Electronic Supplementary Information

Conductive gold nanoparticles assembly linked through interaction between radical cations of ethylene- and propylene-3,4-dioxythiophene mixed tetramer thiolate

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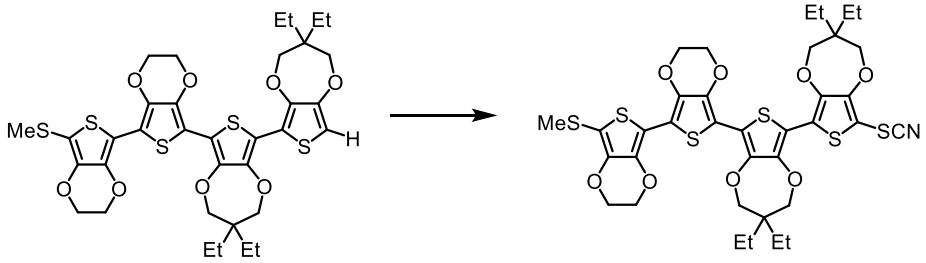
Contents

General

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV500 instrument. Chemical shifts are reported in ppm with reference to tetramethylsilane using the signal of the solvent C_6D_6. APCI mass spectra were recorded on a Bruker MicrOTOFII-SD. Only the more intense or structurally diagnostic mass spectral fragment ion peaks are reported. Electronic absorption spectra were recorded on a SHIMADZU UV-Vis-NIR scanning spectrophotometer (Model UV-3101-PC). Cyclic voltammetry (CV) was performed on a BAS-ALS620B electrochemical analyzer using a standard three-electrode cell consisting of a Pt working electrode, a Pt wire counter electrode, and a Ag/AgCl reference electrode. The potentials were calibrated with ferrocene as an external standard. Transmission electron microscopy (TEM) was carried out using JEOL JEM-3200FS electron microscopes for the drop-cast films on a carbon-supported copper grid. ESR spectra were recorded on a Bruker E500 instrument. The electric conductivity was evaluated using Pt interdigitated array (IDA) electrodes (each array consists of 65 fingers with a 5 μm gap between fingers, 2000 μm finger length, 10 μm finger width, and 100 nm finger height (90 nm Pt and 10 nm Ti)) purchased from BAS Inc. and ADCMT 6241A DC Voltage/Current Source/Monitor. The dichloromethane solution of AuNPs was drop-casted on IDA electrode and dried, then conductivities of the films were measured. These procedures were repeated until the conductivity was saturated. The estimation of conductivities was according to literature.[1] Preparative gel-permeation chromatography (GPC) was performed with a JAI LC–08 chromatograph equipped with JAIGEL 1H and 2H columns.

Commercially available reagents were used as received otherwise noted. Zinc thiocyanate ($Zn(SCN)_2$) was dried with a heat gun in vacuum before use. THF were distilled from relevant drying agents prior to use.

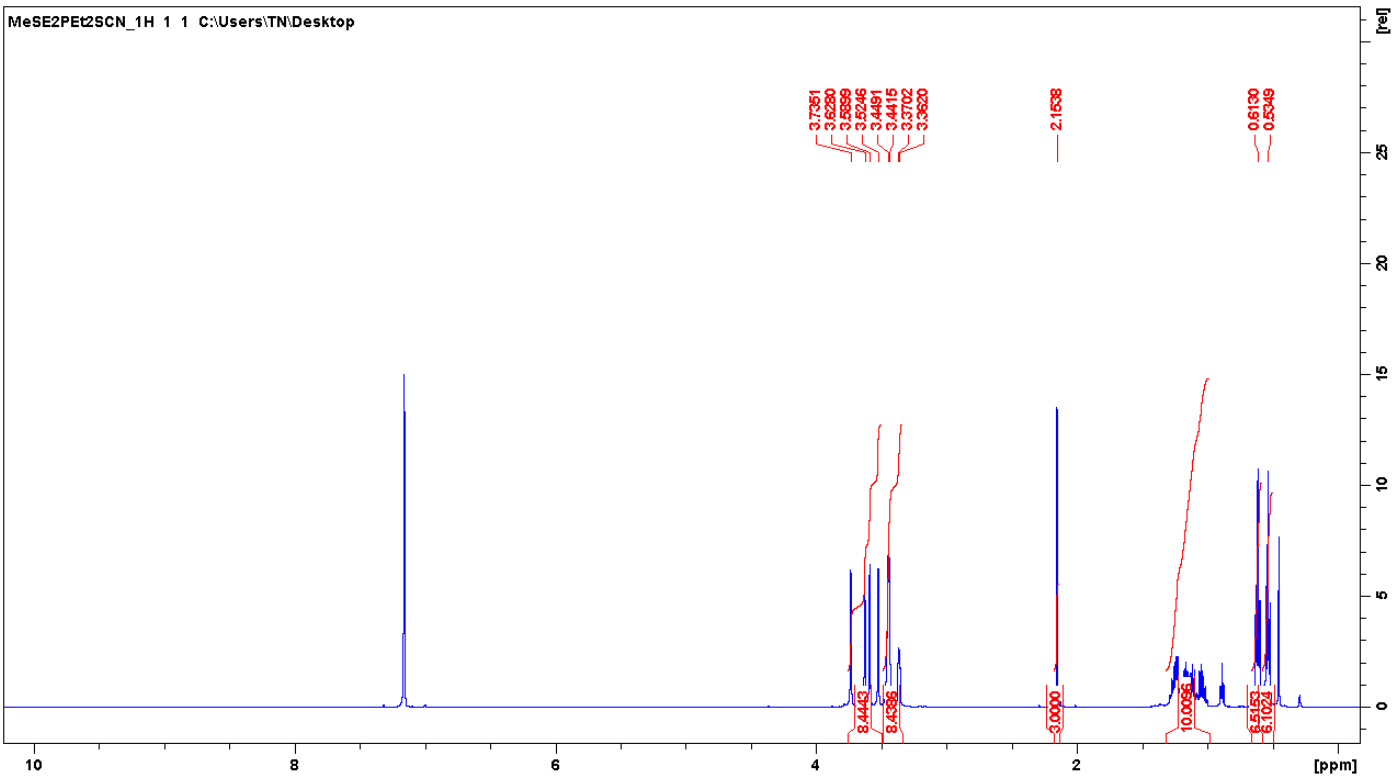
Synthesis



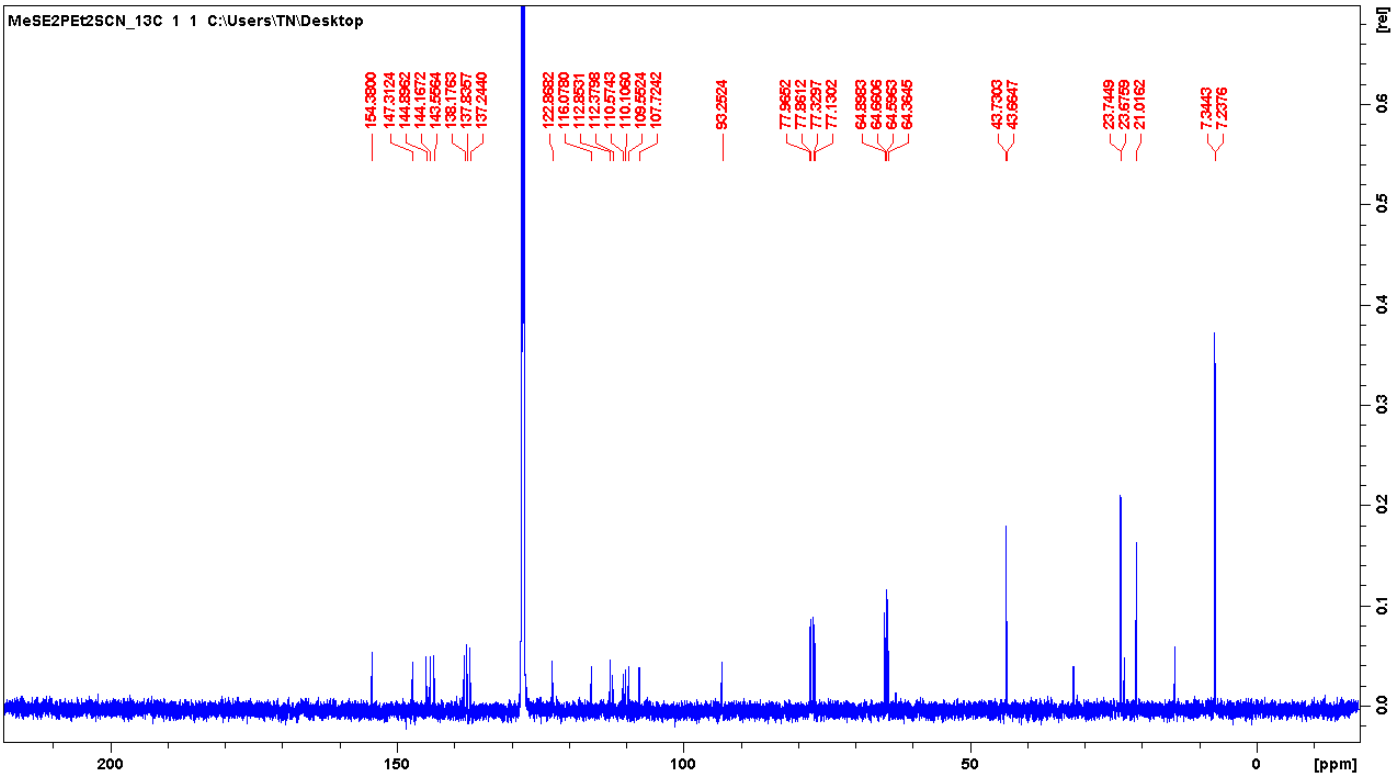
4d **4c**

Synthesis of thiocyanate 4c. A solution of EDOT-ProDOT mixed tetramer **4d**[2] (271 mg, 0.362 mmol) and tetramethylethylenediamine (57 μL, 0.38 mmol) in THF (5 mL) was cooled with liquid N_2-acetone bath, and *n*-BuLi (1.59 M, 0.24 mL, 0.38 mmol) was added at -80 °C under N_2. The reaction mixture was stirred at the temperature for 100 min and then a suspension of $Zn(SCN)_2$ (78 mg, 0.40 mmol) in THF prepared by sonication was added. The mixture was warm to 0 °C with ice bath and stirred for 1 h and a suspension of *N*-chlorosuccinimide (61 mg, 0.40 mmol) in dichloromethane prepared by sonication was added. After 10 min, the reaction mixture was quenched with $NaOH_{aq}$, extracted with ether, and the organic layer was dried over $MgSO_4$. The volatiles were removed in vacuo, and the residue was passed through Al_2O_3 short column eluted with dichloromethane : Hexan = 1 : 1 and purified with preparative recycle GPC eluted with toluene to give **4c** (164 mg, 0.203 mmol, 54%) as deep orange solid: ^{1}H NMR (C_6D_6) δ 3.74(s, 2H), 3.63(s, 2H), 3.59(s, 2H), 3.52(s, 2H), 3.44 (m, 6H), 3.37(m, 2H), 2.15(s, 3H), 1.0-1.3(m, 8H), 0.61(t, 6H), 0.53(t, 6H); ^{13}C NMR (C_6D_6) δ 154.4, 147.3, 144.9, 144.2, 143.6, 138.2, 137.8, 137.2, 122.9, 116.1, 112.9, 112.4, 110.6, 110.1, 109.6, 107.7, 93.3, 78.0, 77.9, 77.3, 77.1, 64.9, 64.7, 64.6, 64.4, 43.73, 43,66, 23.74, 23.68, 21.0, 7.3, 7.2; MS(APCI-TOF) calcd for $C_{36}H_{39}NO_8S_6$ [M+] = 805; found 805.

^{1}H NMR of **4c**



^{13}C NMR of **4c**



Synthesis of AuNPs 2. Dodecylamine (DDA) capped 2.5 nm size AuNPs in dehydrated toluene solution (10 mL) containing 0.1 M didodecyldimethylammonium bromide (DDAB) was prepared according to the literature procedure[3] using $HAuCl_4 \cdot 4H_2O$ (25 mg, 0.36 mmol), DDA (215 mg, 1.16 mmol) and tetrabutylammonium borohydride (TBAB) (60 mg, 0.23 mmol). A solution of TBAB (117 mg, 0.455 mmol) in toluene (5 mL) containing 0.1 M DDAB was added to **4c** (46 mg, 0.057 mmol) in a flask equipped with N_2 balloon and the mixture was sonicated. Then DDA-capped AuNPs solution was added to the mixture. After stirred overnight at rt, methanol (45 mL) was added to the mixture. After standing for additional 24 h, the precipitate was collected with a membrane filter and washed thoroughly with toluene-methanol mixed solvent (1:2) to obtain some of **AuNPs 2**. After evaporation, additional **AuNPs 2** could be collected from the residue by repeating the same filtration and washing procedure.

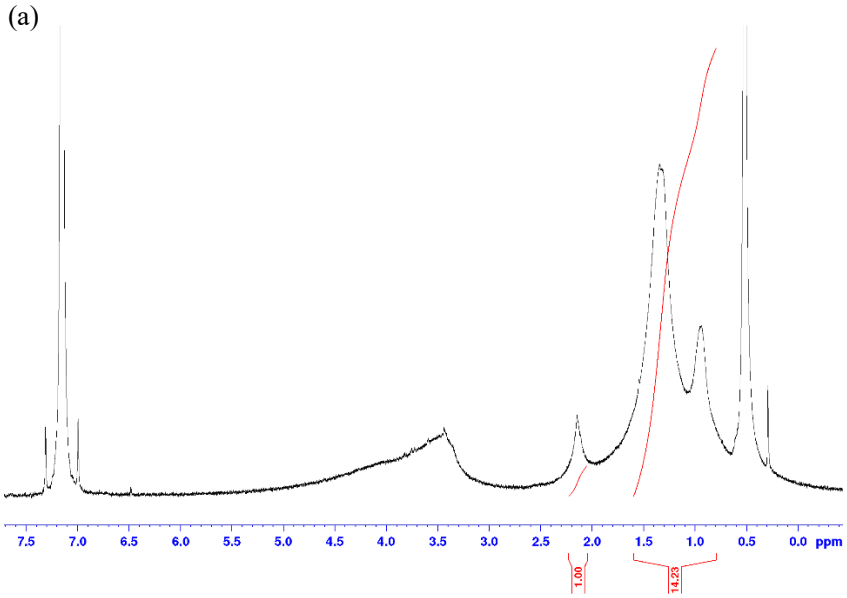


Figure S1 ^{1}H NMR of (a) **2** in C_6D_6. The characteristic signal around δ 2.2 ppm is due to the methyl proton of MeS-group in **4** moiety. The broad signal around δ 0.8-1.6 ppm contains both methylene units of ethyl side chain in ProDOT and DDA (except for the next methylene unit to amine nitrogen). We roughly estimated the ratio between **4** and DDA from the integrals of these signals.

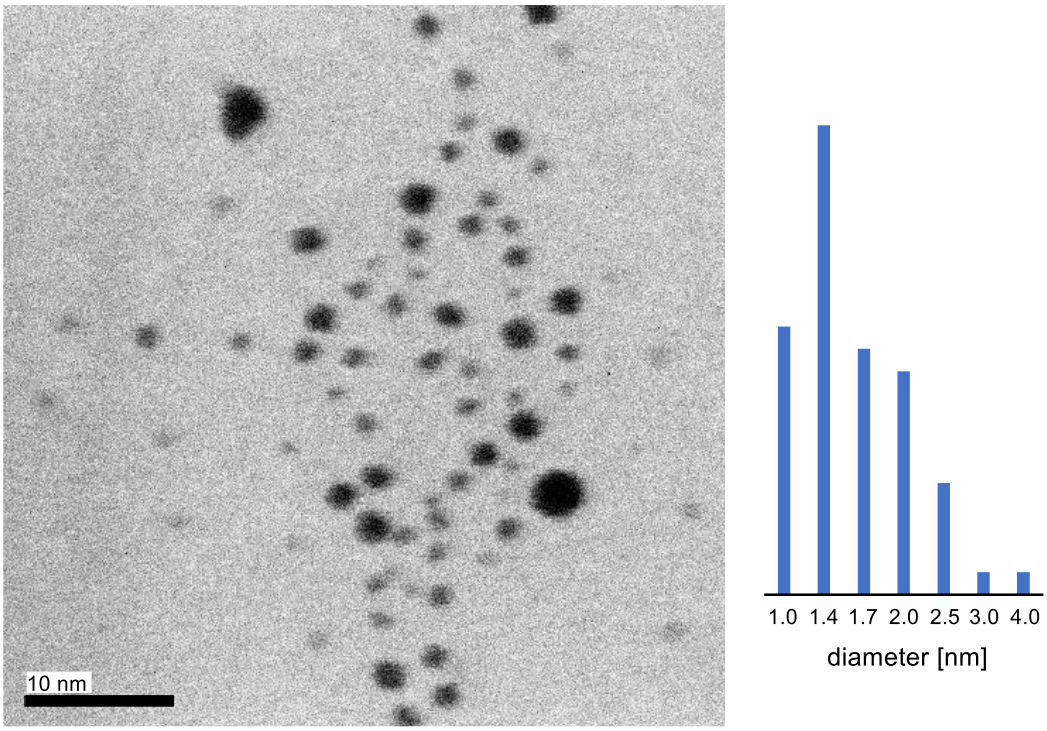


Figure S2 A TEM image and distribution of AuNPs **2**.

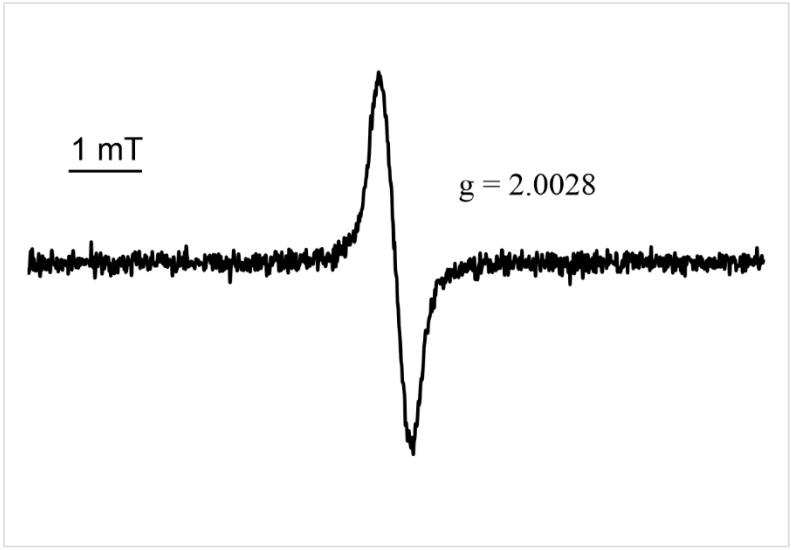


Figure S3 ESR spectra of **2** oxidized with $AgSbF_6$.

Computational Methods

DFT calculations were performed with the Gaussian 09 program.[4] The geometry optimization of the single E_2P_2 thiolate on 12 (=3 × 4) Au atoms in the (111) arrangement and one Au adatom placed on a 2-fold hollow in the neutral and oxidized states were conducted with the M06 method and LanL2DZ (Au) and 6-31G(d) (C,H,O,S) basis sets. The position of only all Au atoms were fixed. The thiolate atom was also restricted so that the distances to the neighboring Au atoms were identical.

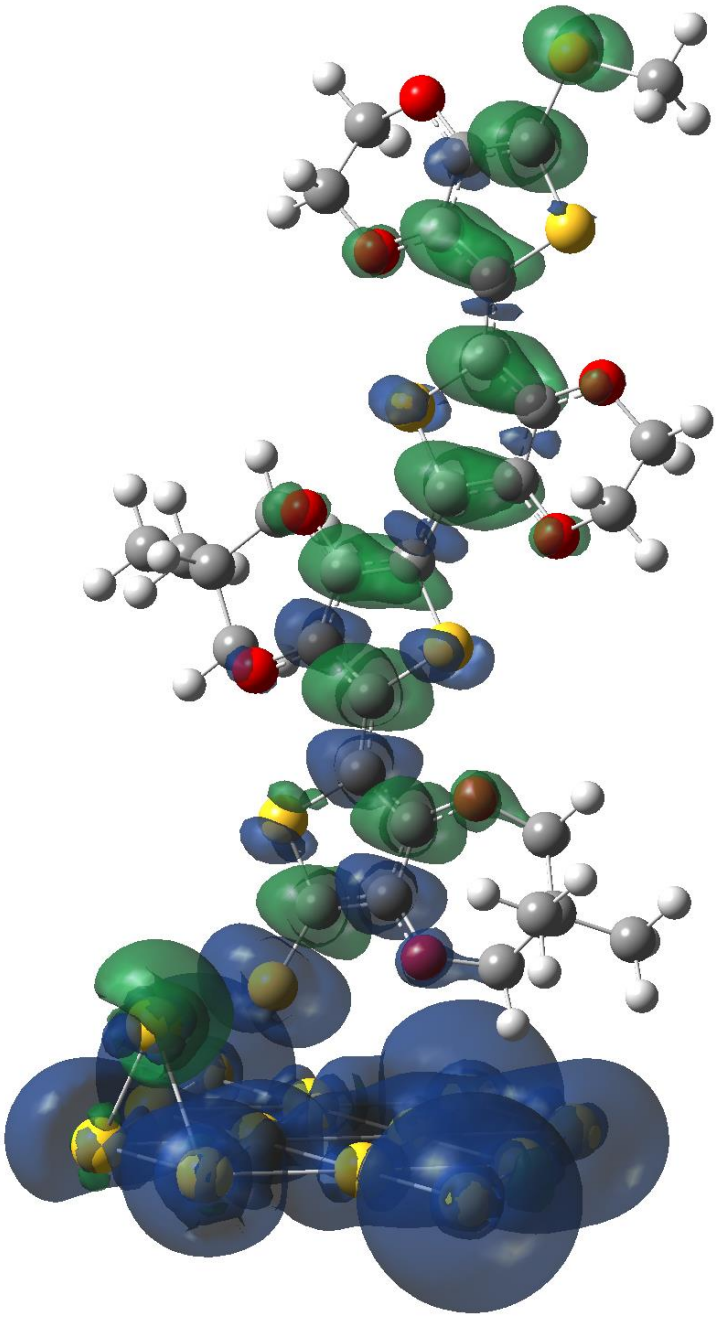


Figure S4 Calculated spin distribution of E_2P_2 thiolate of Au_{13} cluster in the one-electron oxidized state.

Ref.

1. W. P. Wuelfing, S. J. Green, J. J. Pietron, D. E. Cliffel and R. W. Murray, *J. Am. Chem. Soc.*, 2000, **122**, 11465–11472.

2. T. Nishinaga, Y. Kanzaki, D. Shiomi, K. Matsuda, S. Suzuki and K. Okada, *Chem. Eur. J.*, 2018, **24**, 11717–11728.

3. T. Zdobinsky, P. Sankar Maiti and R. Klajn, *J. Am. Chem. Soc.*, 2014, **136**, 2711–2714.

4. Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.: Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

Table S1. Cartesian coordinate of optimized structure of E_2P_2 thiolate of Au_{13} cluster in the neutral state

Au	-3.93202353	-3.23841415	-2.07078379
Au	-3.86980419	-0.60844879	-3.24288116
Au	-3.25136079	1.68167872	-1.60971093
Au	-3.18914145	4.31164408	-2.78180829
Au	-2.63291740	3.97180623	0.02345931
Au	-2.69513675	1.34184088	1.19555668
Au	-3.31358014	-0.94828664	-0.43761356
Au	-3.37579949	-3.57825200	0.73448381
Au	-2.81957545	-3.91808984	3.53975141
Au	-2.75735610	-1.28812448	2.36765404
Au	-2.13891271	1.00200303	4.00082428
Au	-2.07669336	3.63196839	2.82872691
Au	-1.47749977	-2.21040735	-3.17210826
S	-0.51692696	-1.14995103	-0.74165352
C	1.07514078	-0.61415822	-0.81656480
S	2.45984761	-1.68338207	-1.00750369
C	1.49873230	0.72954623	-0.71703466
C	3.58352728	-0.33747422	-0.89465811
C	2.88654767	0.87757128	-0.76951327
O	0.60691827	1.72307837	-0.64130750
C	4.98038036	-0.50021476	-0.89676714
O	3.55864777	2.05084945	-0.78895425
C	0.79756177	2.67308277	0.40335714
S	6.10841485	0.84161793	-0.72782671
C	5.67846596	-1.71029339	-0.96258136
C	3.28297209	2.98887124	0.25235073
C	1.92097857	3.67049515	0.15415467
H	-0.16780606	3.19927765	0.47071742
H	0.95116682	2.13351937	1.35667481
C	7.48072736	-0.24800077	-0.67904451
C	7.06468191	-1.57046137	-0.83526704
O	5.04377280	-2.88689973	-1.15248746
H	3.38896274	2.48213742	1.22856353
H	4.08319064	3.73607705	0.16293910
C	1.84980080	4.70429916	1.27750803
C	1.74453532	4.34768280	-1.20057830
C	8.81188342	0.20639528	-0.51112541
O	7.94885157	-2.59630220	-0.89934800
C	5.26422100	-3.88621798	-0.15626407
H	1.94051530	4.23897265	2.27050239
H	2.64936397	5.45116840	1.17566794
H	0.88879896	5.23640257	1.24522139
H	0.75959981	4.83346288	-1.26131273
H	2.51539464	5.11695703	-1.35134207
H	1.81246986	3.62897279	-2.02462656
C	9.24475337	1.51761381	-0.36317954
S	10.19364803	-0.88562694	-0.44269105
C	7.76478849	-3.63068465	0.06313234
C	6.61704336	-4.58733919	-0.25416267
H	5.13147571	-3.43186993	0.84186266
H	4.45738697	-4.61519683	-0.30894968
C	10.63231713	1.64496669	-0.18502800
O	8.40855626	2.58090172	-0.38051990
C	11.31374666	0.44102063	-0.19546253
H	8.71351439	-4.18475491	0.06715161
H	7.62807375	-3.17723098	1.06162102
C	6.80065061	-5.19940230	-1.63821933

C	6.63319840	−5.67756038	0.81613839
O	11.23979642	2.85114651	−0.01290223
C	9.09835807	3.81833186	−0.53292528
C	12.71607304	0.23556629	−0.03609889
H	7.75682024	−5.73805926	−1.69759840
H	5.99609688	−5.91649634	−1.85226438
H	6.79221145	−4.43459473	−2.42208263
H	5.82886258	−6.40556074	0.64532224
H	7.58466952	−6.22651282	0.79776294
H	6.50292290	−5.26221725	1.82597104
C	10.31290066	3.86009936	0.36505983
H	8.38257874	4.60468403	−0.27444448
H	9.40175290	3.93831916	−1.58380669
C	13.41238447	−0.95771727	−0.06147612
S	13.84555399	1.56545355	0.21340343
H	10.01193957	3.71110985	1.41383850
H	10.83681990	4.81669966	0.27490689
C	14.80769729	−0.82106314	0.11894546
O	12.82301606	−2.16506533	−0.23976175
C	15.20800638	0.48222106	0.28043723
O	15.66154039	−1.87758288	0.12516751
C	13.76182651	−3.18303370	−0.57787617
S	16.87273832	0.95406331	0.53562030
C	14.97468351	−3.10487732	0.32090452
H	14.06309362	−3.06577771	−1.63006247
H	13.23867442	−4.13671007	−0.45897076
C	16.70179100	2.75624002	0.65085200
H	15.68751993	−3.90282762	0.09030333
H	14.66520383	−3.19401150	1.37450861
H	16.09103028	3.04766172	1.51285830
H	17.71412194	3.14777211	0.78868877
H	16.28440091	3.17726417	−0.27085664

Table S2. Cartesian coordinate of optimized structure of **4a**

C	−1.50140547	−1.65643558	−0.20765502
S	−2.55965349	0.68792343	−0.24583614
C	−2.89792836	−1.85989080	−0.12285731
O	−3.45090990	−3.10139687	−0.05267716
O	−0.61688789	−2.69099694	−0.21462529
C	−2.50004307	−4.10460043	0.27570042
H	−2.25967343	−4.05079491	1.34938123
H	−2.97829510	−5.06641770	0.06499294
C	−1.24131810	−3.92475556	−0.54030097
H	−0.51062766	−4.71046477	−0.32405001
H	−1.48436616	−3.94572249	−1.61432997
C	−1.12997489	−0.33221314	−0.27411398
C	−3.63393234	−0.69687566	−0.13298046
C	−5.06173647	−0.56500040	−0.07772584
C	−5.80896848	0.59189998	−0.13354884
S	−6.13303387	−1.94735104	0.04284406
C	−7.21233040	0.38215198	−0.10194978
O	−5.26576786	1.83861534	−0.22846046
O	−8.10617391	1.40046941	−0.15868133
C	−6.20579294	2.78255757	−0.72096782
C	−7.50514058	2.67185888	0.04284853
H	−6.38308960	2.60562842	−1.79374442
H	−5.75363411	3.77098646	−0.59165975
H	−8.23097682	3.41550458	−0.30232849
H	−7.31656906	2.82796778	1.11716715

C	-7.56024248	-0.94136357	-0.01694803
S	-9.16532725	-1.63598154	0.03466339
C	-9.63561644	-1.20954741	1.74834213
H	-9.69154375	-0.12293134	1.86875940
H	-10.62421987	-1.64447337	1.93017635
H	-8.91676629	-1.63135961	2.45832902
C	0.19706435	0.20596725	-0.35139491
C	0.56703815	1.53315243	-0.39792106
S	1.61829733	-0.82118131	-0.43176047
C	1.96796989	1.73044824	-0.46457032
O	-0.33738049	2.54994192	-0.41710105
C	2.69583738	0.56179221	-0.46683234
O	2.55233546	2.95514531	-0.55027821
C	-0.21929483	3.48304155	0.65023891
C	4.12521341	0.42658850	-0.43787151
C	2.27899343	3.83531000	0.53325933
C	0.90531718	4.50138220	0.46934810
H	-1.18495862	4.00691750	0.68176561
H	-0.09748470	2.93513784	1.60237376
C	4.85471582	-0.74340522	-0.44106568
S	5.20438448	1.80200174	-0.35489221
H	2.40028192	3.28968939	1.48710092
H	3.06150325	4.60529019	0.48009685
C	0.73866544	5.24160581	-0.85286809
C	0.82430140	5.48098484	1.63842679
C	6.26185996	-0.55198376	-0.33800643
O	4.26378228	-1.95932789	-0.60205543
C	6.61380680	0.77333460	-0.26994655
H	-0.23161180	5.75683981	-0.88684825
H	1.52709284	5.99726715	-0.97577391
H	0.78901734	4.55434865	-1.70376208
H	1.60801649	6.24654800	1.55933835
H	-0.14435636	5.99905276	1.64749873
H	0.94420725	4.97426825	2.60714294
O	7.16343823	-1.56379655	-0.34044021
C	4.49206987	-2.89627661	0.44070903
S	8.22150618	1.46129052	-0.15808613
C	6.98040397	-2.55010310	0.66450971
C	5.86665764	-3.55906869	0.38644665
H	4.33814922	-2.40338373	1.41856398
H	3.70983027	-3.65900005	0.31862934
C	8.46483019	1.37224910	1.65036471
H	7.94103452	-3.08118082	0.71846268
H	6.80922693	-2.05516684	1.63884252
C	5.91275268	-4.60115322	1.50208331
C	6.08275833	-4.22368730	-0.96801155
H	8.49037188	0.32980050	1.98686792
H	9.42862146	1.84316428	1.87201890
H	7.66938280	1.91450528	2.17271397
H	5.76374806	-4.14721827	2.49284007
H	5.13202028	-5.36070053	1.35956266
H	6.88077307	-5.12039997	1.51234562
H	7.05587746	-4.73371094	-0.99679649
H	5.30217056	-4.97335251	-1.15938474
H	6.05939981	-3.49088595	-1.78110638

Table S3. Cartesian coordinate of optimized structure of E_2P_2 thiolate of Au_{13} cluster in the one-electron oxidized state

Au	-3.86633346	-3.07700565	-2.37228734

Au	-3.95077046	-0.33695538	-3.25512149
Au	-3.36743723	1.79094996	-1.40413730
Au	-3.45187423	4.53100024	-2.28697145
Au	-2.78410398	3.91885530	0.44684689
Au	-2.69966698	1.17880502	1.32968105
Au	-3.28300022	-0.94910031	-0.52130314
Au	-3.19856321	-3.68915059	0.36153101
Au	-2.53079297	-4.30129553	3.09534936
Au	-2.61522998	-1.56124525	2.21251520
Au	-2.03189674	0.56666009	4.06349939
Au	-2.11633374	3.30671036	3.18066524
Au	-1.49522687	-1.83152735	-3.43107806
S	-0.50086014	-0.99678234	-0.93538627
C	1.06964633	-0.44709735	-0.82323109
S	2.45467100	-1.52731403	-0.76873023
C	1.48285719	0.91474558	-0.74811821
C	3.56907677	-0.16968609	-0.64123412
C	2.85771049	1.06351006	-0.64393214
O	0.57295328	1.88805709	-0.83355745
C	4.94766089	-0.32435430	-0.58283453
O	3.54704747	2.22071824	-0.63694700
C	0.64878022	2.93947802	0.12474905
S	6.09144435	1.01918386	-0.53629235
C	5.63847741	-1.56233835	-0.56368890
C	3.13004942	3.25821208	0.25912835
C	1.79752105	3.91408083	-0.08525485
H	-0.31132121	3.46704753	0.02371529
H	0.68466590	2.49665376	1.13772325
C	7.45169151	-0.08734233	-0.45104662
C	7.01478298	-1.43088312	-0.48322459
O	4.96184639	-2.71671824	-0.67062188
H	3.09939804	2.84845409	1.28364190
H	3.93912583	3.99749890	0.20437902
C	1.58745595	5.05356026	0.91294942
C	1.79366599	4.44913390	-1.51267714
C	8.78195490	0.33206445	-0.38350220
O	7.91068064	-2.43871819	-0.50459773
C	5.23267729	-3.74376079	0.29097259
H	1.54908925	4.68935977	1.95048696
H	2.39454777	5.79485797	0.84018334
H	0.64020496	5.57163820	0.70803554
H	0.81916890	4.90253216	-1.74498631
H	2.56667758	5.21947417	-1.64063713
H	1.97663848	3.65573208	-2.24600733
C	9.25694953	1.65311493	-0.36736637
S	10.14764745	-0.79180368	-0.32771554
C	7.72883386	-3.49262121	0.44276188
C	6.57807877	-4.44031625	0.12010938
H	5.14265882	-3.31113348	1.30252760
H	4.41772385	-4.46469762	0.15133144
C	10.64247172	1.75843907	-0.28973544
O	8.44307317	2.72224359	-0.42807567
C	11.30247228	0.52663091	-0.25843458
H	8.67885826	-4.04230091	0.42629888
H	7.60029120	-3.05295441	1.44770044
C	6.72000982	-5.00781079	-1.28783395
C	6.62758092	-5.56407112	1.15563340
O	11.29232954	2.94564049	-0.24108882
C	9.14731088	3.93187690	-0.72564626
C	12.69305600	0.31015079	-0.18129942

H	7.68034376	-5.53032586	-1.39713698
H	5.91952181	-5.73156593	-1.49263082
H	6.67170292	-4.22442247	-2.05220328
H	5.81942174	-6.28753574	0.98582532
H	7.57792219	-6.11063465	1.08867935
H	6.52880792	-5.18232263	2.18222132
C	10.41538325	4.01863171	0.09194373
H	8.46316804	4.75158694	-0.49065950
H	9.38182488	3.95103877	-1.79941838
C	13.36524975	-0.91131130	-0.19010948
S	13.86818156	1.62706368	-0.08912097
H	10.18024117	3.97663936	1.16605250
H	10.95898195	4.94325122	-0.12137968
C	14.76315761	-0.79895681	-0.11387871
O	12.73688500	-2.09794598	-0.26745873
C	15.19996792	0.50864295	-0.05007689
O	15.59412178	-1.86683685	-0.09782359
C	13.62810410	-3.17876686	-0.57178774
S	16.87894906	0.93253368	0.06991853
C	14.90006735	-3.06277398	0.23650138
H	13.85396346	-3.15906976	-1.64744258
H	13.08421287	-4.09704358	-0.33364899
C	16.77415022	2.74206179	0.14749911
H	15.57977605	-3.89100279	0.01640871
H	14.66738039	-3.06481974	1.31254680
H	16.20135024	3.06903226	1.02255307
H	17.80325603	3.09913771	0.24625829
H	16.34442707	3.15544330	-0.77179178