Electronic Supplementary Information

Novel tetranuclear triarylantimony(V) complexes with (±)-mandelic acid ligand: synthesis, characterization, *in vitro* cytotoxicity and DNA binding properties

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General procedures:

All operations were carried out under a pure nitrogen atmosphere using standard Schlenk tube techniques. All solvents were dried by standard procedures and degassed prior to use. Elemental analyses were performed on a PE-2400-II elemental analyzer. ^{1}H, ^{13}C NMR spectra were recorded on Varian Mercury Plus400 spectrometer, using 5 mm tuneable broad-band probe. Appropriate chemical shifts in ^{1}H and ^{13}C NMR spectra were related to the residual signals of the solvents (DMSO-d_6: $\delta(^{1}H)$ = 2.50 ppm and $\delta(^{13}C)$ = 39.52 ppm). X-single crystal structures were performed on a Bruker Smart-1000 CCD diffractometer. Fluorescent spectra were performed on a Hitachi F-7000 fluorescence spectrophotometer. ESI-Q-TOF detection is performed with a Bruker microTOF-Q mass spectrometer (Bruker Daltonics Inc., Billerica, MA), and the mass spectra are obtained in the positive mode. MS image analysis is performed with DataAnalysis, a proprietary software program provided by Bruker. A 500 mL syringe is obtained from Hamilton (Bonaduz AG, Switzerland).

Experimental Section

All operations on air-sensitive compounds were carried out under a nitrogen atmosphere with the use of Schlenk techniques. All solvents were dried by standard procedures and degassed prior to use.

Ⅰ The synthesis of fluoro-substituted triarylantimony dichloride (see Scheme S1)

1: $(4\text{-}FC_6H_4)_3Sb$, $(3\text{-}FC_6H_4)_3Sb$ and $(3, 4, 5\text{-}F_3C_6H_2)_3Sb$

1) $(4\text{-}FC_6H_4)_3Sb$: $4\text{-}FC_6H_4Br$ (0.5 mol), dissolved in dry ether, was added dropwise to 12.5 g of Mg turnings at 0 °C. The Grignard solution was cooled to - 12 °C and 0.15 mol of $SbCl_3$ (34.2 g), dissolved in 50 ml ether slowly added. After completion of the reaction, the mixture was treated with saturated NH_4Cl solution; the ether layer separated and dried over Na_2SO_4, and evaporated *in vacuo*, the residue being recrystallized from dichloromethane (Yield 46.4 g, 76% based on $SbCl_3$).

2) $(3\text{-}FC_6H_4)_3Sb$ was obtained in the similar manner as $(4\text{-}FC_6H_4)_3Sb$: $3\text{-}FC_6H_4Br$ (0.5 mol), $SbCl_3$ (34.2 g, 0.15 mol). Yield 48.8 g, 80% based on $SbCl_3$.

3) $(3, 4, 5\text{-}F_3C_6H_2)_3Sb$ was obtained in the similar manner as $(4\text{-}FC_6H_4)_3Sb$: $3, 4, 5\text{-}F_3C_6H_2Br$ (0.5 mol), $SbCl_3$ (34.2 g, 0.15 mol). Yield 52.5 g, 68% based on $SbCl_3$.

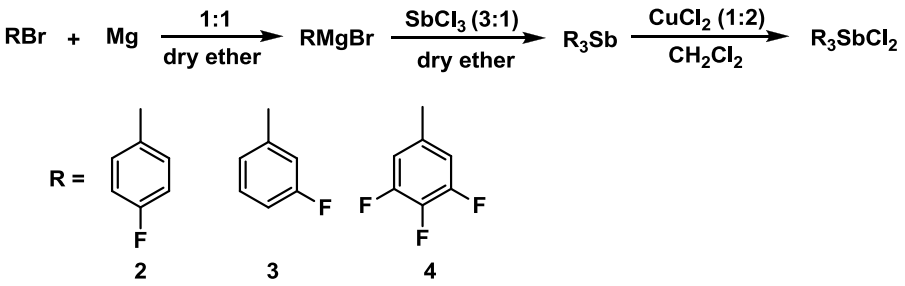
2: $(4\text{-}FC_6H_4)_3SbCl_2$, $(3\text{-}FC_6H_4)_3SbCl_2$ and $(3, 4, 5\text{-}F_3C_6H_2)_3SbCl_2$

1) $(4\text{-}FC_6H_4)_3SbCl_2$: $(4\text{-}FC_6H_4)_3Sb$ (40.7 g, 0.1 mol) was dissolved in dichloromethane at 6 °C and then 0.2 mol of $CuCl_2$ (26.9 g), dissolved in 50 ml ethanol slowly added. After completion of the reaction, the liquid was separated and evaporated *in vacuo*. The obtained white powder was recrystallized from dichloromethane (Yield 31.1 g, 65% based on $(4\text{-}FC_6H_4)_3Sb$).

2) $(3\text{-}FC_6H_4)_3SbCl_2$ was obtained in the similar manner as $(4\text{-}FC_6H_4)_3SbCl_2$: $(3\text{-}FC_6H_4)_3Sb$ (40.7 g, 0.1 mol), $CuCl_2$ (26.9 g, 0.2 mol). The obtained white powder was recrystallized from dichloromethane (Yield 33.5 g, 70% based on $(3\text{-}FC_6H_4)_3Sb$).

3) $(3, 4, 5\text{-}F_3C_6H_2)_3SbCl_2$ was obtained in the similar manner as $(4\text{-}FC_6H_4)_3SbCl_2$: $(3, 4, 5\text{-}F_3C_6H_2)_3Sb$ (51.5 g, 0.1 mol), $CuCl_2$ (26.9 g, 0.2 mol). The obtained white powder was recrystallized from dichloromethane (Yield 30.5 g, 52% based on $(3, 4, 5\text{-}F_3C_6H_2)_3Sb$).

The molecular structures of fluoro-substituted triarylantimony dichloride were unambiguously determined by the single-crystal X-ray diffraction analysis (Fig. S1) together with the partial atomic numbering scheme.



Scheme S1 Preparation of the fluoro-substituted triarylantimony dichloride studied

Crystallographic data: **a**$_2$: $C_{18}H_{12}Cl_2F_3Sb$, M=477.93, monoclinic, $P2_1/c$, T=298(2) K, a=14.6332(8), b=18.2552(7), c=15.3949(9) Å, β=118.235(7)°, V=3623.2(3) Å^3, Z=8, ρ_{calcd}=1.752 g cm^{-3}, μ=1.843 mm^{-1}, 0.45×0.42×0.35 mm^3, $2\theta_{max}$=50.04; 23794 reflections collected, 6406 independent and used in the structure refinement of 433 parameters. R_{int}=0.0655, R_1=0.0424 (I >2σ(I)), wR_2=0.0755 (all data), min./max. residual electron density: 0.468/-0.415 eÅ^{-3}, CCDC 915548. **a**$_3$: $C_{18}H_{11}Cl_2F_3Sb$, M=476.92, monoclinic, $C2/c$, T=298(2) K, a=15.7459(13), b=10.8520(9), c=10.6081(11) Å, β=106.4830(10)°, V=1738.2(3) Å^3, Z=4, ρ_{calcd}=1.822 g cm^{-3}, μ=1.920 mm^{-1}, 0.48×0.42×0.41 mm^3, $2\theta_{max}$=50.04; 4209 reflections collected, 1532 independent and used in the structure refinement of 116 parameters. R_{int}=0.0387, R_1=0.0335 (I >2σ(I)), wR_2=0.0877 (all data), min./max. residual electron density: 0.700/-1.509 eÅ^{-3}, CCDC 915546. **a**$_4$: $C_{18}H_6Cl_2F_9Sb$, M=585.88, monoclinic, $C2/c$, T=298(2) K, a=16.3902(13), b=11.1424(6), c=10.7202(5) Å, β=103.8220(10)°, V=1901.1(2) Å^3, Z=4, ρ_{calcd}=2.047 g cm^{-3}, μ=1.820 mm^{-1}, 0.43×0.42×0.35 mm^3, $2\theta_{max}$=50.04; 4637 reflections collected, 1681 independent and used in the structure refinement of 138 parameters. R_{int}=0.0499, R_1=0.0374 (I >2σ(I)), wR_2=0.0717 (all data), min./max. residual electron density: 0.528/-0.609 eÅ^{-3}, CCDC 915547.

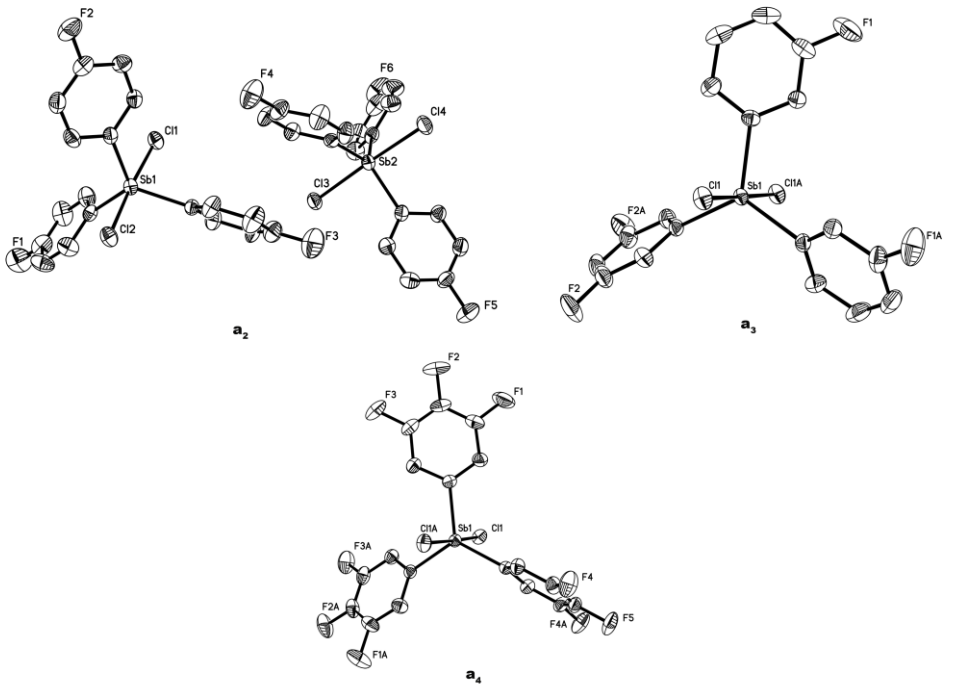


Fig. S1 Molecular structures of fluoro-substituted triarylantimony dichloride **a**$_2$-**a**$_4$, with ellipsoids set at 30% probability. Hydrogen atoms are omitted for clarity.

Ⅱ The synthesis of tetranuclear triaryl antimony(V) complexes

1: Sodium ethoxide (4 mmol) was added to a stirring solution of (±)-mandelic acid (0.608 g, 4 mmol) in methanol (30 ml) and heated under reflux for 0.5 h. After the addition of $(C_6H_5)_3SbCl_2$ (0.848 g, 2 mmol) to the reactor, the resulting mixture was stirred and refluxed for additional 8 h. The reaction solution thus obtained was filtered and evaporated in vacuo forming a white solid. Colorless single crystals of **c**$_1$ were obtained by re-crystallization from ethyl ether-petroleum ether solution (v/v 1.5:1) at room temperature. Yield 0.48 g, 46%; m.p. 151-153°C. Found: C 61.8; H 4.7. Calc. for $C_{108}H_{94}O_{13}Sb_4$: C 62.2; H 4.5%. ^{1}H NMR (400 MHz, DMSO-d$_6$, 25°C): δ 7.59 (d, 24H, *ortho*-Ph), 7.43 (t, 12H, *para*-Ph), 7.40 (t, 24H, *meta*-Ph), 7.38 (d, 8H, *ortho*-(-C(H)Ph-)), 7.17~7.22 (m, 12H, *meta*- and *para*-(-C(H)Ph-)), 5.17 (s, 4H, -C(H)Ph-), 3.36 (q, 4H, -OCH_2-), 1.07 ppm (t, 6H, -OCH_2CH_3). ^{13}C NMR (100 MHz, DMSO-d$_6$, 25°C): δ 175.1 (COO), 143.7, 142.0, 134.9, 130.5, 129.3, 128.1, 127.9, 127.3 (Ph and -C(H)Ph-), 74.7 (-C(H)Ph-), 65.6 (-OCH_2-), 15.9 ppm (-OCH_2CH_3). The ESI-Q-TOF MS: *m/z* 383.0325 ((R1)$_3$Sb+CH_3O^-), 1029.0772 (((R1)$_3$Sb)$_2$L$_2$+Na^+) and 1531.1463 (((R1)$_3$Sb)$_3$L$_3$+Na^+).

2: Complex **c**$_2$ was prepared in the similar way as **c**$_1$: $(4\text{-}FC_6H_4)_3SbCl_2$ (0.956 g, 2 mmol). Colorless single crystals of **2** were obtained by re-crystallization from ethyl ether-petroleum ether solution (v/v 3:1) at room temperature.

Yield 0.62 g, 54%; m.p. 162-168°C. Found: C 56.5; H 3.2. Calc. for $C_{108}H_{82}F_{12}O_{13}Sb_4$: C 56.3; H 3.6%. ^{1}H NMR (400 MHz, DMSO-d_6, 25°C): δ 7.62~7.45 (m, 48H, *ortho*- and *meta*-Ph), 7.36 (d, 8H, *ortho*-(-C(H)Ph-)), 7.15~7.28 (m, 12H, *meta*- and *para*-(-C(H)Ph-)), 5.18 (s, 4H, -C(H)Ph-). ^{13}C NMR (100 MHz, DMSO-d_6, 25°C): δ 174.9 (COO), 165.1, 162.6, 141.5, 139.0, 137.0, 136.6, 127.5, 116.5 (Ph and -C(H)Ph-), 74.6 (-C(H)Ph-). The ESI-Q-TOF MS: *m/z* 437.0028 ($(R2)_3Sb+CH_3O^-$), 955.0180 ($((R2)_3Sb)_2L+CH_3O^-$), 1695.0772 ($((R2)_3Sb)_3L_3+Na^+$).

3: Complex $\mathbf{c_3}$ was prepared in the similar way as $\mathbf{c_1}$: $(3\text{-}FC_6H_4)_3SbCl_2$ (0.956 g, 2 mmol). Colorless single crystals of **3** were obtained by re-crystallization from ethyl ether-petroleum ether solution (v/v 1.5:1) at room temperature. Yield 0.56 g, 50%; m.p. 179-184°C. Found: C 55.8; H 3.7. Calc. for $C_{104}H_{72}F_{12}O_{12}Sb_4$: C 56.0; H 3.3%. ^{1}H NMR (400 MHz, DMSO-d_6, 25°C): δ 7.55~7.50 (m, 48H, *ortho*-, *meta*- and *para*-Ph), 7.33 (d, 8H, *ortho*-(-C(H)Ph-)), 7.19~7.27 (m, 12H, *meta*- and *para* -C(H)Ph-), 5.26 (s, 4H, -C(H)Ph-). ^{13}C NMR (100 MHz, DMSO-d_6, 25°C): δ 174.8 (COO), 145.9，141.3，130.7，128.8，127.8，127.3，121.1，118.0 (Ph and -C(H)Ph-), 74.1 (-C(H)Ph-).The ESI-Q-TOF MS: *m/z* 437.0038 ($(R3)_3Sb+CH_3O^-$), 594.9764 ($(R3)_3SbL+K^+$), 995.0200 ($((R3)_3Sb)_2L+CH_3O^-$), 1711.0548 ($((R3)_3Sb)_3L_3+K^+$).

4: Complex $\mathbf{c_4}$ was prepared in the similar way as $\mathbf{c_1}$: $(3,4,5\text{-}F_3C_6H_2)_3SbCl_2$ (1.172 g, 2 mmol). Colorless single crystals of **4** were obtained by re-crystallization from ethyl ether-petroleum ether solution (v/v 3:1) at room temperature. Yield 0.80 g, 60%; m.p. 215-217°C. Found: C 47.6; H 2.4. Calc. for $C_{108}H_{58}F_{36}O_{13}Sb_4$: C 47.4; H 2.1%. ^{1}H NMR (400 MHz, DMSO-d_6, 25°C): δ 7.92 (d, 24H, *ortho*-Ph), 7.64 (d, 8H, *ortho*-(-C(H)Ph-)), 7.30~7.43 (m, 12H, *meta*- and *para*-(-C(H)Ph-)), 5.32 (s, 4H, -C(H)Ph-). ^{13}C NMR (100 MHz, DMSO-d_6, 25°C): δ 167.9 (COO), 152.5, 149.9, 142.2, 139.2, 133.2, 129.8, 127.7, 118.9 (Ph and -C(H)Ph-), 74.5 (-C(H)Ph-). The ESI-Q-TOF MS: *m/z* 702.9186 ($(R4)_3SbL+K^+$), 1352.9208 ($((R4)_3Sb)_2L_2+Na^+$), 2016.9386 ($((R4)_3Sb)_3L_3+Na^+$).

Crystallographic data: $\mathbf{c_1}$: $C_{108}H_{94}O_{13}Sb_4$, M=2086.83, monoclinic, $P2_1/c$, T=298(2) K, a=14.0440(13), b=42.816(3), c=17.3410(16) Å, β=114.915(2)°, V=9456.8(14) Å^3, Z=4, ρ_{calcd}=1.466 g cm^{-3}, μ=1.193 mm^{-1}, 0.46×0.45×0.43 mm^3, $2\theta_{max}$=50.04; 46810 reflections collected, 16675 independent and used in the structure refinement of 1128 parameters. R_{int}=0.0594, R_1=0.0693 (I >2σ(I)), wR_2=0.1497 (all data), min./max. residual electron density: 1.335/-2.007 eÅ^{-3}, CCDC 888519. $\mathbf{c_2}$: $C_{108}H_{82}F_{12}O_{13}Sb_4$, M=2302.82, Triclinic, $P\bar{1}$, T=120 K, a= 11.6366(7), b= 14.5216(8), c= 16.3719(10) Å, α= 75.2460(10) °, β=84.121(2) °, γ=72.0700(10) °, V=2544.5(3) Å^3, Z=1, ρ_{calcd}=1.551 g cm^{-3}, μ=1.136 mm^{-1}, 0.45×0.40×0.36 mm^3, $2\theta_{max}$=50.04; 15668 reflections collected, 8965 independent and used in the structure refinement of 642 parameters. R_{int}=0.0538, R_1=0.0475 (I >2σ(I)), wR_2=0.1185 (all data), min./max. residual electron density: 1.331/-0.680eÅ^{-3}, CCDC 931285. $\mathbf{c_3}$: $C_{104}H_{72}F_{12}O_{12}Sb_4$, M=2228.62,

Triclinic, $P\bar{1}$, T=298(2) K, a=13.7102(12), b=14.5439(14), c=23.0914(19) Å, α=87.3790(10)°, β=85.6180(10)°, γ=89.104(2)°, V=4585.8(7) Å^3, Z=2, ρ_{calcd}=1.614 g cm^{-3}, μ=1.253 mm^{-1}, 0.46×0.42×0.39 mm^3, $2\theta_{max}$=50.04; 22038 reflections collected, 15732 independent and used in the structure refinement of 1189 parameters. R_{int}=0.0899, R_1=0.0928 (I >2σ(I)), wR_2=0.2833 (all data), min./max. residual electron density: 1.812/-1.254 eÅ^{-3}, CCDC 905087.

c$_4$: $C_{108}H_{58}F_{36}O_{13}Sb_4$, M=2734.54, Monoclinic, $C2/c$, T=120 K, a= 25.7941(9), b= 16.1264(6), c= 49.486(2) Å, β= 103.146°, V= 20045.0(14) Å^3, Z=8, ρ_{calcd}=1.812 g cm^{-3}, μ= 1.199 mm^{-1}, 0.46×0.42×0.36 mm^3, $2\theta_{max}$=50.04; 38166 reflections collected, 17662 independent and used in the structure refinement of 1484 parameters. R_{int}= 0.0651, R_1= 0.0726 (I >2σ(I)), wR_2= 0.1359 (all data), min./max. residual electron density: 1.459 / -1.138 eÅ^{-3}, CCDC 905275.

Cytotoxicity Assays

The cell lines, human lung carcinoma cell line (A549), human colon adenocarcinoma (Caco-2), human colon carcinoma cell line (HCT-116) and rat hepatocytes cell line (BRL) were used for screening. Cell lines were grown and maintained in the logarithmic phase at 37 ℃ in humidified incubators in an atmosphere of 5% CO_2 using the following culture media containing 10% fetal bovine serum and 1% antibiotics (100 units·mL^{-1} penicillin and 100 μg·mL^{-1} streptomycin): (i) DMEM medium for A549 cell, (ii) IMDM medium for Caco-2 cell, (iii) McCoy's 5a medium for HCT-116 cell, (iv) RPMI-1640 medium for BRL cell. Cell viability in compound-treated cultures was evaluated by using a system based on the tetrazolium compound MTT assay. The light absorption was measured at 490 nm using ELx808 Absorbance Microplate Reader (Bio-Tek Co., USA).

The colorimetric MTT assay was used to determine the cytotoxicity of compounds. All cells were seeded onto a 96-well plate at a concentration of 1000-1500 cells/well, respectively, in 100 μL of growth medium and were incubated for 12 h. The medium was then removed, and 200 μL of new growth medium containing various concentrations of complexes was added. After the medium was removed 48 h later, 100 μL of a 0.5 mg/mL solution of MTT in medium was added, and the plate was incubated for an additional 4 h. The medium/MTT mixture was aspirated, after that 100 μL of DMSO were added to dissolve the insoluble purple formazan precipitates produced by MTT reduction. The plate was shaken for 20 min on a plate shaker to ensure complete dissolution. The optical density of each well was measured at 490 nm wavelength. The cytotoxic activity was determined by expressing the mean optical densities for drug-treated cells at the concentration as a percentage of those for untreated cells. IC_{50} values were extrapolated from the resulting curves. The reported IC_{50} values are the averages from at least three independent experiments, each of which consisted of three replicates per concentration level. Dilutions of compounds in growth medium were prepared from concentrated solutions (20, 15, 10, 5, 1 μM) in DMSO.

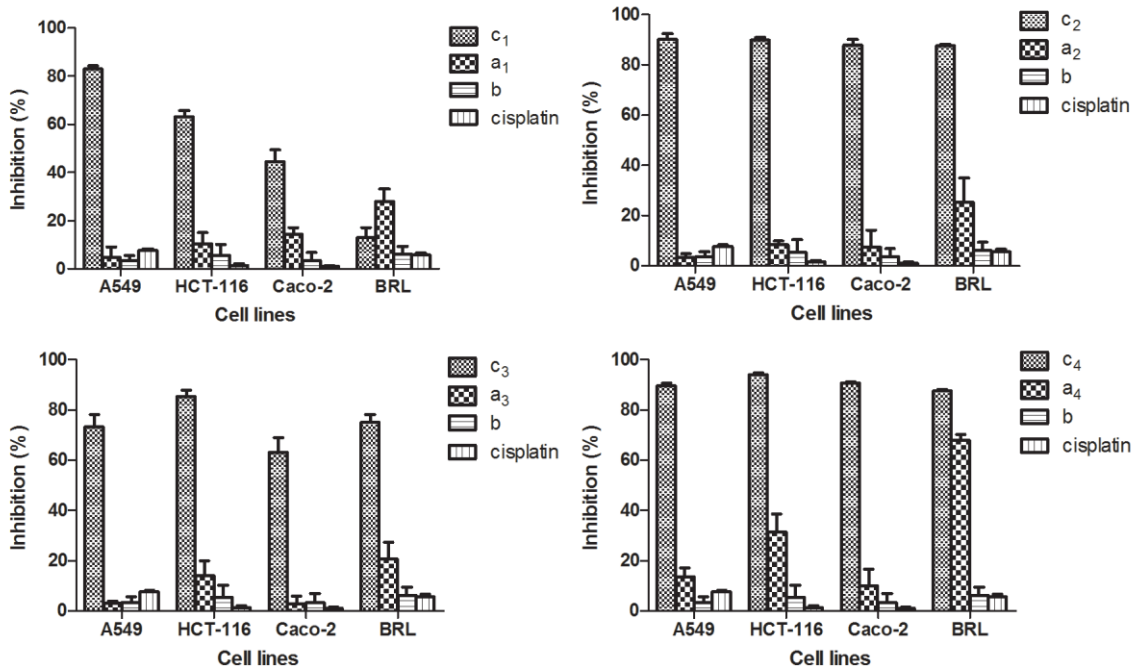


Fig. S2 Cytotoxic activity of all compounds against three human tumor cell lines and one normal cell line with dose level of 10 μM.

Fluorescent spectra

In order to investigate the interaction between complexes and DNA, ethidium bromide (EB) is used as a probe. EB is a weak fluorescent reagent, but in the presence of DNA, its emission intensity can be greatly enhanced because of its strong intercalation between the adjacent DNA base pairs. It has been reported that this enhanced fluorescence could be quenched, at least partly by the addition of another molecule.[1] So the fluorescence quenching assays of EB bound to excess of DNA is utilized to differentiate intercalating and non-intercalative ligands.

The fluorescence quenching curves of EB-DNA system were determined in different concentrations of DMSO solution of complexes (they are stable in DMSO). From the fluorescent emissive spectra of complexes, we could see that the fluorescence emission at *ca.* 590 nm had been quenched obviously after the coordination with antimony, while the EB-DNA system had a strong fluorescence emission. The quenching of the fluorescent spectra of EB-DNA-organoantimony (V) complexes system could be utilized to investigate the interaction between complexes and DNA. With the increasing of concentration of complexes, fluorescence quenching of EB-DNA system were occurred in different extent, and this may be because complexes bind to DNA in an intercalative mode in different degree. The fluorescence quenching curve of EB-DNA by complexes were shown in Fig. 1S, and we can see that the addition of samples to DNA pretreated with EB causes appreciable reduction in the emission intensity, indicating the replacement of EB by complexes. According to the classical Stern-Volmer equation:[2] $I_0/I = 1 + K_{sv}r$ where I_0 and I represent fluorescence intensities in the absence and presence of samples respectively, and r corresponds to the concentration ratio of complexes to DNA. K_{sv}, linear Stern-Volmer constant, can be obtained from the slope of I_0/I versus r linear plot and depends on the ratio of the concentration of EB bond to DNA.

CT-DNA and EB were dissolved in 10 mmol•L^{-1} trihydroxymethylaminomethane (tris)-HCl buffer solution and the CT-DNA concentration per nucleotide was determined by absorption spectroscopy using the molar absorption coefficient (6600 L•mol^{-1}•cm^{-1}) at 260 nm, while the EB concentration was calculated by the ratio of the mass to their molecular weight. Compounds were dissolved in DMSO and the concentration was determined as EB. The sample was added to the solution containing 25μmol•L^{-1} CT-DNA and 3μmol•L^{-1} EB at different concentrations (0~125μmol•L^{-1}). After two hours, the fluorescence quenching spectra were recorded at 530~700 nm with all samples

excited at 258 nm.

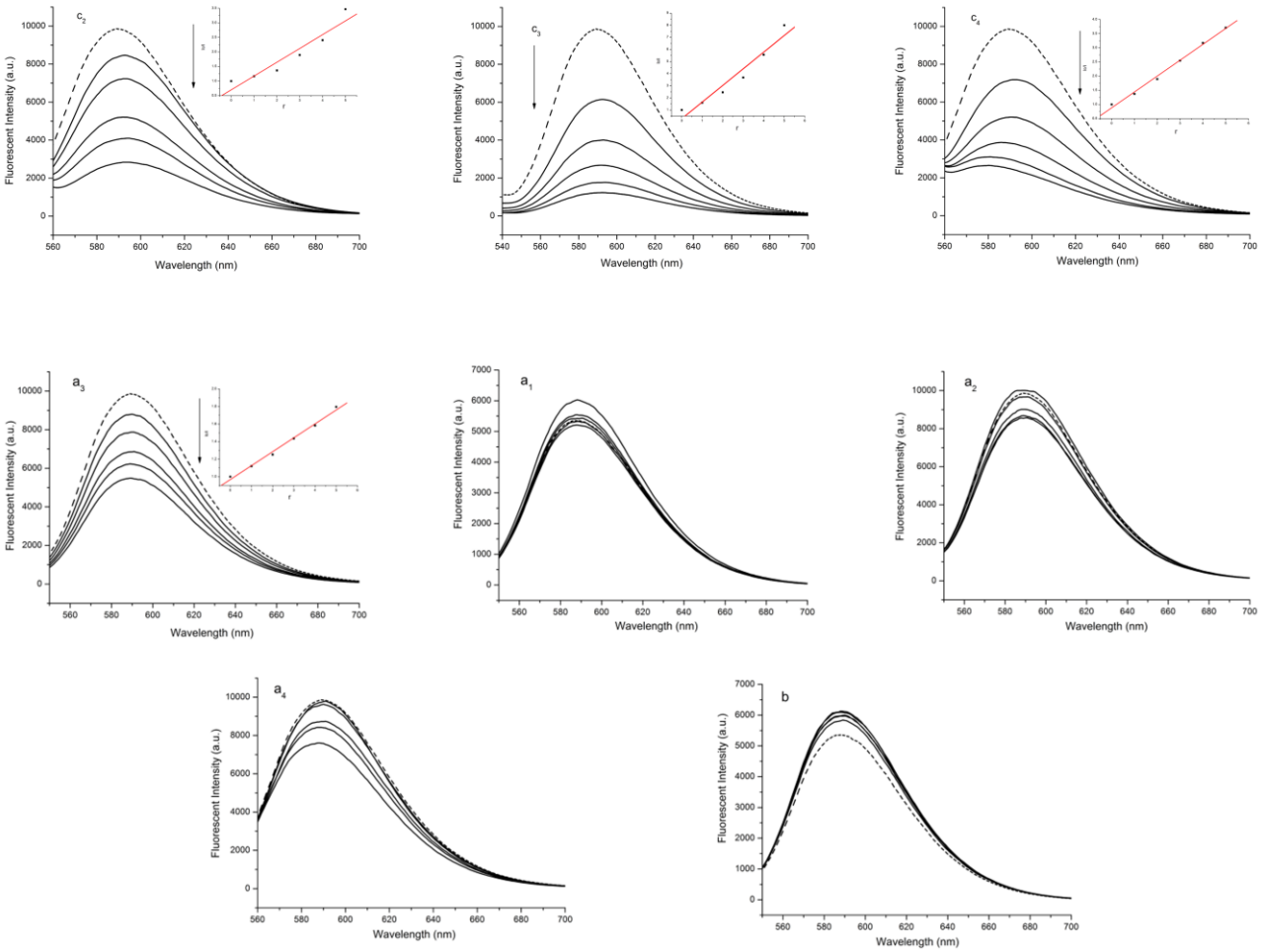


Fig. S3 Emission spectra from EB bound DNA in the absence (---) and in the presence of [complexes] 0-125 μM concentration, [DNA] 25 μM; [EB] 3 μM. Arrow shows changes in the emission intensity upon addition of increasing concentration of the complexes. Inset: Plots of I_0/I vs r (r= [Complex]/[DNA]) with experimental data points. λ_{ex} = 258 nm.

Table S1 Selected bond lengths (Å) and angles (°) for $\mathbf{c_1}$

Bond lengths			
Sb(1)-O(1)	1.994(6)	Sb(1)-O(2)	2.170(5)
Sb(1)-O(6)	2.337(6)	Sb(1)-C(1)	2.138(8)
Sb(1)-C(7)	2.147(9)	Sb(1)-C(13)	2.136(8)
C(19)-O(2)	1.266(10)	C(19)-O(3)	1.246(10)
C(20)-O(1)	1.395(10)	C(19)-C(20)	1.544(12)
Sb(2)-O(4)	1.973(6)	Sb(2)-O(5)	2.181(6)
Sb(2)-O(9)	2.465(6)	Sb(2)-C(27)	2.146(9)
Sb(2)-C(33)	2.129(10)	Sb(2)-C(39)	2.137(9)
C(45)-O(5)	1.265(9)	C(45)-O(6)	1.233(9)
C(46)-O(4)	1.416(10)	C(45)-C(46)	1.530(11)
Sb(3)-O(7)	1.979(5)	Sb(3)-O(8)	2.197(5)
Sb(3)-O(12)	2.349(6)	Sb(3)-C(53)	2.125(9)
Sb(3)-C(59)	2.149(9)	Sb(3)-C(65)	2.140(10)
C(71)-O(8)	1.272(10)	C(71)-O(9)	1.248(10)
C(72)-O(7)	1.397(9)	C(71)-C(72)	1.517(12)
Sb(4)-O(3)	2.359(6)	Sb(4)-O(10)	1.982(6)
Sb(4)-O(11)	2.190(6)	Sb(4)-C(79)	2.158(9)
Sb(4)-C(85)	2.131(10)	Sb(4)-C(91)	2.139(9)
C(97)-O(11)	1.262(10)	C(97)-O(12)	1.259(10)
C(98)-O(10)	1.415(10)	C(97)-C(98)	1.513(12)
Bond angles			
O(1)-Sb(1)-C(1)	158.5(3)	O(1)-Sb(1)-C(7)	94.2(3)
O(1)-Sb(1)-C(13)	93.6(3)	O(1)-Sb(1)-O(2)	77.6(2)
O(1)-Sb(1)-O(6)	82.7(2)	O(2)-Sb(1)-C(1)	84.0(3)
O(2)-Sb(1)-C(7)	92.7(3)	O(2)-Sb(1)-C(13)	164.3(3)

O(2)-Sb(1)-O(6)	78.4(2)	O(6)-Sb(1)-C(1)	82.8(3)
O(6)-Sb(1)-C(7)	171.0(3)	O(6)-Sb(1)-C(13)	87.7(3)
C(1) -Sb(1)-C(7)	97.8(3)	C(1)-Sb(1)-C(13)	101.6(3)
C(7)-Sb(1)-C(13)	100.9(4)	O(1)-C(20)-C(19)	111.1(7)
O(2)-C(19)-C(20)	116.3(7)	C(20)-O(1)-Sb(1)	117.6(5)
C(19)-O(2)-Sb(1)	113.7(5)		
O(4)-Sb(2)-C(27)	91.0(3)	O(4)-Sb(2)-C(33)	100.2(3)
O(4)-Sb(2)-C(39)	154.3(3)	O(4)-Sb(2)-O(5)	76.7(2)
O(4)-Sb(2)-O(9)	81.4(2)	O(5)-Sb(2)-C(27)	163.0(3)
O(5)-Sb(2)-C(33)	95.0(3)	O(5)-Sb(2)-C(39)	85.1(3)
O(5)-Sb(2)-O(9)	76.8(2)	O(9)-Sb(2)-C(27)	89.9(3)
O(9)-Sb(2)-C(33)	171.2(3)	O(9)-Sb(2)-C(39)	76.9(3)
C(27) -Sb(2)-C(33)	98.7(4)	C(27)-Sb(2)-C(39)	102.4(4)
C(33)-Sb(2)-C(39)	99.4(3)	O(4)-C(46)-C(45)	110.0(6)
O(5)-C(45)-C(46)	116.2(7)	C(46)-O(4)-Sb(2)	118.8(5)
C(45)-O(5)-Sb(2)	114.9(5)		
O(7)-Sb(3)-C(53)	91.9(3)	O(7)-Sb(3)-C(59)	156.4(3)
O(7)-Sb(3)-C(65)	94.5(3)	O(7)-Sb(3)-O(8)	76.6(2)
O(7)-Sb(3)-O(12)	81.5(2)	O(8)-Sb(3)-C(53)	164.0(3)
O(8)-Sb(3)-C(59)	85.3(3)	O(8)-Sb(3)-C(65)	91.4(3)
O(8)-Sb(3)-O(12)	79.9(2)	O(12)-Sb(3)-C(53)	87.5(3)
O(12)-Sb(3)-C(59)	80.4(3)	O(12)-Sb(3)-C(65)	171.1(3)
C(53) -Sb(3)-C(59)	102.4(4)	C(53)-Sb(3)-C(65)	100.7(4)
C(59)-Sb(3)-C(65)	101.2(4)	O(7)-C(72)-C(71)	111.0(7)
O(8)-C(71)-C(72)	116.6(7)	C(72)-O(7)-Sb(3)	119.1(5)
C(71)-O(8)-Sb(3)	113.9(5)		
O(3)-Sb(4)-C(79)	80.8(3)	O(3)-Sb(4)-C(85)	169.7(3)
O(3)-Sb(4)-C(91)	88.7(3)	O(3)-Sb(4)-O(10)	83.4(2)

O(3)-Sb(4)-O(11)	74.5(2)	O(10)-Sb(4)-C(79)	159.7(3)
O(10)-Sb(4)-C(85)	94.1(3)	O(10)-Sb(4)-C(91)	91.4(3)
O(10)-Sb(4)-O(11)	77.2(2)	O(11)-Sb(4)-C(79)	86.3(3)
O(11)-Sb(4)-C(85)	95.2(3)	O(11)-Sb(4)-C(91)	160.6(3)
C(79) -Sb(4)-C(85)	99.2(4)	C(79)-Sb(4)-C(91)	100.9(4)
C(85)-Sb(4)-C(91)	101.3(4)	O(10)-C(98)-C(97)	110.7(7)
O(11)-C(97)-C(98)	117.6(8)	C(98)-O(10)-Sb(4)	118.2(5)
C(97)-O(11)-Sb(4)	113.0(5)		

Table S2 Selected bond lengths (Å) and angles (°) for **c_2**

Bond lengths			
Sb(1)-O(1)	1.995(4)	Sb(1)-O(2)	2.182(4)
Sb(1)-O(6)	2.322(4)	Sb(1)-C(9)	2.130(6)
Sb(1)-C(15)	2.131(5)	Sb(1)-C(21)	2.148(6)
C(1)-O(2)	1.265(7)	C(2)-O(1)	1.418(6)
C(2)-C(3)	1.513(8)	C(1)-C(2)	1.541(7)
Sb(2)-O(4)	1.986(4)	Sb(2)-O(5)	2.186(4)
Sb(2)-O(3) #1	2.403(3)	Sb(2)-C(35)	2.130(5)
Sb(2)-C(41)	2.128(6)	Sb(2)-C(47)	2.142(6)
C(27)-O(5)	2.186(4)	C(28)-O(4)	1.428(6)
C(27)-C(28)	1.518(7)	C(28)-C(29)	1.508(8)
Bond angles			
O(1)-Sb(1)-C(9)	92.6(2)	O(1)-Sb(1)-C(15)	91.5(2)
O(1)-Sb(1)-C(21)	158.13(18)	O(1)-Sb(1)-O(2)	77.28(14)
O(1)-Sb(1)-O(6)	75.04(15)	O(2)-Sb(1)-C(9)	90.71(18)
O(2)-Sb(1)-C(15)	163.54(18)	O(2)-Sb(1)-C(21)	86.07(18)
O(2)-Sb(1)-O(6)	76.74(13)	O(6)-Sb(1)-C(9)	169.1(4)
O(6)-Sb(1)-C(15)	89.4(5)	O(6)-Sb(1)-C(21)	163.95(19)
C(9)-Sb(1)-C(15)	101.9(2)	C(9)-Sb(1)-C(21)	101.8(2)
C(15)-Sb(1)-C(21)	101.4(2)	O(1)-C(2)-C(1)	110.5(5)
C(2)-O(1)-Sb(1)	113.4(7)	C(1)-O(2)-Sb(1)	118.1(7)
O(2)-C(1)-C(2)	116.3(5)		
O(4)-Sb(2)-C(35)	95.9(2)	O(4)-Sb(2)-C(41)	90.3(2)
O(4)-Sb(2)-C(47)	157.29(18)	O(4)-Sb(2)-O(5)	77.65(15)
O(4)-Sb(2)-O(3) #1	82.65(14)	O(5)-Sb(2)-C(35)	91.52(18)
O(5)-Sb(2)-C(41)	162.45(19)	O(5)-Sb(2)-C(47)	85.59(19)

O(5)- Sb(2)-O(3) #1	77.44(13)	O(3) #1-Sb(2)-C(35)	168.93(18)
O(3) #1-Sb(2)-C(41)	88.50(17)	O(3) #1-Sb(2)-C(47)	78.79(18)
C(35)-Sb(2)-C(41)	102.5(2)	C(35)-Sb(2)-C(47)	102.5(2)
C(41)-Sb(2)-C(47)	102.1(2)	O(5)-C(27)-C(28)	117.5(5)
O(4)-C(28)-C(27)	110.5(5)	C(27)-O(5)-Sb(2)	112.0(3)
C(28)-O(4)-Sb(2)	117.7(3)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y+1,-z

Table S3 Selected bond lengths (Å) and angles (°) for **c_3**

Bond lengths			
Sb(1)-O(2)	1.972(10)	Sb(1)-O(8)	2.316(11)
Sb(1)-O(9)	2.193(10)	Sb(1)-C(9)	2.155(14)
Sb(1)-C(15)	2.132(19)	Sb(1)-C(21)	2.123(15)
C(1)-O(9)	1.236(18)	C(2)-O(2)	1.394(17)
C(53)-O(8)	1.242(18)	C(1)-C(2)	1.56(2)
Sb(2)-O(4)	2.335(10)	Sb(2)-O(5)	2.177(11)
Sb(2)-O(11)	1.981(9)	Sb(2)-C(35)	2.136(17)
Sb(2)-C(41)	2.139(16)	Sb(2)-C(47)	2.152(17)
C(1)-O(4)	1.243(17)	C(27)-O(5)	1.268(17)
C(28)-O(11)	1.418(17)	C(27)-C(28)	1.51(2)
Sb(3)-O(6)	2.200(11)	Sb(3)-O(10)	1.988(11)
Sb(3)-O(12)	2.366(10)	Sb(3)-C(61)	2.129(16)
Sb(3)-C(67)	2.10(2)	Sb(3)-C(73)	2.149(15)
C(53)-O(6)	1.271(18)	C(54)-O(10)	1.376(17)
C(79)-O(12)	1.223(17)	C(53)-C(54)	1.52(2)
Sb(4)-O(1)	2.184(10)	Sb(4)-O(3)	2.360(11)
Sb(4)-O(7)	1.992(10)	Sb(4)-C(87)	2.147(17)
Sb(4)-C(93)	2.139(17)	Sb(4)-C(99)	2.133(17)
C(79)-O(1)	1.295(17)	C(80)-O(7)	1.401(17)
C(79)-O(12)	1.223(17)	C(79)-C(80)	1.53(2)
Bond angles			
O(2)-Sb(1)-C(9)	93.0(5)	O(2)-Sb(1)-C(15)	156.2(6)
O(2)-Sb(1)-C(21)	94.6(5)	O(2)-Sb(1)-O(8)	84.6(4)
O(2)-Sb(1)-O(9)	75.9(4)	O(8)-Sb(1)-C(9)	85.1(5)

O(8)-Sb(1)-C(15)	82.0(6)	O(8)-Sb(1)-C(21)	173.3(5)
O(8)- Sb(1)-O(9)	77.8(4)	O(9)-Sb(1)-C(9)	160.3(5)
O(9)-Sb(1)-C(15)	82.1(6)	O(9)-Sb(1)-C(21)	95.5(5)
C(9)-Sb(1)-C(15)	105.3(7)	C(9)-Sb(1)-C(21)	101.6(6)
C(15)-Sb(1)-C(21)	96.4(7)	O(9)-C(1)-C(2)	116.6(13)
O(2)-C(2)-C(1)	108.7(13)	C(2)-O(2)-Sb(1)	118.3(9)
C(1)-O(9)-Sb(1)	113.6(10)		
O(4)-Sb(2)-C(35)	89.6(5)	O(4)-Sb(2)-C(41)	77.6(5)
O(4)-Sb(2)-C(47)	169.1(5)	O(4)-Sb(2)-O(5)	77.1(4)
O(4)-Sb(2)-O(11)	83.2(4)	O(5)-Sb(2)-C(35)	162.8(6)
O(5)-Sb(2)-C(41)	87.8(5)	O(5)-Sb(2)-C(47)	92.2(5)
O(5)- Sb(2)-O(11)	77.0(4)	O(11)-Sb(2)-C(35)	90.7(5)
O(11)-Sb(2)-C(41)	157.8(5)	O(11)-Sb(2)-C(47)	96.8(6)
C(35)-Sb(2)-C(41)	100.1(6)	C(35)-Sb(2)-C(47)	101.3(6)
C(41)-Sb(2)-C(47)	99.9(6)	O(5)-C(27)-C(28)	116.4(15)
O(11)-C(28)-C(27)	111.0(13)	C(27)-O(5)-Sb(2)	115.3(11)
C(28)-O(11)-Sb(2)	118.8(9)		
O(6)-Sb(3)-C(61)	163.2(5)	O(6)-Sb(3)-C(67)	93.2(8)
O(6)-Sb(3)-C(73)	82.7(5)	O(6)-Sb(3)-O(10)	75.8(4)
O(6)-Sb(3)-O(12)	78.4(4)	O(10)-Sb(3)-C(61)	92.6(6)
O(10)-Sb(3)-C(67)	95.3(9)	O(10)-Sb(3)-C(73)	154.1(5)
O(10)- Sb(3)-O(12)	82.9(4)	O(12)-Sb(3)-C(61)	88.2(5)
O(12)-Sb(3)-C(67)	171.6(8)	O(12)-Sb(3)-C(73)	78.8(5)
C(61)-Sb(3)-C(67)	100.0(9)	C(61)-Sb(3)-C(73)	104.8(6)
C(67)-Sb(3)-C(73)	100.2(8)	O(6)-C(53)-C(54)	115.9(14)
O(10)-C(54)-C(53)	111.2(13)	C(53)-O(6)-Sb(3)	112.9(10)
C(54)-O(10)-Sb(3)	117.9(9)		
O(1)-Sb(4)-C(87)	84.8(5)	O(1)-Sb(4)-C(93)	94.7(6)

O(1)-Sb(4)-C(99)	161.3(5)	O(1)-Sb(4)-O(3)	77.4(4)
O(1)-Sb(4)-O(7)	78.0(4)	O(3)-Sb(4)-C(87)	81.6(6)
O(3)-Sb(4)-C(93)	171.7(6)	O(3)-Sb(4)-C(99)	85.1(6)
O(3)- Sb(4)-O(7)	82.5(4)	O(7)-Sb(4)-C(87)	158.7(6)
O(7)-Sb(4)-C(93)	93.4(6)	O(7)-Sb(4)-C(99)	93.2(5)
C(87)-Sb(4)-C(93)	100.6(7)	C(87)-Sb(4)-C(99)	99.3(6)
C(93)-Sb(4)-C(99)	102.4(7)	O(1)-C(79)-C(80)	116.3(13)
O(7)-C(80)-C(79)	111.9(13)	C(79)-O(1)-Sb(4)	111.9(9)
C(80)-O(7)-Sb(4)	117.7(9)		

Table S4 Selected bond lengths (Å) and angles (°) for **c_4**

Bond lengths			
Sb(1)-O(1)	2.178(6)	Sb(1)-O(3)	1.973(5)
Sb(1)-O(4)	2.383(5)	Sb(1)-C(33)	2.122(8)
Sb(1)-C(39)	2.137(8)	Sb(1)-C(45)	2.125(9)
C(1)-O(1)	1.255(9)	C(2)-O(3)	1.411(9)
C(9)-O(4)	1.257(8)	C(1)-C(2)	1.517(10)
Sb(2)-O(5)	2.144(5)	Sb(2)-O(6)	1.975(5)
Sb(2)-O(7)	2.367(5)	Sb(2)-C(51)	2.136(8)
Sb(2)-C(57)	2.123(8)	Sb(2)-C(63)	2.159(8)
C(9)-O(5)	1.270(8)	C(10)-O(6)	1.419(8)
C(17)-O(7)	1.232(9)	C(9)-C(10)	1.528(11)
Sb(3)-O(2)	2.266(5)	Sb(3)-O(10)	2.172(5)
Sb(3)-O(12)	1.977(5)	Sb(3)-C(69)	2.151(9)
Sb(3)-C(75)	2.154(7)	Sb(3)-C(81)	2.124(8)
C(25)-O(10)	1.285(9)	C(26)-O(12)	1.414(9)
C(1)-O(2)	1.255(9)	C(25)-C(26)	1.534(11)
Sb(4)-O(8)	2.181(5)	Sb(4)-O(9)	1.975(5)
Sb(4)-O(11)	2.313(5)	Sb(4)-C(87)	2.123(8)
Sb(4)-C(93)	2.137(8)	Sb(4)-C(99)	2.135(8)
C(17)-O(8)	1.289(9)	C(18)-O(9)	1.417(8)
C(25)-O(11)	1.250(9)	C(17)-C(18)	1.516(11)
Bond angles			
O(1)-Sb(1)-C(33)	84.1(3)	O(1)-Sb(1)-C(39)	168.6(3)
O(1)-Sb(1)-C(45)	93.6(3)	O(1)-Sb(1)-O(3)	77.4(2)
O(1)-Sb(1)-O(4)	81.6(2)	O(3)-Sb(1)-C(33)	154.2(3)
O(3)-Sb(1)-C(39)	95.1(3)	O(3)-Sb(1)-C(45)	104.0(3)
O(3)- Sb(1)-O(4)	81.6(2)	O(4)-Sb(1)-C(33)	77.8(3)

O(4)-Sb(1)-C(39)	89.5(3)	O(4)-Sb(1)-C(45)	174.2(3)
C(33)-Sb(1)-C(39)	100.0(3)	C(33)-Sb(1)-C(45)	104.0(3)
C(39)-Sb(1)-C(45)	95.6(3)	O(1)-C(1)-C(2)	118.1(7)
O(3)-C(2)-C(1)	110.0(6)	C(1)-O(1)-Sb(1)	112.6(5)
C(2)-O(3)-Sb(1)	117.4(4)		
O(5)-Sb(2)-C(51)	164.1(2)	O(5)-Sb(2)-C(57)	93.7(3)
O(5)-Sb(2)-C(63)	84.3(2)	O(5)-Sb(2)-O(6)	78.12(19)
O(5)-Sb(2)-O(7)	79.08(19)	O(6)-Sb(2)-C(51)	90.4(3)
O(6)-Sb(2)-C(57)	95.7(3)	O(6)-Sb(2)-C(63)	156.0(2)
O(6)- Sb(2)-O(7)	82.2(2)	O(7)-Sb(2)-C(51)	88.5(2)
O(7)-Sb(2)-C(57)	172.7(3)	O(7)-Sb(2)-C(63)	78.5(2)
C(51)-Sb(2)-C(57)	98.5(3)	C(51)-Sb(2)-C(63)	103.1(3)
C(57)-Sb(2)-C(63)	101.7(3)	O(5)-C(9)-C(10)	116.3(6)
O(6)-C(10)-C(9)	110.7(6)	C(9)-O(5)-Sb(2)	113.7(5)
C(10)-O(6)-Sb(2)	117.2(4)		
O(2)-Sb(3)-C(69)	84.0(3)	O(2)-Sb(3)-C(75)	171.5(3)
O(2)-Sb(3)-C(81)	86.3(2)	O(2)-Sb(3)-O(10)	78.15(19)
O(2)-Sb(3)-O(12)	84.9(2)	O(10)-Sb(3)-C(69)	84.5(3)
O(10)-Sb(3)-C(75)	93.8(3)	O(10)-Sb(3)-C(81)	162.2(3)
O(10)- Sb(3)-O(12)	77.7(2)	O(12)-Sb(3)-C(69)	160.6(3)
O(12)-Sb(3)-C(75)	90.8(3)	O(12)-Sb(3)-C(81)	92.5(3)
C(69)-Sb(3)-C(75)	98.1(3)	C(69)-Sb(3)-C(81)	102.6(3)
C(75)-Sb(3)-C(81)	101.3(3)	O(10)-C(25)-C(26)	117.3(7)
O(12)-C(26)-C(25)	109.6(6)	C(25)-O(10)-Sb(3)	112.5(5)
C(26)-O(12)-Sb(3)	117.8(4)		
O(8)-Sb(4)-C(87)	162.4(3)	O(8)-Sb(4)-C(93)	93.1(2)
O(8)-Sb(4)-C(99)	84.0(2)	O(8)-Sb(4)-O(9)	77.3(2)
O(8)-Sb(4)-O(11)	76.88(18)	O(9)-Sb(4)-C(87)	90.1(3)

O(9)-Sb(4)-C(93)	96.3(3)	O(9)-Sb(4)-C(99)	156.9(3)
O(9)- Sb(4)-O(11)	85.4(2)	O(11)-Sb(4)-C(87)	90.0(2)
O(11)-Sb(4)-C(93)	169.3(3)	O(11)-Sb(4)-C(99)	77.2(2)
C(87)-Sb(4)-C(93)	100.6(3)	C(87)-Sb(4)-C(99)	104.7(3)
C(93)-Sb(4)-C(99)	98.1(3)	O(8)-C(17)-C(18)	116.8(7)
O(9)-C(18)-C(17)	110.5(6)	C(17)-O(8)-Sb(4)	110.5(6)
C(18)-O(9)-Sb(4)	119.4(5)		

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