

1 **Electronic Supplementary Information (ESI)**

2 **Hydrogen bond breakage by Fluoride anion in a simple CdTe quantum dot/Gold**
3 **nanoparticle FRET system and its analytical application**

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1 **1. Experimental Section**

2 **Materials.** Hydrogen tetrachloroaurate (III) ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), trisodium citrate, cadmium acetate
3 dihydrate (98.5%), tellurium powder (300 mesh, 99%), sodium hydrogen boride (99%) and
4 potassium fluoride were purchased from China Medicine Group Shanghai Chemical Reagent
5 Corporation. Thioglycolic acid (TGA) were obtained from Sigma-Aldrich. All other reagents were
6 analytical reagent grade. Water used in the experiment was purified with Mill-Q ($18.2 \text{ M}\Omega \cdot \text{cm}^{-1}$)
7 water system. 100k Nanosep filter (Pall Corporation, USA) was used as ultra-purification
8 instrumentation.

9 **Instrumentation and methods.** Fluorimetric spectra were collected with an Edinburgh FLS920
10 spectrofluorimeter (Edinburgh Instruments Ltd, England) equipped with a xenon lamp and a
11 quartz cuvette (1.0 cm optical path) as the container. Absorption spectra were recorded on an
12 UV-1700 spectrophotometer (Shimadzu Corp. Kyoto, Japan). Transmission electron microscopy
13 (TEM) images were collected on a Hitachi Model H-800 instrument. Acidity measurements were
14 made with a Model pHs-3C meter (Shanghai Leici Equipment Factory, China). Centrifugation
15 was done on the instrument of Sigma 3K 15 Centrifuge. Capillary electrophoresis (CE) was
16 performed by using a QL-1000 instrument with UV/Vis detector (Shandong Normal University).
17 Experimental conditions: capillary with 50 cm effective (55 cm total) length and $75 \mu\text{m}$ inner
18 diameter. $\text{Na}_2\text{B}_4\text{O}_7$ solution (20 mM, pH 9.2) was used as running buffer. The applied voltage was
19 12 kV. The samples were introduced to the capillary by pressure for 10s.

20 **Preparation of water-soluble CdTe quantum dots (QDs) and its purification.**

21 *Preparation of NaHTe.*

22 In a two-necked flask (25 mL), 11.3 mg tellurium powder and 10 mL water were deaerated with
23 argon for 10 min. Then 30 mg NaBH_4 was added and the resulting suspension was stirred under
24 argon until NaBH_4 was completely dissolved. After that, the resulting suspension was heated to 35
25 $^\circ\text{C}$ under vigorous stirring and argon bubbling. During fifteen minutes, the colored suspension
26 changed its characteristic color from violet to colorless. Fresh NaHTe was obtained and was
27 cooled to room temperature.

28 *Preparation and purification of TGA/ CdTe QDs.*

29 In a three-necked flask (250 mL) equipped with a reflux condenser, cadmium acetate dihydrate (2
30 mmol) was dissolved in 100 mL water. After thioglycolic acid (TGA, 1.0 mmol) was added, the
31 solution was adjusted to pH 10 with aqueous NaOH (1.0 M) and stirred under argon at room
32 temperature for 30 min. Then 2mL NaHTe solution was injected under argon and the mixture was
33 refluxed. The colour of the precursors mixture turned from colorless to orange, supporting the
34 growth of the nanocrystals. After refluxing for particular time, stable water-compatible
35 TGA-capped CdTe QDs were obtained.¹ To remove excess TGA, the as-prepared QDs were
36 precipitated with an equivalent amount of 2-propanol. The pellet of purified QDs was dried
37 overnight at room temperature in vacuum, and the final product in the powder form could be
38 redissolved in ultrapure water (20 mL). The aggregated nanoparticles that formed in the process of
39 redissolving were removed by ultrafiltration using 100k Nanosep filter under centrifugation
40 (12000 rpm , 5 min). The upper phase was discarded, leaving the obtained homogeneous QDs in
41 lower phase as the stock solution. The obtained QDs were characterized by fluorescence
42 spectroscopy and UV/Vis spectroscopy. According to the excitonic absorption peak value and the
43 extinction coefficient per mole (ϵ) of CdTe nanoparticles² The final concentration of CdTe-QDs is

1 6.4×10^{-7} mol/L. We denote the concentration of purified QDs solution to be $1 \times$.

2 **Preparation of citrate modified Au nanoparticles (AuNPs).**

3 The monodispersed AuNPs was prepared using the classical citrate reduction route pioneered by
4 Frens.³ Briefly, trisodium citrate (1%, 5.25 mL) was added rapidly to an aliquot of 0.01% HAuCl₄
5 (150 mL) that was brought to a reflux while stirring. This mixture was refluxed for an additional
6 15 min, during which time the color changed to deep red. Then the solution was set aside to cool
7 to room temperature. This result in citrate ion stabilized AuNPs with net negative charges. Next,
8 unbound citrate was removed by repeated centrifugation (12000 rpm, 5 min), followed by
9 redispersing the red precipitate in ultrapure water (15 mL) to get the pure AuNPs. The AuNPs
10 were characterized by UV/Vis absorption spectroscopy as well as transmission electron
11 microscopy (TEM). The final concentration of AuNPs was calculated to be approximately 2.0 nM
12 (1.2×10^{15} particles/L)⁴ with a high molar extinction coefficient (ϵ at 520 nm) of 6.1×10^8 M⁻¹ cm⁻¹.
13 Please note that we denote the concentration of the as-prepared AuNPs solution to be $2 \times$.

14 **Fluorescence quenching.**

15 100 μ L of the prepared CdTe QDs ($0.1 \times$), 100 μ L of 0.10 M (pH=7.0) buffer solution and different
16 concentrations of AuNPs solution were added to 1.50 mL colorimetric tube, sequentially. Each
17 sample solution was diluted with pure water to a final volume of 1.00 mL. For an equilibration
18 period of 20 min to make reaction completely, the fluorescence spectra were collected .

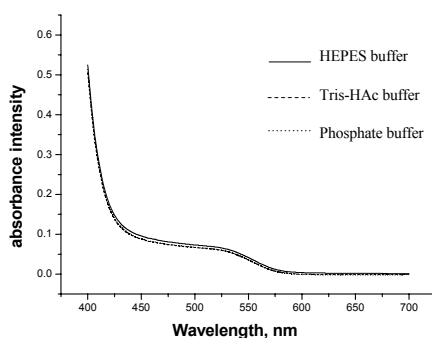
19 **Fluorescence detection of fluoride ion.**

20 100 μ L of 0.10 M (pH=7.0) buffer solution and 200 μ L of AuNPs solution ($2 \times$) were added into
21 100 μ L of the prepared CdTe QDs ($0.1 \times$) as the probe solution. Equilibration period of 20 min was
22 performed to make the reaction completely. Afterwards, different concentrations of F⁻ were added.
23 Each sample solution was diluted with pure water to a final volume of 1.00 mL. After 5 minutes'
24 reaction, the fluorescence spectra were obtained .

26 **references**

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32 **2. Results and Discussion**



49 **Fig.S1** The absorption spectra of CdTe QDs ($0.1 \times$). Solutions were prepared in 10 mM buffer solution (pH 7.0).

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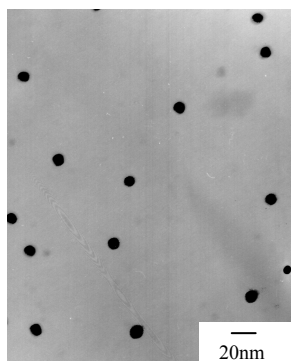


Fig.S2 TEM images of the as-synthesized AuNPs.

21 **Interactions between water-soluble CdTe QDs and AuNPs studied by fluorescence spectra.**

22 *Effect of acidity*

23 In order to monitor the fluorescence intensity changes related to pH variations, three buffer
24 solutions are chosen, including sodium phosphate buffer, Tris-HAc buffer and HEPES buffer. The
25 concentration of QDs was fixed to be $0.1\times$, volume was $100\ \mu\text{L}$. The concentration of AuNPs was
26 fixed at $2\times$, volume was $200\ \mu\text{L}$. For phosphate buffer system, the effect of pH was in the range of
27 $5.5\sim 9.0$. In acid condition, fluorescence quenching is obvious(Fig. S3a). When increasing pH,
28 fluorescence quenching efficiency decreased, but the fluorescence peak is still at $520\ \text{nm}$. Similar
29 results was observed in Tris-HAc buffer solution ($\text{pH}=7.0\sim 9.8$) and HEPES buffer solution
30 ($\text{pH}=6.4\sim 9.0$). Therefore, the pH of the solution play an important role in the interactions between
31 water-soluble CdTe QDs and AuNPs. Finally, considering the stability of CdTe QDs and AuNPs, a
32 buffer solution of pH 7.0 was recommended.

33 *Effect of buffer concentration*

34 When the concentration of phosphate buffer solution was more than $25\ \text{mM}$, the solution
35 color changed from red to light purple. For Tris-HAc buffer solution, the solution color turned to
36 light purple when the concentration was $30\ \text{mM}$. However, for HEPES buffer, the solution color
37 changed a little even when the concentration reached $30\ \text{mM}$. These results indicated that the
38 concentration of buffer solution affects the stabilization of AuNPs. In the high ionic strength
39 solutions, the solution color changed from red to light purple resulted from the self-aggregation of
40 AuNPs. While in HEPES buffer, AuNPs are relatively stable due to the non-ionic property of the
41 buffer. As shown in Fig. S3b, fluorescence quenching efficiency of AuNPs decreased with the
42 increasing of buffer concentration. In the following experiments, $10\ \text{mM}$ buffer solution (pH 7.0)
43 was chosen.

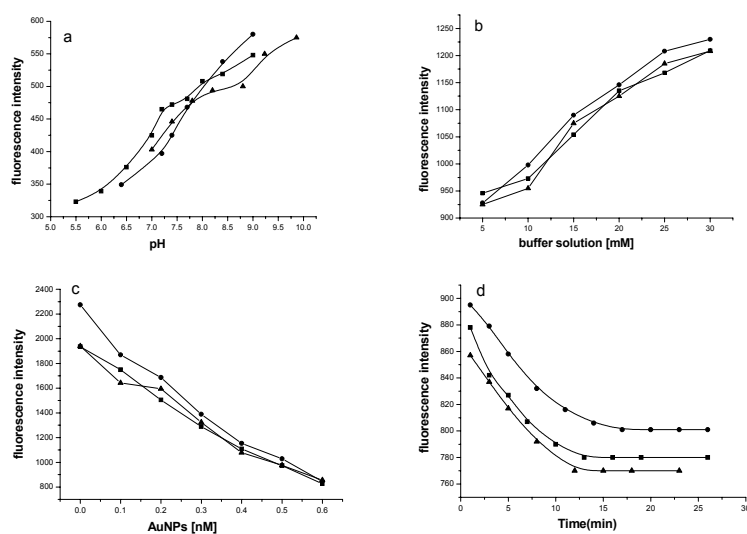
44 *The concentration ratio of the CdTe QDs to AuNPs*

45 Fig. S3c shows the effect of AuNPs amounts on photoluminescence (PL) intensity during
46 adding $50\sim 300\ \mu\text{L}$ of $2\ \text{nM}$ ($2\times$) AuNPs. When the concentration and volume of QDs is stabilized
47 at $0.1\times$ and $100\ \mu\text{L}$, a regular decrease in the fluorescence emission of QDs was observed. The
48 experiment results show that the fluorescence quenching efficiency of AuNPs is almost same in
49 different buffer solutions.

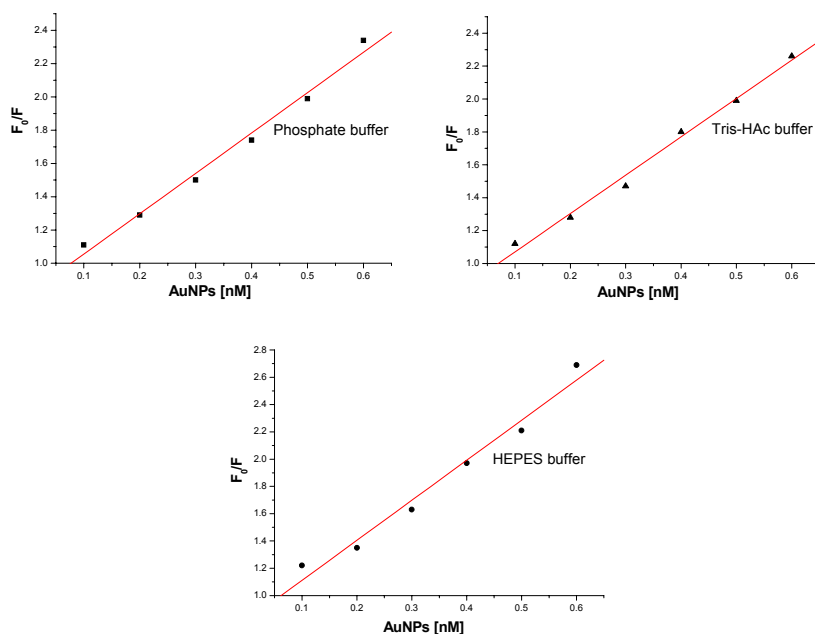
50 *Effect of interaction time*

51 Fig. S3d shows the decrease of fluorescence intensity along time after adding AuNPs to the
52 QDs solution in the presence of $10\ \text{mM}$ buffer solutions. The fluorescence intensity gradually

1 decreased along the reaction time and reached a plateau after 15 min. Therefore, reaction time of 20
2 min was selected to obtain the best sensitivity.



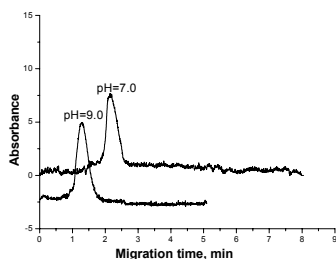
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41 **Fig.S3** In all the experiments, CdTe QDs are fixed at $0.1 \times 100 \mu\text{L}$. (■) phosphate buffer, (▲) Tris-HAc buffer, (●)
42 HEPES buffer. (a) Effects of pH (5.5~10.0) on the fluorescence spectra of CdTe-AuNPs assemblies. AuNPs($2 \times$,
43 $200 \mu\text{L}$). Three buffer concentrations are fixed at 10 mM; (b) Effect of buffer concentrations on the fluorescence
44 spectra of CdTe-AuNPs assemblies, AuNPs($2 \times, 200 \mu\text{L}$), pH 7.0; (c) PL quenching of CdTe QDs upon adding
45 AuNPs, three buffer concentrations are fixed at 10 mM, pH 7.0; (d) The changes of fluorescence intensity with
46 increasing incubation time. AuNPs ($2 \times, 200 \mu\text{L}$). Three buffer concentrations are fixed at 10 mM, pH 7.0.



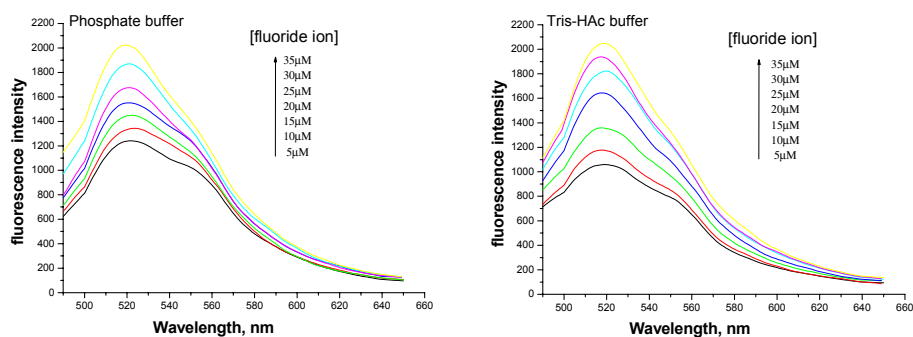
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80 **Fig.S4** Stern-Volmer plot of F_0/F versus [AuNPs]. The buffer concentration is fixed at 10 mM, pH 7.0.

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82 Fig.S5 shows the electropherograms of free QDs in different pH by capillary electrophoresis
83 obtained with a UV-visible detector at 350 nm. In the alkaline buffer solution, CdTe QDs possess
84 negative charges and migrate to the anode in the electric field. As pH decreased, the QDs was

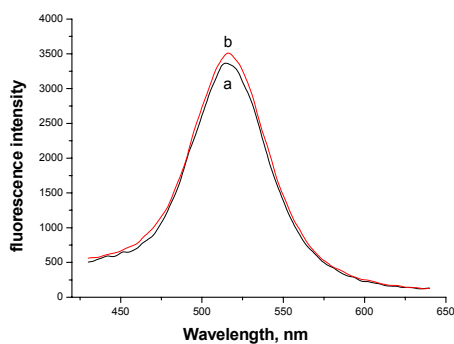
1 detected at a longer migration time. This indicated that the negative charges on the surface of
2 CdTe QDs decreased.



20 Fig.S5 Electropherograms of CdTe QDs($0.10\text{mg}\cdot\text{ml}^{-1}$) obtained by capillary electrophoresis at 350 nm.



43 Fig.S6 Fluorescence response after different concentrations of F^- were added to the analytical system in the
44 optimal conditions. The buffer concentration is fixed at 10 mM, pH 7.0.



66 Fig. S7 (a) Fluorescence spectra of CdTe QDs ($0.1\times$). (b) Fluorescence response after F^- ($50\mu\text{M}$) were added to the
67 QDs solution. Solutions were prepared in 10 mM HEPES buffer solution (pH 7.0).

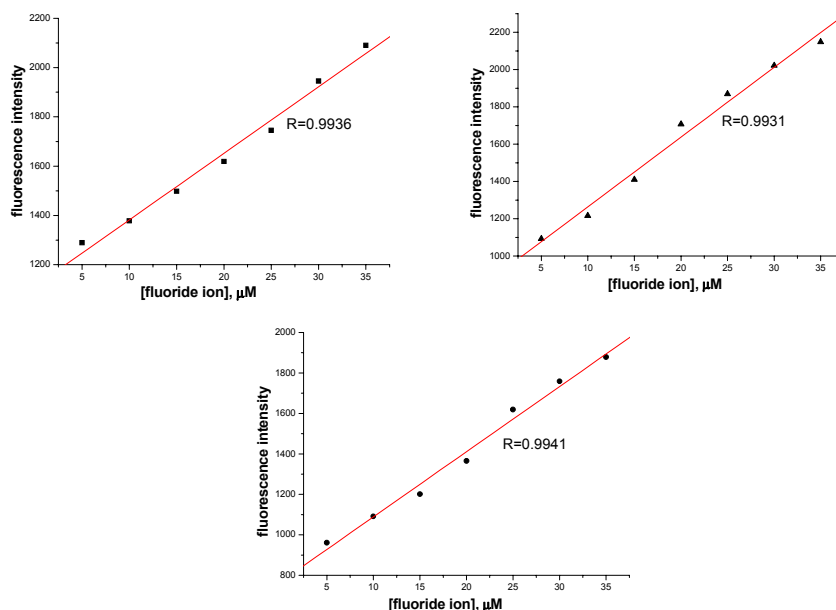


Fig. S8 A linear correlation between the fluorescence intensity and the concentrations of F^- . (■) Phosphate buffer, (▲) Tris-HAc buffer, (●) HEPES buffer.

Table S1. The detection limit and the relative standard deviation (RSD).

	Phosphate buffer	Tris-HAc buffer	HEPES buffer
Detection limit	115 nM	84 nM	97 nM
RSD ($n=11$)	2.1 %	1.8 %	1.1 %

Effects of various anions and cations on the nanoprobe.

To assess the selectivity of the assemblies for F^- , the effects of various anions and cations on the determination of F^- were examined in the tested three buffer solutions. Although the nano-assemblies can detect F^- in phosphate buffer solution, AuNPs became unstable after adding higher concentration of anions, which may be due to the high ionic strength of solution. For Tris-HAc buffer solution, the influence was much better. In HEPES buffer solution, the influence was small. Finally, HEPES buffer was chosen. Table S2 shows that the relative error of most species in HEPES buffer solution.

Table S2. Interferences of various coexisting anions and cations in the presence of 20 μM F^- (HEPES buffer).

Coexisting substances	Concentration / mol·L ⁻¹	Relative error / %
Cl ⁻	5.0×10^{-4}	1.5
Br ⁻	5.0×10^{-4}	1.3
I ⁻	5.0×10^{-4}	1.2
SO ₄ ²⁻	5.0×10^{-4}	0.5

NO ₃ ⁻	5.0×10 ⁻⁴	0.6
CH ₃ COO ⁻	5.0×10 ⁻⁴	1.8
HCO ₃ ⁻	5.0×10 ⁻⁴	2.7
HPO ₄ ²⁻	5.0×10 ⁻⁴	2.4
NO ₂ ⁻	5.0×10 ⁻⁴	0.3
Na ⁺	1.0×10 ⁻³	-0.4
K ⁺	1.0×10 ⁻³	-0.9
Ag ⁺	1.0×10 ⁻³	-1.6
Mg ²⁺	1.0×10 ⁻³	-2.2
Ca ²⁺	1.0×10 ⁻³	-2.8
Fe ²⁺	1.0×10 ⁻³	-1.8
Zn ²⁺	1.0×10 ⁻³	-1.5
Cu ²⁺	1.0×10 ⁻³	-2.4
Hg ²⁺	1.0×10 ⁻³	-2.8
Al ³⁺	1.0×10 ⁻³	-1.5
Fe ³⁺	1.0×10 ⁻³	-2.2

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Table S3. Analytical results of F⁻ in tap water samples (HEPES buffer).

	Measured ^a (μM)	Added (μM)	Recovered ^a (μM)	RSD (%)	Recovery (%)	Measured ^b (μM)
Tap water	20.92	10.00	31.17	1.2	102	20.85

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^a Mean value of six determinations by the proposed method.

^b Mean value of six determinations by using electrodes prepared from LaF₃.

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3. Theoretical Calculations

10 Calculated geometries were initially optimized with the Gaussian 03¹ package at the DFT level
11 of theory by using the B3LYP functional ²(Becke's three parameters hybrid functional ³ with the
12 Lee-Yang-Parr correlation functional ⁴) and the 6-31+G(d,p) basis set. The resulting stationary
13 points were confirmed by frequency calculations. Reported total electronic energies are
14 uncorrected for the ZPVE (zero point vibrational energy) and computed in the gas-phase. Bond
15 orders were characterized by the Wiberg's bond index ⁵ (WBI) and calculated at the
16 B3LYP/6-311G** level with the natural bond orbital (NBO) method ⁶ as the sum of squares of the
17 off-diagonal density matrix elements between atoms, as formulated in terms of the natural atomic
18 orbital (NAO) basis set.

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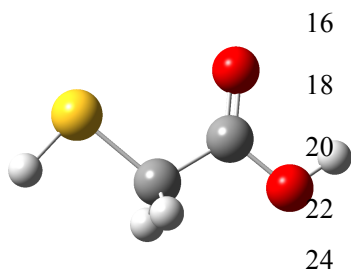
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2 D.Daniels, M. C.Strain, O.Farkas, D. K.Malick, A.D.Rabuck, K.Raghavachari, J. B.Foresman, J. V.Ortiz, Q.Cui,
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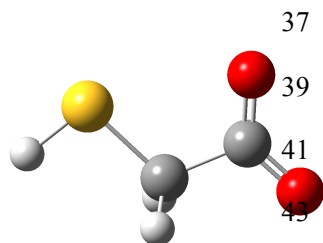
13 **Calculated structures, energies and cartesian coordinates (B3LYP/6-31+G**) for model**
14 **compounds and relevant complexes.**



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26 E = -627.283884 au

27	C	-0.96037300	0.10671300	0.00040400
28	O	-0.92755900	1.31567500	0.00000100
29	O	-2.11635600	-0.60309600	-0.00020400
30	H	-2.84786000	0.03789000	-0.00050700
31	C	0.23344100	-0.82270500	0.00016400
32	S	1.78996300	0.15139200	-0.00008100
33	H	2.58963400	-0.93558100	-0.00030200
34	H	0.16601000	-1.46464900	0.88369700
35	H	0.16571200	-1.46461800	-0.88336900



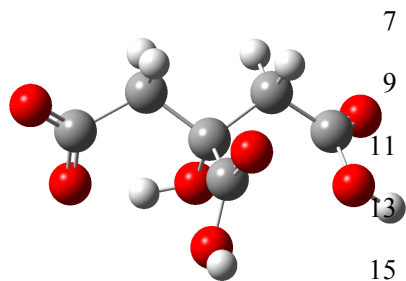
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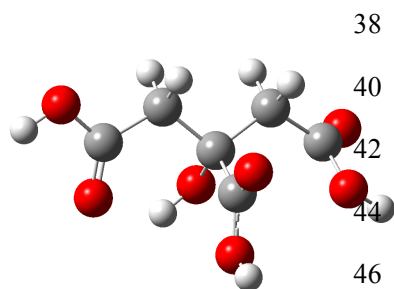
48	C	1.10947100	0.08806300	0.00002200
49	O	0.90871700	1.32597300	0.00001300
50	O	2.18741400	-0.56204800	-0.00002200

1	C	-0.15461100	-0.83669800	0.00001300
2	S	-1.73048000	0.14146400	-0.00001700
3	H	-2.56434100	-0.93084600	0.00012000
4	H	-0.12308700	-1.47607900	-0.88696500
5	H	-0.12310300	-1.47608400	0.88698500



16 E= -759.5891344 au

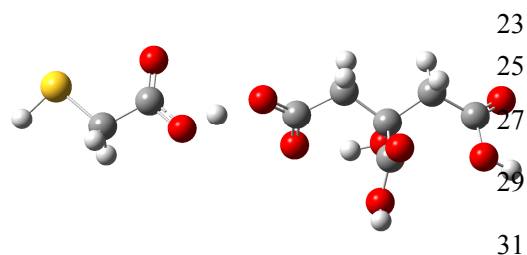
17	C	-0.01439800	-0.22275900	-0.11678800
18	C	1.23029200	-0.73284700	-0.88679200
19	H	1.10098100	-1.79544000	-1.09661400
20	H	1.31879400	-0.18704400	-1.83305900
21	C	-1.30723300	-0.68064100	-0.85872200
22	H	-1.18793100	-1.74924100	-1.08133900
23	H	-1.41988900	-0.14978800	-1.80699200
24	C	-2.62860300	-0.55259300	-0.03035400
25	C	2.53275400	-0.60036700	-0.13449800
26	O	-2.49879500	-0.69576600	1.23293900
27	O	3.34239700	-1.49195700	0.04016900
28	O	2.76640200	0.66049600	0.31404100
29	H	3.59405100	0.62080700	0.82047500
30	O	0.03054500	-0.74329000	1.18075300
31	H	-0.95372300	-0.77741600	1.45567100
32	C	-0.00404900	1.32607900	-0.14972100
33	O	0.17215800	1.98577400	-1.16114600
34	O	-0.26077700	1.90627600	1.03847000
35	H	-0.29709100	2.86087500	0.86062500
36	O	-3.67790100	-0.37703100	-0.67741600



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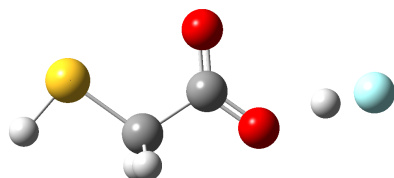
48 E=-760.1174145 au

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3	H	1.12395600	-2.03911700	-0.62880000
4	H	1.23519300	-0.66469800	-1.75537800
5	C	-1.26793400	-0.90825600	-0.59387100
6	H	-1.22379700	-1.99704100	-0.47454600
7	H	-1.34536200	-0.69693900	-1.66416100
8	C	-2.52911300	-0.43059000	0.08805800
9	C	2.58199400	-0.61613700	-0.09981800
10	O	-2.57361200	0.24274200	1.10123400
11	O	3.38670100	-1.42907500	0.29619500
12	O	2.82423200	0.71700000	-0.09821800
13	H	3.69495600	0.85222500	0.31266000
14	O	0.14824300	-0.57183300	1.37549700
15	H	-0.57768300	-0.12321300	1.83968500
16	C	0.00683600	1.22600400	-0.31380500
17	O	-0.14531900	1.65816200	-1.43840300
18	O	0.13825800	2.00461100	0.77056200
19	H	0.09859300	2.92764900	0.46674300
20	O	-3.63869300	-0.85634600	-0.54859500
21	H	-4.40772500	-0.53410700	-0.04684900



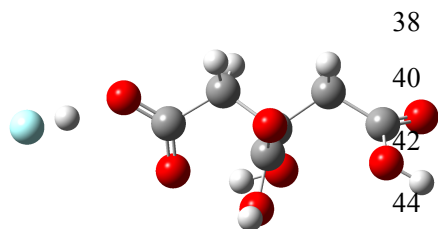
32	E=-1386.9093501 au			
33	C	-2.52344000	-0.21249700	0.08305100
34	C	-3.70352000	-0.98027500	0.72497200
35	H	-3.43511700	-2.03425700	0.80825900
36	H	-3.89162500	-0.57749200	1.72645300
37	C	-1.20768900	-0.58403600	0.82623100
38	H	-1.15454900	-1.67918700	0.87022700
39	H	-1.22045600	-0.20644300	1.85091300
40	C	0.08524100	-0.11511600	0.11836500
41	C	-4.99283800	-0.92546300	-0.06149900
42	O	0.07452900	-0.02513700	-1.13549600
43	O	-5.66702400	-1.88704500	-0.37489100
44	O	-5.37933900	0.34099400	-0.36088300
45	H	-6.18515300	0.26437100	-0.89771000
46	O	-2.46267300	-0.57508000	-1.27116000
47	H	-1.51900900	-0.38072500	-1.53806300

1	C	-2.74919300	1.30595300	0.29281600
2	O	-3.01244600	1.80597800	1.37243500
3	O	-2.57862900	2.04618300	-0.81789100
4	H	-2.67728800	2.97206500	-0.53941400
5	O	1.07072500	0.09727600	0.89057400
6	H	2.34301000	0.41454500	0.37283500
7	O	3.29266800	0.78727800	0.03173900
8	C	4.31505300	-0.02277700	0.16251500
9	O	4.32543100	-1.13565700	0.66972200
10	C	5.57537200	0.61372500	-0.43366000
11	S	7.03674500	-0.47597400	-0.17073700
12	H	5.40623500	0.77503100	-1.50186000
13	H	5.73365700	1.58758900	0.03667200
14	H	7.91252000	0.36467000	-0.76645900



26 E= -727.2324566au

27	C	0.00000000	0.00000000	0.00000000
28	O	0.00000000	0.00000000	1.24036380
29	O	0.98862448	0.00000000	-0.81048234
30	H	2.36841312	0.01246771	-0.41992939
31	C	-1.35545923	0.00035299	-0.75259712
32	S	-2.77867870	0.00148495	0.42725481
33	H	-3.73830895	0.00041239	-0.53009986
34	H	-1.40175146	0.88599721	-1.39213873
35	H	-1.40247176	-0.88597729	-1.39117034
36	F	3.36831961	0.02717314	-0.27724966



46

47	E= -860.07928au			
48	C	0.52134400	-0.22494800	-0.10182900
49	C	1.75124400	-0.78849900	-0.85364800

1	H	1.60358100	-1.85655400	-1.01918300
2	H	1.84250200	-0.28446200	-1.82235000
3	C	-0.77689700	-0.68590200	-0.82649500
4	H	-0.69517800	-1.76921600	-0.98308400
5	H	-0.86421200	-0.21089000	-1.80615800
6	C	-2.08472600	-0.46026100	-0.02353100
7	C	3.06240600	-0.64590900	-0.11627200
8	O	-2.00870600	-0.48567700	1.23374400
9	O	3.86071000	-1.54196100	0.07945800
10	O	3.31232400	0.62648000	0.28523600
11	H	4.14703200	0.60048000	0.78112000
12	O	0.56566800	-0.70578300	1.21505400
13	H	-0.38793800	-0.66033800	1.52492900
14	C	0.56096000	1.32167700	-0.18318700
15	O	0.72289100	1.93945900	-1.22146200
16	O	0.34873500	1.94026500	0.99264900
17	H	0.32586900	2.89118300	0.79337500
18	O	-3.12545400	-0.31768200	-0.72790200
19	H	-4.49112200	-0.21111900	-0.18779900
20	F	-5.45509600	-0.13742600	0.05496700
21				
22				
23				