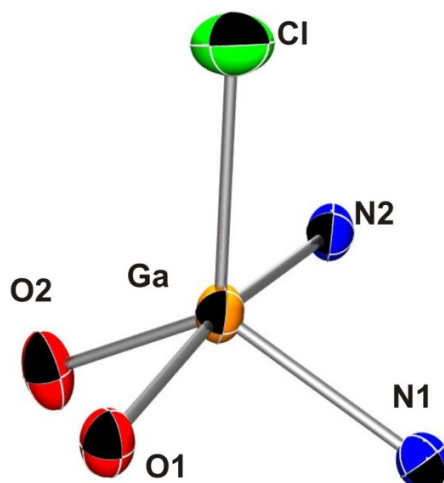


Figure S4. View of the coordination around the Ga center in **4**.

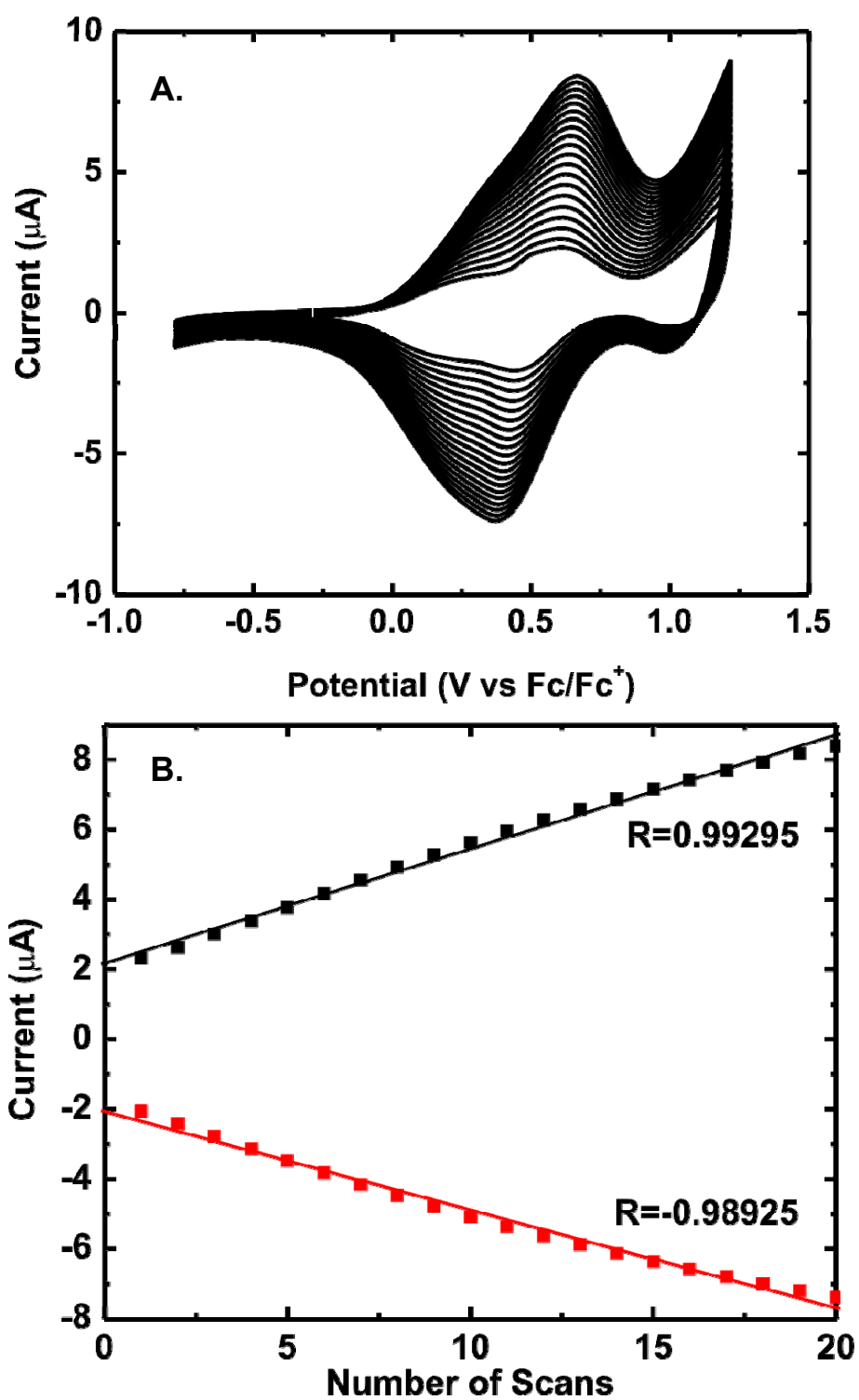


Figure S5. A. Electropolymerization of a 2×10^{-4} M CH_2Cl_2 solution of 2, 0.1 M TBAPF₆, Pt button (1.6 mm) electrode. B. The oxidative (black) and reductive (red) peak current versus the number of scans.

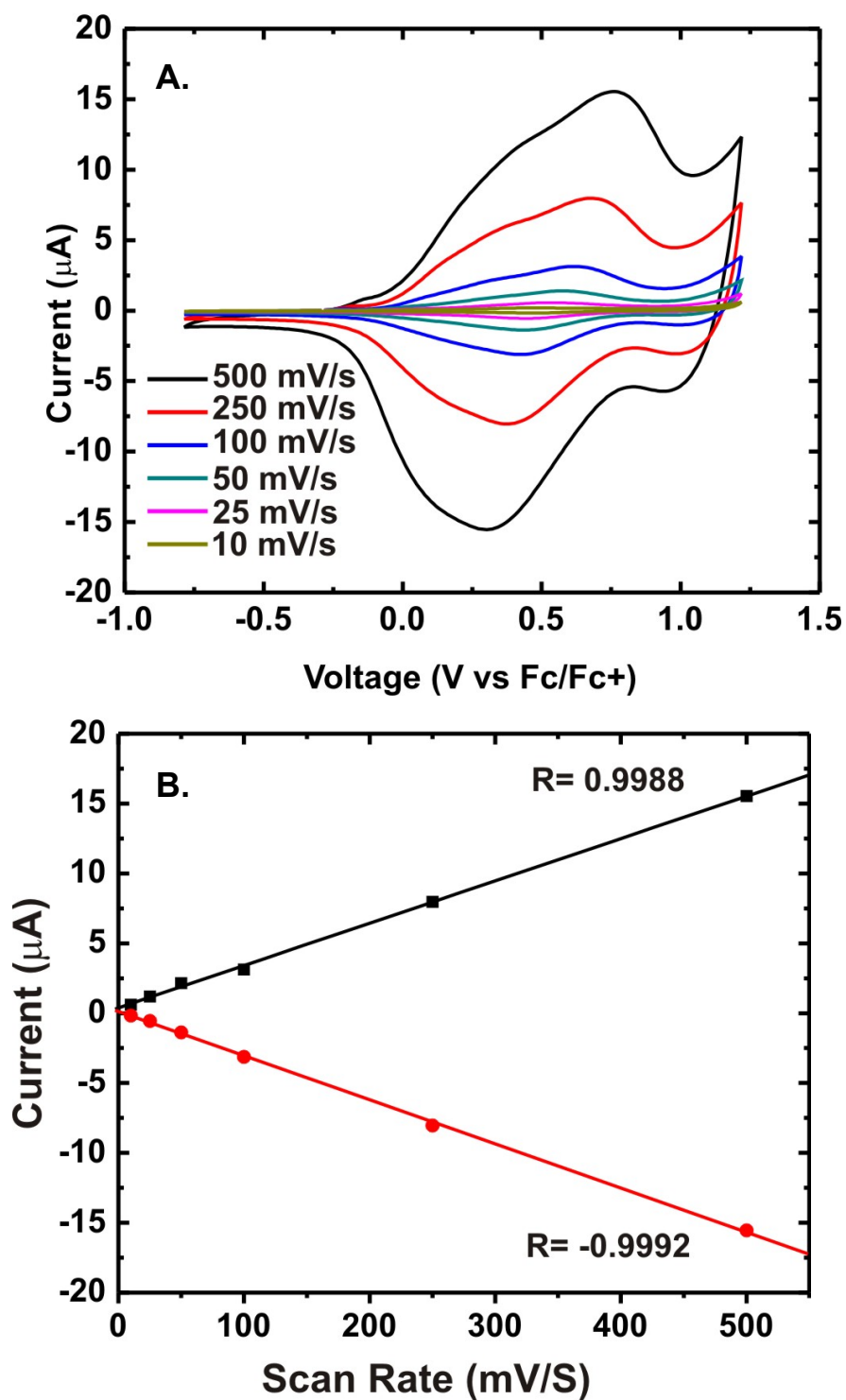


Figure S6. A. Scan rate dependence study of **2** grown on Pt button electrode (1.6 mm diameter). B. The oxidative (black) and reductive (red) peak current versus scan rate.

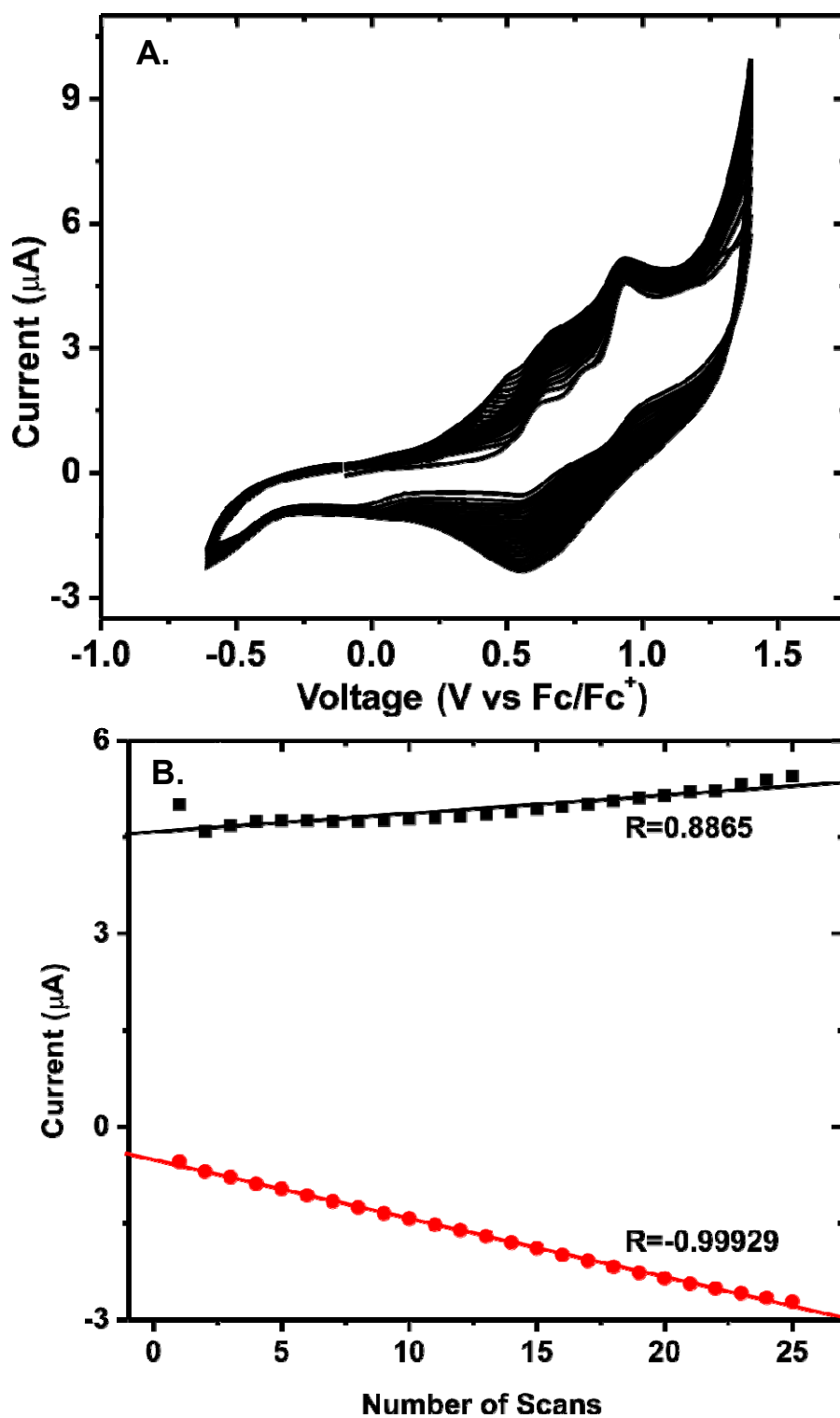


Figure S7. A. Electropolymerization of a 2×10^{-4} M CH_2Cl_2 solution of **6**, 0.1 M TBAPF_6 , Pt button (1.6 mm) electrode. B. The oxidative (black) and reductive (red) peak current versus the number of scans.

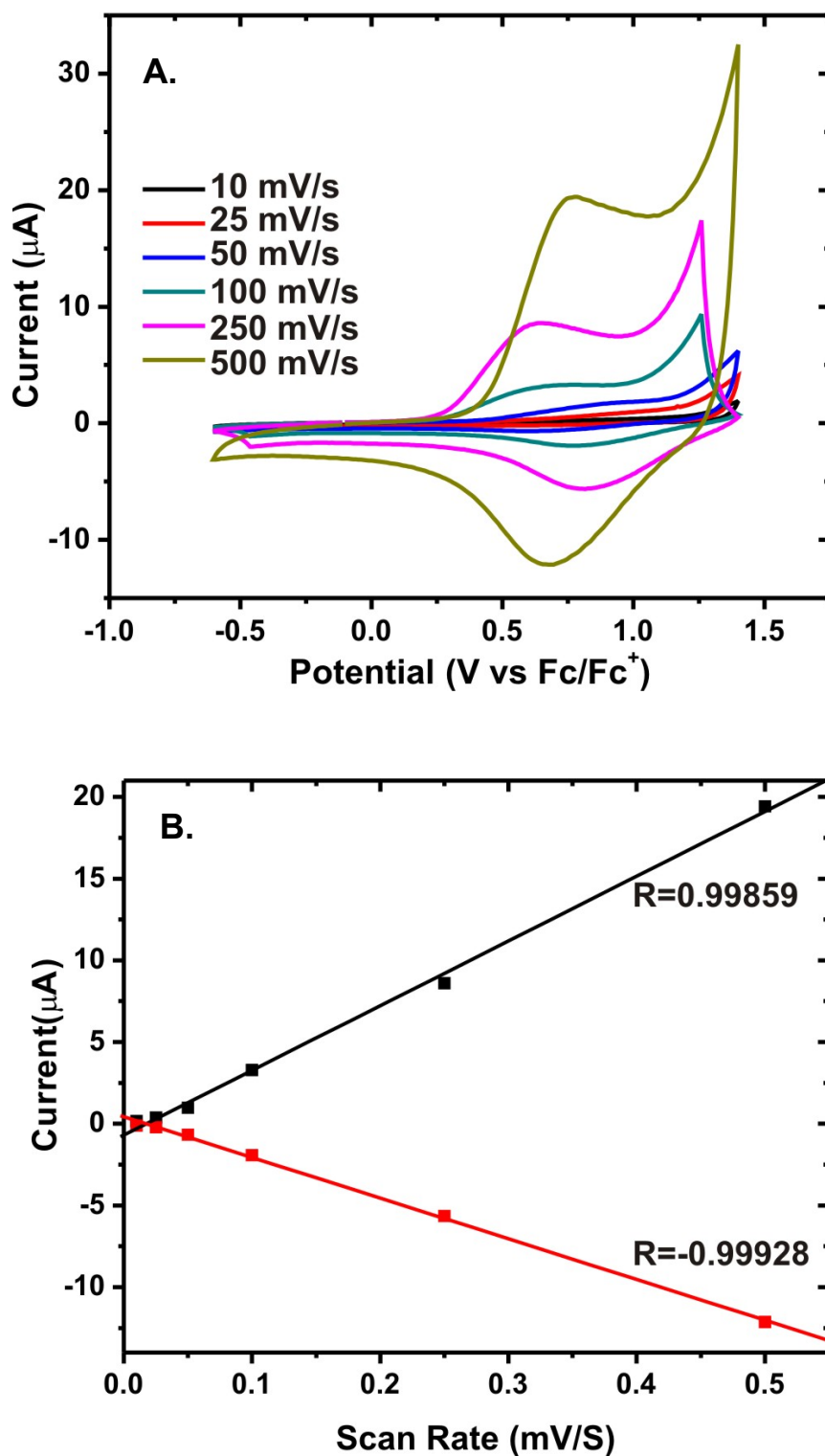


Figure S8. A. Scan rate dependence study of **6** grown on Pt button electrode (1.6 mm diameter). B. The oxidative (black) and reductive (red) peak current versus scan rate.

References

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- (2) Tang, Z.; Chen, X.; Pang, X.; Yang, Y.; Zhang, X.; Jing, X. *Biomacromolecules*, **2004**, *5*, 967.
- (3) Sheldrick, G. M. (1994) SHELXL97. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- (4) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, vol. 4 (1974), Table 2.2A.