$Ti_2S@D_{3h}(24109)$-C_{78}: A sulfide cluster metallofullerene containing only transition metals inside the cage

Fang-Fang Li,[a] Ning Chen,[a,c] Marc Mulet-Gas,[b] Vivian Triana,[a] Jesse Murillo,[a] Antonio Rodríguez-Fortea,[*b] Josep M. Poblet,[*b] and Luis Echegoyen[*a]

[a] *Department of Chemistry, University of Texas at El Paso, El Paso, Texas 79968, United States*
[b] *Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, 43007 Tarragona, Spain*
[c] *Current address: College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, Jiangsu, 212163, China. Email:chenning@suda.edu.cn*
Email: antonio.rodriguezf@urv.cat, josepmaria.poblet@urv.cat, echegoyen@utep.edu

Experimental sections:

The separation and purification of $Ti_2S@C_{78}$ were preformed by multistep HPLC using Waters HPLC system equipped with a 2707 autosampler, a 2535 quaternary gradient module, a 2489 UV−vis detector, and a fraction collector III and DyChrom Recycling HPLC system. MALDI−TOF MS was conducted on a Bruker Microflex LRF mass spectrometer. The UV−vis−NIR spectra were recorded using a Cary 5000 UV−vis−NIR spectrophotometer. CV studies were conducted in a one-compartment cell connected to a CHI 660 workstation in a solution of *o*-DCB containing 0.05 M *n*-Bu_4NPF_6. A 2 mm diameter glassy carbon disk, platinum wire and silver wire were used as the working, counter and pseudo reference electrodes, respectively. Ferrocene (Fc) was added to the solution at the end of the experiment as an internal potential standard.

Figure S1 shows the multistage HPLC procedures utilized to isolate and purify $Ti_2S@C_{78}$. The HPLC-MALDI-TOF MS analysis shows that, on a 5PYE column, the $Ti_2S@C_{78}$ fraction is overlapped with those of C_{88}, C_{90}, C_{92} and $Ti_2@C_{84}$ as shown in Figure S1a. The fraction containing $Ti_2S@C_{78}$ was further separated by recycling HPLC using a Buckyprep column, resulting in the isolation of five fractions (Figure S1b). The MALDI-TOF-MS analysis reveals a mass of 1064 appeared in the third fraction (label with blue rectangle), indicating the involvement of $Ti_2S@C_{78}$. The isolated fraction was further processed by recycling HPLC using a Buckyprep-M column resulting in another four fractions (Figure S1c). MALDI-TOF-MS analysis reveals the mass at 1064 appeared in the last fraction (labeled with a pink rectangle). The isolated $Ti_2S@C_{78}$ was further purified by recycling HPLC running with a Buckyprep-M column as illustrated in Figure S1d.

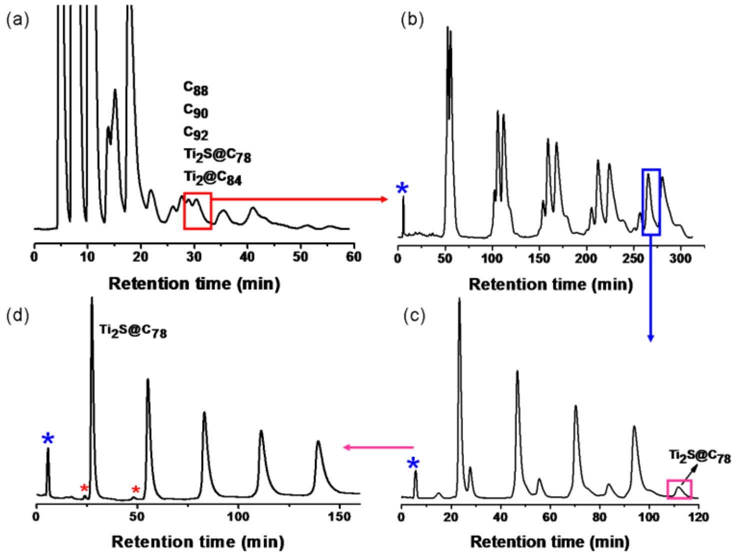

Figure S1. HPLC separation processes of $Ti_2S@C_{78}$. (a) Chromatogram from the initial HPLC of extract on a 5PYE column. (b) Chromatogram from the 2nd-step HPLC isolation of fraction labeled by the red rectangle by recycling HPLC (Buckyprep column). (c) Chromatogram from the 3rd-step HPLC isolation of fraction labeled by the blue rectangle by recycling HPLC (Buckyprep-M column). (d) Chromatogram of the isolated $Ti_2S@C_{78}$ (Buckyprep-M column), the fraction labeled by the red star was removed during the 2nd cycle. The peaks labeled with blue stars are from solvent. Conditions: λ = 320 nm; mobile phase, toluene; flow rate, 4.00 mL/min.

Computational results:

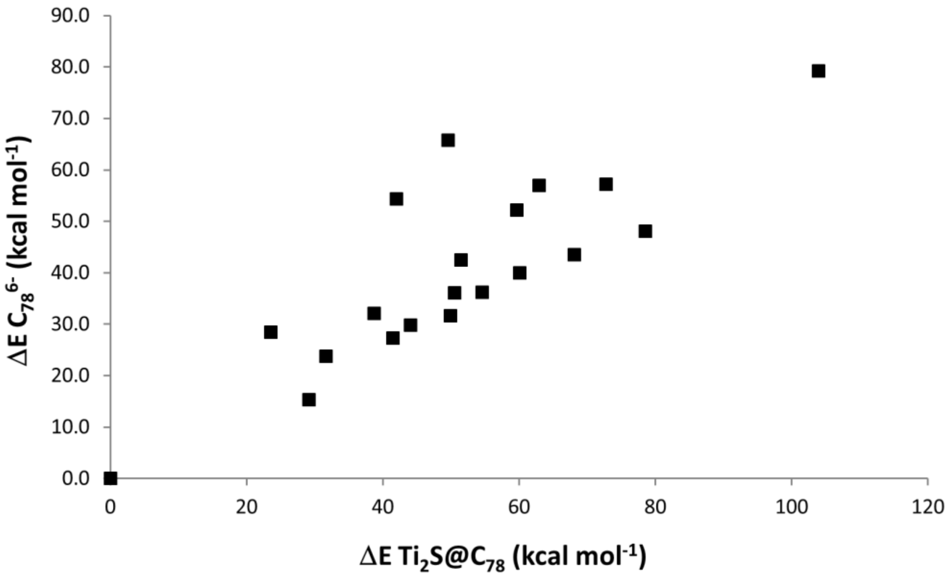

Figure S2. Plot of the energy of the lowest-energy hexaanions with respect to the corresponding clusterfullerenes at DFT level.

Table S1. Relative energies for all computed orientations of Ti_2S in $Ti_2S@D_{3h}(24109)$-C_{78}. Ti-Ti distances in Angstroms and Ti-S-Ti angles in degrees.

Orientation	ΔE (kcal mol^{-1})	Ti-Ti	Ti-S-Ti
1	27.51	3.99	121.28
2	18.10	3.63	104.64
3	33.91	3.69	107.58
4	29.93	3.14	86.63
5	13.93	3.80	111.86
6	30.75	3.93	118.71
7	15.35	4.00	121.82
8	30.39	3.97	120.76
9	18.20	3.63	104.93
10	18.23	3.62	104.07
11	30.74	3.94	118.97
12	34.04	3.69	107.52
13	14.01	3.80	111.71
14	19.24	3.84	114.84
15	18.36	4.20	131.91
16	19.17	3.84	114.91
17	15.18	4.00	121.89
18	0.00	4.69	171.71
19	18.22	3.64	105.10

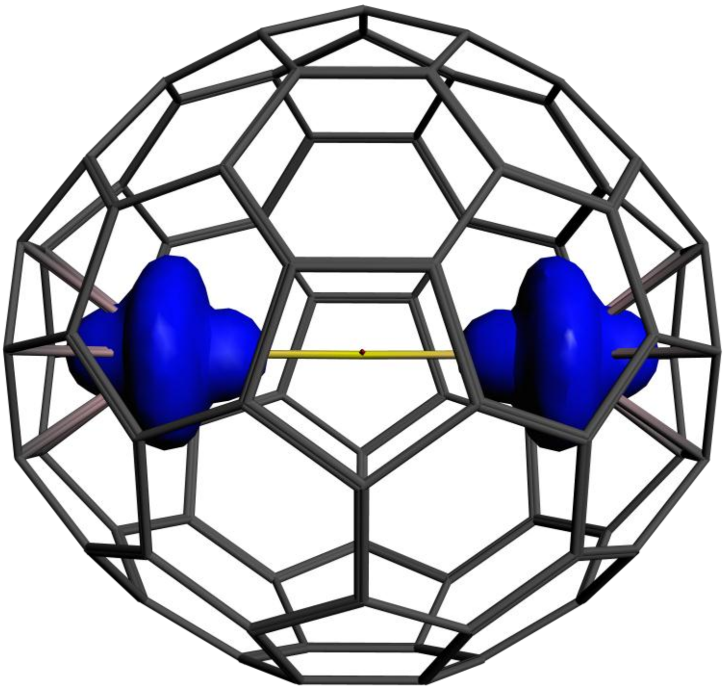

Figure S3. Spin density representation for the monoreduced $Ti_2S@D_{3h}(24109)$-C_{78}.

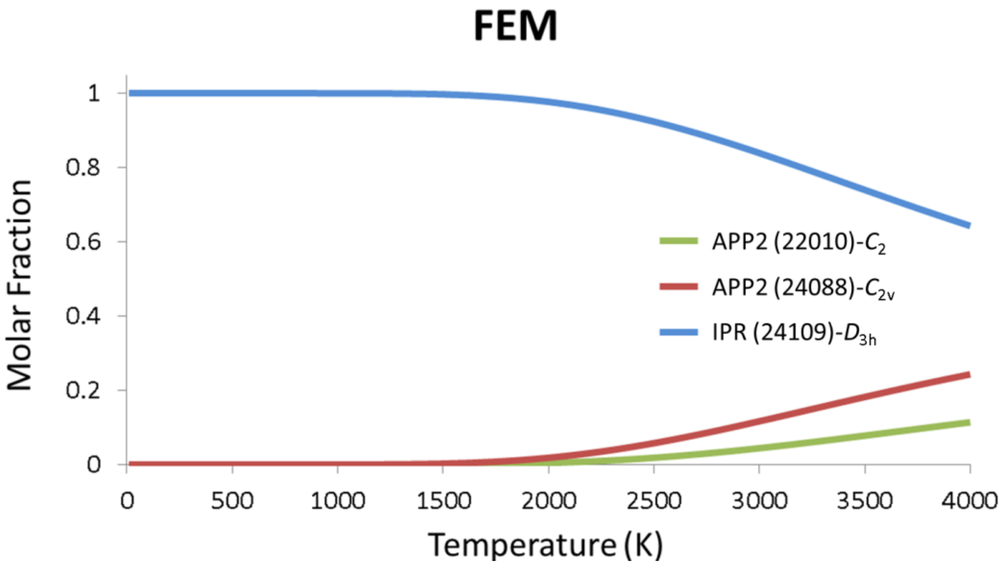

Figure S4. Predicted molar fractions within the FEM approximation as a function of temperature for three different isomers of $Ti_2S@C_{78}$. In the RRHO the molar fraction for the $Ti_2S@D_{3h}$(24109)-C_{78} isomer from 0 to 4000 K.

Table S2. TDDFT predictions for the most intense lowest-energy excitations in the absorption spectrum of $Ti_2S@D_{3h}$(24109)-C_{78}.

E (eV)	λ (nm)	f [a)]	Leading configurations[b)] (%)
1.1685	1061	0.00420	HOMO → LUMO+3 (98)
1.3204	938	0.00553	HOMO → LUMO+4 (96)
1.5036	825	0.00259	HOMO-3 → LUMO+1 (97)
1.5731	788	0.01134	HOMO-3 → LUMO+2 (93)
			HOMO-2 → LUMO+1 (36)
1.6536	750	0.01823	HOMO-1 → LUMO+5 (28)
			HOMO-1 → LUMO+2 (23)
1.7243	719	0.00355	HOMO-5 → LUMO (92)

[a] Only excitations with *f* (oscillator strength) > 0.001 are listed. [b] Contributions less than 10% are omitted.

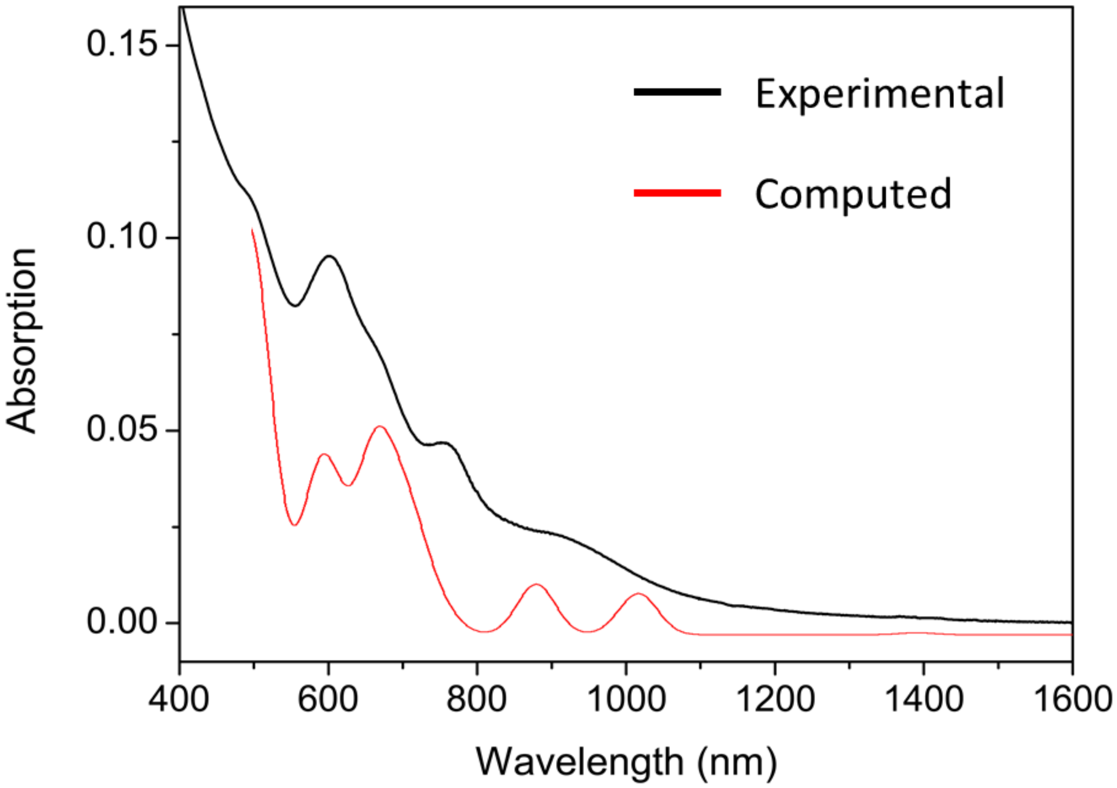

Figure S5. Experimental (black) and computed UV-Vis-NIR spectra (red).

Optimized cartesian coordinates of $Ti_2S@D_{3h}$(24109)-C_{78}.

C	-0.716544	-3.988044	1.259800
C	-1.451109	-4.011639	0.000843
C	-2.575978	-3.117458	0.145240
C	-2.602550	-2.651883	1.508048
C	-1.409206	-3.115136	2.168383
C	0.716544	-3.988044	1.259800
C	1.451109	-4.011639	0.000843
C	0.732762	-4.048903	-1.249282
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C	-1.165838	-3.111167	-2.264638
C	-2.375422	-2.318265	-2.197122
C	-3.114024	-2.320566	-0.931642
C	-3.837264	-1.167393	-0.556331
C	-3.886345	-0.710797	0.826946
C	-3.224299	-1.426735	1.867033
C	-2.648200	-0.710864	2.955338
C	-1.421660	-1.164783	3.601823
C	-0.734231	-2.317979	3.161096
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C	2.602550	-2.651883	1.508048
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C	2.375422	-2.318265	-2.197122
C	1.165838	-3.111167	-2.264638
C	0.000000	-2.631272	-2.955689
C	0.000000	-1.416731	-3.694540
C	-1.233559	-0.711082	-3.750440
C	-2.406557	-1.166758	-3.013606
C	-3.133710	0.000000	-2.602249
C	-3.833786	0.000000	-1.391246
C	-3.837264	1.167393	-0.556331
C	-3.886345	0.710797	0.826946
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C	-2.648200	0.710864	2.955338
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C	-0.700802	0.000000	4.022462
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C	3.833786	0.000000	-1.391246
C	3.133710	0.000000	-2.602249
C	2.406557	-1.166758	-3.013606
C	1.233559	-0.711082	-3.750440
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C	2.575978	3.117458	0.145240
C	1.451109	4.011639	0.000843
C	0.732762	4.048903	-1.249282
S	0.000000	0.000000	0.045127
Ti	0.000000	2.348839	-0.125720
Ti	0.000000	-2.348839	-0.125720