Supporting Information

# *Elucidating Ligand Effects in Thiolate-Protected Metal Clusters Using $Au_{24}Pt(TBBT)_{18}$ as A Model Cluster*

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## 1. Additional Tables

### Table S1. Comparison of Bond Lengths between Clusters 1 and 2

| Bond type | Cluster **1** | Cluster **2** |
|---|---|---|
| $Au_{surf}$−$Au_{staple}$ [a] | 3.259±0.055 | 3.192±0.017 |
| $Au_{staple}$−S [a] | 2.304±0.006 | 2.303±0.003 |

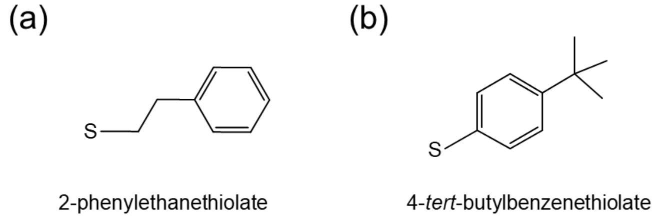
[a] See Figure S7.

### Table S2. Redox Potentials and HOMO−LUMO Gap Obtained from SWV Curves for Clusters 1 and 2

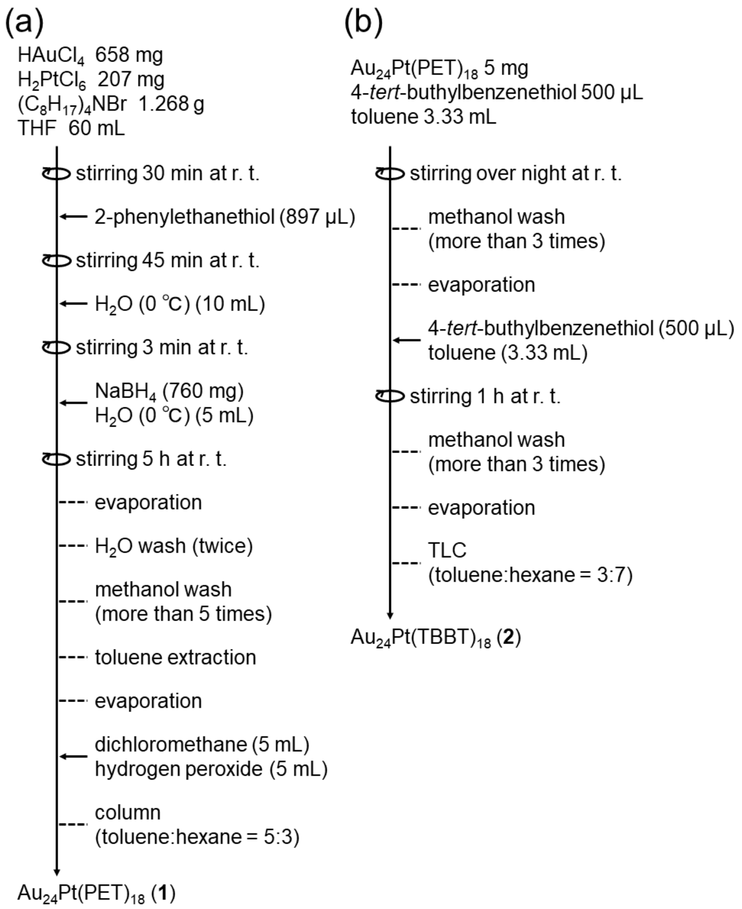
| Cluster | $E_{O2}$ (V) [a] | $E_{O1}$ (V) [a] | $E_{R1}$ (V) [a] | $E_{R2}$ (V) [a] | $E_{R1} - E_{O1}$ (V) [a] | $E_{O1} - E_{O2}$ (V) [b] | H−L gap (V) [c] |
|---|---|---|---|---|---|---|---|
| Cluster **1** | −0.03 | −0.20 | −0.67 | −0.95 | 0.47 | 0.17 | 0.30 |
| Cluster **2** | 0.25 | −0.05 | −0.68 | −0.93 | 0.63 | 0.30 | 0.33 |

[a] These values were estimated from the SWV curve (Figure 7(b)). [b] This value corresponds to the charging energy[1]. [c] This value is the HOMO−LUMO gap of the cluster that was estimated from the SWV curve (Figure 7(b)).

## 2. Schemes



**Scheme S1**. Geometrical structures of thiolates used: (a) 2-phenylethanethiolate (PET) and (b) 4-*tert*-butylbenzenethiolate (TBBT).



**Scheme S2.** Protocol used for the synthesis of (a) clusters **1** and (b) **2**.

## 3. Additional Figures

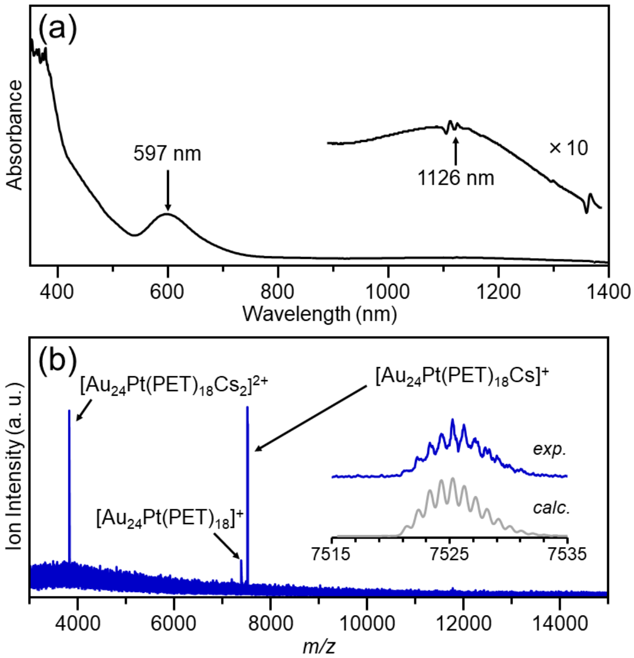


**Figure S1.** Cluster **1** used as a precursor cluster in the synthesis of cluster **2**, (a) optical absorption spectrum and (b) positive-ion ESI mass spectrum. In the mass spectrometry, $Cs^+$ ion ($CH_3COOCs$ salt) was added to the solution as the cation source.

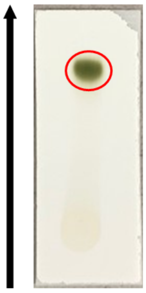


**Figure S2.** Photograph of thin-layer chromatography for the purification of product (cluster **2**). In this separation, a mixture of solvent, toluene:hexane = 3:7, was used as a mobile phase.

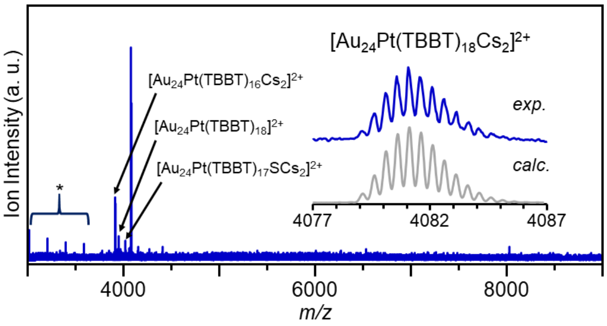


**Figure S3.** Positive-ion ESI mass spectrum of cluster **2**. In this mass spectrometry, Cs ion ($CH_3COOCs$ salt) was added to the solution as the cation source. The asterisks are assigned to the $(CH_3COOCs)_nCs^+$.

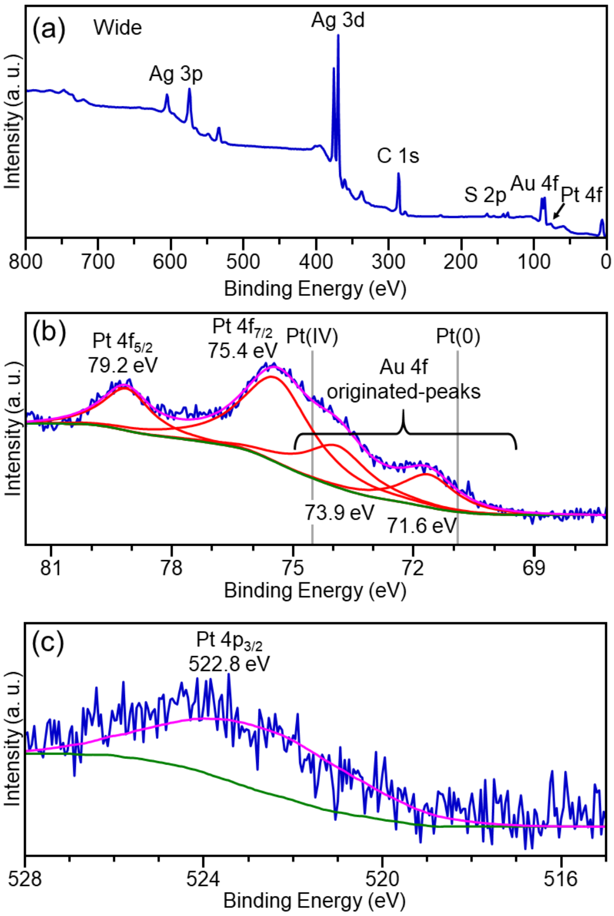


**Figure S4.** X-ray photoelectron spectrum of cluster **2**; (a) wide, (b) Pt 4f, and (c) Pt 4p regions. This result indicates that a Pt atom is included in cluster **2**. In (b), peaks from Au 4f are also observed.

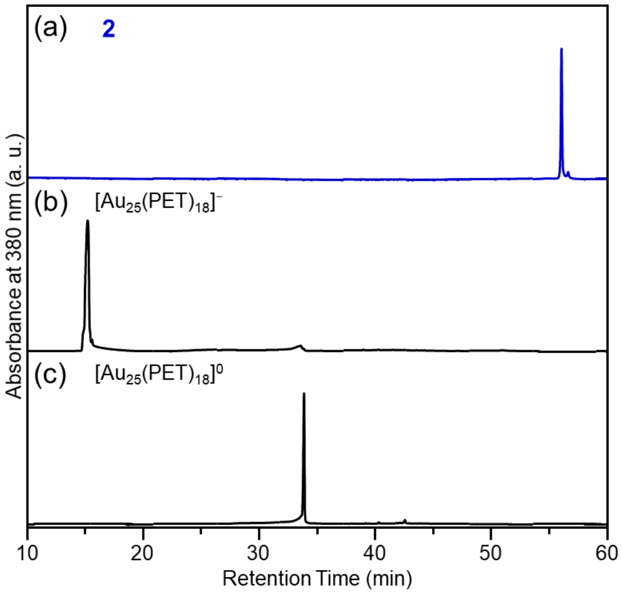


**Figure S5.** Chromatogram obtained using reversed-phase high-performance liquid chromatography for (a) cluster **2**, (b) [Au$_{25}$(PET)$_{18}$]$^0$, and (c) [Au$_{25}$(PET)$_{18}$]$^-$. [Au$_{25}$(PET)$_{18}$]$^0$ was obtained by oxidation of [Au$_{25}$(PET)$_{18}$]$^-$. The peak of cluster **2** is very sharp, indicating that the purity of the product is very high. In this experimental condition, the charged cluster elutes at an early retention time as seen in (b). However, the retention time of cluster **2** is very long (> 55 min), consisting with the interpretation that the product is the neutral [Au$_{24}$Pt(TBBT)$_{18}$]$^0$.

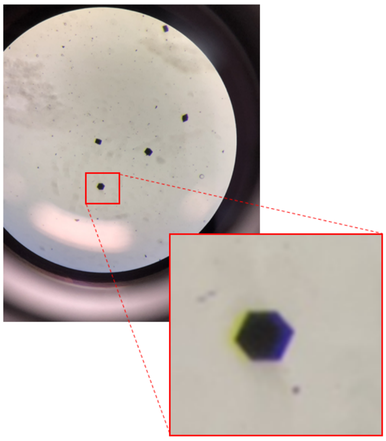


**Figure S6.** Photographs of hexagonal-shaped crystal of cluster **2**.

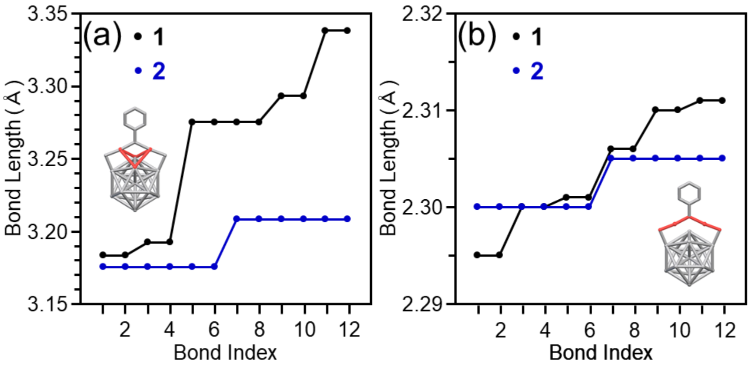


**Figure S7.** Comparison of bond lengths between clusters **1** and **2**; (a) $Au_{surf}$–$Au_{staple}$ and (b) $Au_{staple}$–S. The average bond lengths of these bonds are listed in Table S1.

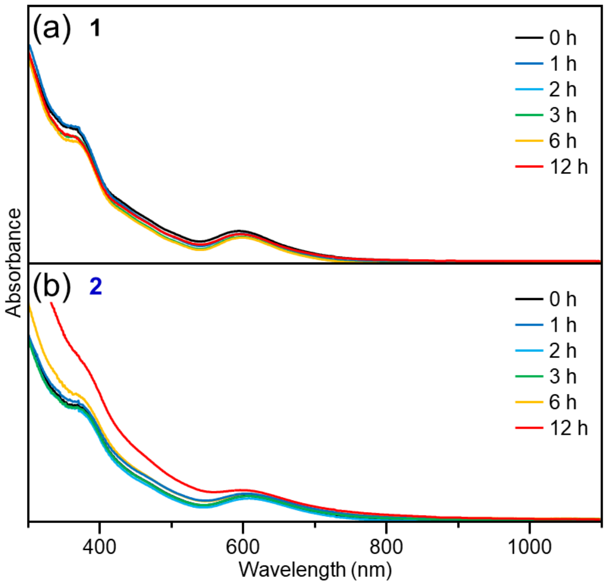


**Figure S8.** Time dependences of absorption spectra of (a) cluster **1** in toluene (1 × $10^{-5}$ M) at 60 °C and (b) cluster **2** in toluene (1 × $10^{-5}$ M) at 60 °C.

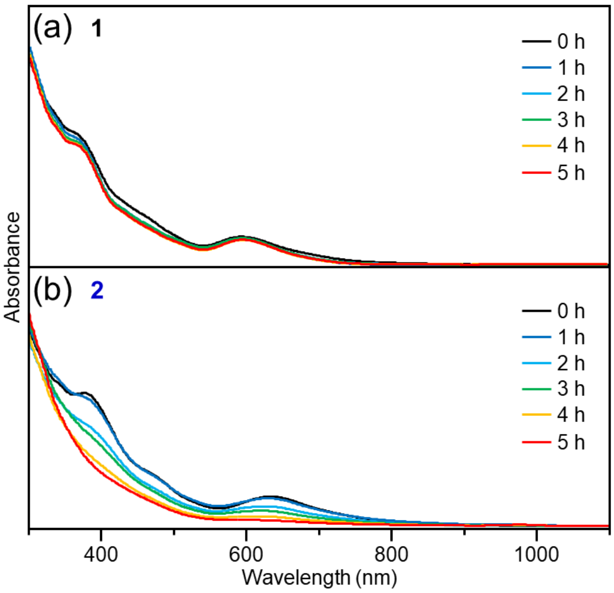


**Figure S9.** Time dependences of absorption spectra of (a) cluster **1** in THF ($1 \times 10^{-5}$ M) at 60 °C and (b) cluster **2** in THF ($1 \times 10^{-5}$ M) at 60 °C.

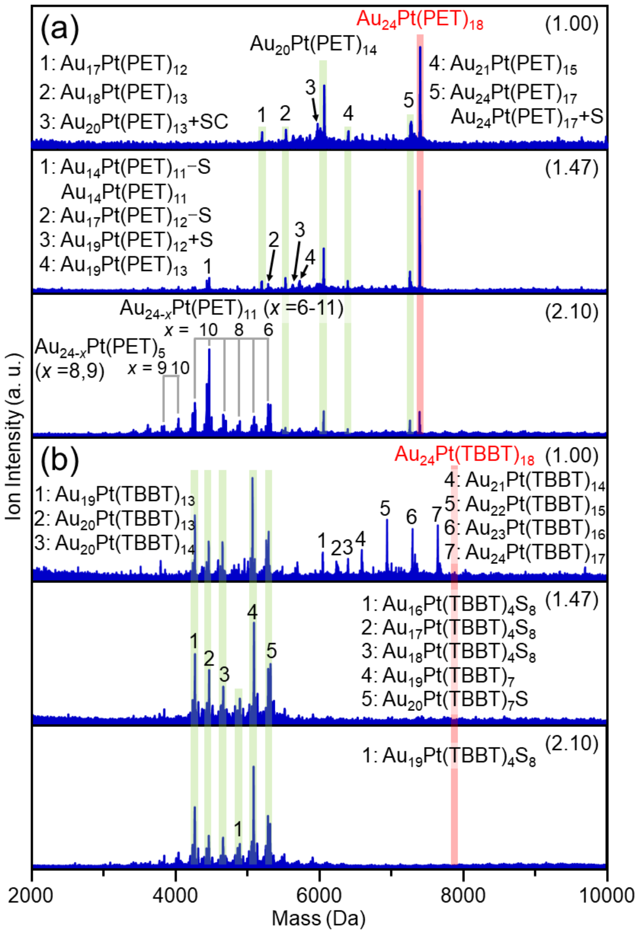


**Figure S10.** Negative-ion MALDI mass spectra of (a) clusters **1** and (b) **2** recorded at four laser fluences. Values in parentheses indicate the laser fluence in arbitrary units; (1.00) in (a) represents the same laser fluence as (1.00) in (b). The chemical compositions of the main fragment ions are described in the mass spectra.

## 4. Additional Information for Crystalized Clusters

### 4.1. Crystal Data

Crystal data and some important structural refinement parameters for cluster **2** are given below.

$C_{180}H_{72}Au_{24}PtS_{18}$; $M_w$. 7733.58 g/mol; trigonal, R-3 (No. 148); a = b = 26.9072(2) Å, c=24.2457(2) Å, $\alpha$ = $\beta$= 90 °, $\gamma$= 120 °; V= 15202.1(3) Å$^3$ ; T=100 K; Z=3; $\mu$ (Cu K$\alpha$) =35.022 /mm; total 117032 reflections measured (5.26° ≤ 2Θ ≤ 147.204°) and unique reflections are 6802 ($R_{int}$ = 0.0720), which were used in all calculations. Final *wR2* of all data was 0.1271 and *R1* was 0.0450 (I > 2σ (I)). All crystal-data details and structural refinement parameters are tabulated in Table S3.

**Table S3: Details of Crystal Data and Structural Refinement Parameters in Cluster 2**

| | |
|---|---|
| Empirical formula | $C_{180}H_{72}Au_{24}PtS_{18}$ |
| Formula weight | 7733.58 |
| Temperature/K | 100(2) |
| Crystal system | trigonal |
| Space group | R-3 |
| A (Å) | 26.9072(2) |
| B (Å) | 26.9072(2) |
| C (Å) | 24.2457(2) |
| Α (°) | 90 |
| Β (°) | 90 |
| Γ (°) | 120 |
| Volume (Å$^3$) | 15202.1(3) |
| Z | 3.00006 |
| $\rho_{calc}$g (cm$^3$) | 2.534 |
| Μ (/mm) | 35.022 |
| F(000) | 10242.0 |
| Crystal size (mm$^3$) | 0.6 × 0.6 × 0.1 |
| Radiation MoKα | CuKα (λ = 1.54184) |
| 2Θ range for data collection (°) | 5.26 to 147.204 |
| Index ranges | $-33 \le h \le 33$, $-33 \le k \le 32$, $-29 \le l \le 30$ |
| Reflections collected | 117032 |
| Independent reflections | 6802 [$R_{int}$ = 0.0720, $R_{sigma}$ = 0.0183] |
| Data/restraints/parameters | 6802/630/384 |
| Goodness-of-fit on F$^2$ | 1.063 |
| Final R indexes (I > 2σ (I)) | $R_1$ = 0.0427, $wR_2$ = 0.1255 |
| Final R indexes [all data] | $R_1$ = 0.0450, $wR_2$ = 0.1271 |
| Largest diff. peak/hole (e/Å$^3$) | 1.43/−2.03 |

### 4.2. Structure Quality Indicators and Refinement Details

CrysAlisPro Version 1.171.39.20a was used for absorption correction of the crystal. Initial model of the product structure that contains heavy atoms (metal, sulfur) and most carbon atoms of thiolates were solved by SIR-92 using direct method.[2] Total cluster structures were refined by the full-matrix least-squares method against F$^2$ by SHELXL-2018/3[3] using Olex2 software.[4] The cluster has few disordered-*tert*-butyl groups of thiolate ligands, which were modeled (by using PART command and SADI restrains) and refined (details of occupancies are given in Table S4). In both structures, hydrogen atoms were placed at calculated positions, except for disordered H atoms that were attached with t-butyl groups, and their positions were refined with a riding model. During overall refinement, few aromatic rings were modelled by using hexagonal restrain AFIX 66.

**Table S4: Atomic Occupancy of Disordered Carbons of *tert*-Butyl Groups in Cluster 2**

| Atom | Occupancy | | Atom | Occupancy | | Atom | Occupancy |
|---|---|---|---|---|---|---|---|
| C27 | 0.64(14) | | C30 | 0.64(14) | | C17 | 0.72(4) |
| C29 | 0.64(14) | | C21 | 0.72(4) | | C22 | 0.72(4) |
| C31 | 0.60(3) | | C32 | 0.60(3) | | C33 | 0.60(3) |
| C33A | 0.40(3) | | C32A | 0.40(3) | | C31A | 0.40(3) |
| C17A | 0.28(4) | | C21A | 0.28(4) | | C22A | 0.28(4) |
| C30A | 0.36(14) | | C29A | 0.36(14) | | C27A | 0.36(14) |

The additional refinement product details are given below.

1. Fixed Uiso
 At 1.2 times of: All C(H) groups
2. Restrained distances
 C31-C32 ≈ C31-C33 ≈ C32-C33 ≈ C33A-C32A ≈ C33A-C31A ≈C32A-C31A with sigma of 0.04
 C1-C00G ≈ C1-C31 ≈ C1-C32 ≈ C1-C33 ≈ C1-C33A ≈ C1-C32A≈ C1-C31A with sigma of 0.02
 C17-C21 ≈ C17-C22 ≈ C21-C22 ≈ C17A-C21A ≈ C17A-C22A ≈C21A-C22A with sigma of 0.04
 C15-C00C ≈ C15-C17 ≈ C15-C21 ≈ C15-C22 ≈ C15-C17A ≈C15-C21A ≈ C15-C22A with sigma of 0.02
 C27-C30 ≈ C27-C29 ≈ C30-C29 ≈ C30A-C29A ≈ C30A-C27A ≈C29A-C27A with sigma of 0.04
 C28-C00J ≈ C28-C27 ≈ C28-C30 ≈ C28-C29 ≈ C28-C30A ≈C28-C29A ≈ C28-C27A with sigma of 0.02
3. Uiso/Uaniso restraints and constraints
C009 ≈ C8 ≈ C00I ≈ C00C ≈ C9 ≈ C11 ≈ C00A ≈ C00E≈ C00D ≈ C00J ≈ C26 ≈ C25 ≈ C00B ≈ C00H ≈ C4 ≈C00G ≈ C6 ≈ C00F ≈ C27 ≈ C28 ≈ C30 ≈ C15 ≈ C17≈ C29 ≈ C21 ≈ C22: within 1.7A with sigma of 0.04 and sigma for terminal atoms of 0.08
C31 ≈ C1 ≈ C33 ≈ C32: within 2A with sigma of 0.04 and sigma for terminal atoms of 0.08
C1 ≈ C31 ≈ C32A ≈ C32 ≈ C33A ≈ C33 ≈ C31A: within 1.7A with sigma of 0.04 and sigma for terminal atoms of 0.08
C15 ≈ C22 ≈ C22A ≈ C17A ≈ C17 ≈ C21 ≈ C21A: within 1.7A with sigma of 0.04 and sigma for terminal atoms of 0.08
C29 ≈ C27A ≈ C27 ≈ C28 ≈ C29A ≈ C30 ≈ C30A: within 1.7A with sigma of 0.04 and sigma for terminal atoms of 0.08
4. Rigid body (RIGU) restrains
 C009, C8, C00I, C00C, C9, C11, C00A, C00E, C00D, C00J, C26, C25, C00B, C00H, C4, C00G, C6, C00F, C27, C28, C30, C15, C17, C29, C21, C22 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 C33, C1, C31, C32 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 C1, C31, C32A, C32, C33A, C33, C31A with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 C21, C15, C21A, C17, C17A, C22, C22A with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
5. Others
 Sof(C33A)=Sof(C32A)=Sof(C31A)=1-FVAR(1)
 Sof(C31)=Sof(C32)=Sof(C33)=FVAR(1)
 Sof(C17A)=Sof(C21A)=Sof(C22A)=1-FVAR(2)
 Sof(C17)=Sof(C21)=Sof(C22)=FVAR(2)
 Sof(C30A)=Sof(C29A)=Sof(C27A)=1-FVAR(3)
 Sof(C27)=Sof(C30)=Sof(C29)=FVAR(3)
6.a Aromatic/amide H refined with riding coordinates:
 C8(H8), C00I(H00I), C9(H9), C11(H11), C00E(H00E), C00D(H00D), C26(H26), C25(H25), C00H(H00H), C4(H4), C6(H6), C00F(H00F)
6.b Fitted hexagon refined as free rotating group:
 C009(C8,C00I,C00C,C9,C11), C00A(C00E,C00D,C00J,C26,C25), C00B(C00H,C4,C00G,C6,C00F)

## 5. References

1. R. Guo and R. W. Murray, *J. Am. Chem. Soc.*, 2005, **127**, 12140−12143.
2. A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Cryst.*, 1994, **27**, 435−436.
3. G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.
4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339−341.