Electronic Supplementary Information (ESI)

Molybdenum(VI) Tris(Dithiolene) Complexes as a New Class of Three-Dimensional Two-Photon Absorption Chromophores at Telecommunications Wavelengths

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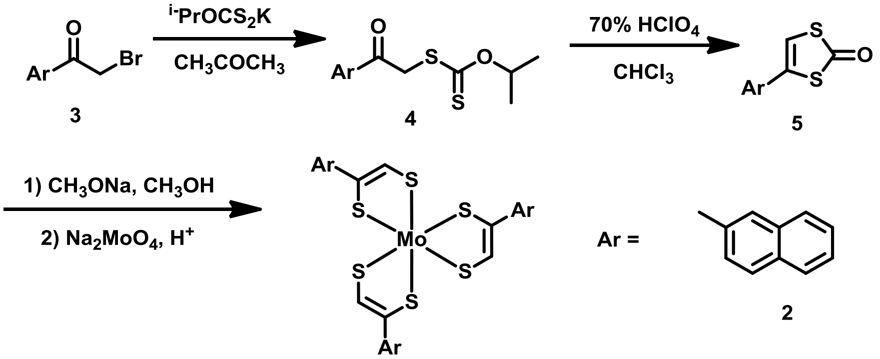
S1 Synthetic procedures and characterization data

S1.1 Instruments

^{1}H and ^{13}C NMR spectroscopies were conducted with a Varian Mercury300 spectrometer using tetramethylsilane (TMS; δ=0 ppm) as an internal standard. Elemental analysis was performed by Vario EL III (German). UV-visible spectra were obtained using a Schimadzu UV- 2550 spectrometer. Cyclic voltammetry (CV) was carried out on a CHI voltammetric analyzer in a three-electrode cell with a Pt counter electrode, a Ag/AgCl reference electrode, and a glassy carbon working electrode at a scan rate of 10mV/s. The potential values obtained were converted to values versus the ferrocenium/ferrocene (Fc$^+$/Fc) standard. All chemicals are commercially available and were used as received.

S1.2 Synthesis



Scheme **S1** Synthesis route for compound **2**

The synthetic route of compound **2** is shown in Scheme **S1**. Compound **1** was synthesized as described in the literature.[S1] ^{1}H NMR (300Hz, $CDCl_3$) δ 7.38(9H, m), 7.79(6H, d), 9.50(3H, s). ^{13}C NMR (150Hz, $CDCl_3$) δ 128.04, 129.07, 129.60, 139.55, 160.78, 177.81. MS (EI): 595.8(M^+). Anal. Calcd. for $C_{24}H_{18}MoS_6$: C, 48.47; H, 3.05. Found: C, 48.93; H, 2.88 (%).

*Synthesis of 4-(naphthalen-2-yl)-1,3-dithiol-2-one (**5**)*: Compound **3** (3 g, 15 mmol) and potassium O-isopropylxanthate (2.63 g, 15 mmol) were dissolved in 50 ml acetone, reflux for 1 h. The mixture was cooled to room temperature, filtered and washed with chloroform. The filtrates were combined, washed with water followed by brine and dried with anhydrous Na_2SO_4. The solvent was removed in vacuum, producing O-isopropyl S-2-(naphthalen-2-yl) dithiocarbamate (**4**) as orange oil mass which was used directly in next step. Crude product of compound **4** was dissolved in 50 ml chloroform than perchloroic acid (70 %, 4 ml) was added dropwise. The mixture was then refluxed for 5 h. The resulting dark product was poured into ice–water followed by its extraction with chloroform. The combined extract was dried with anhydrous Na_2SO_4, then chromatographed on a silica gel (eluent: petroleum: chloroform = 4: 1), affording a white solid (2.1 g, two steps yield 57.4%). ^{1}H NMR (300Hz, $CDCl_3$) δ 6.97 (1H, s), 7.52-7.59 (3H, m), 7.83-7.88 (4H, m). Anal. Calcd. for $C_{13}H_8N_2OS_2$: C, 63.90; H, 3.30. Found: C, 63.43; H, 2.97 (%).

*Synthesis of compound **2***: Compound **5** (1.0 g, 4.09 mmol) and sodium methoxide (1.08 g, 20 mmol) were suspended in degassed methanol and stirred under argon for 1 h, affording an orange solution. Then the mixture was cooled to -78°C and acidified by concentrated hydrochloric acid (5 ml). $(NH_4)_2MoO_4$ (0.28 g, 1.36 mmol) was added, and the resulting reaction mixture was stirred at room temperature for 1 h. The target product was obtained by filtration and recrystallization from chloroform/ethanol to afford a dark green solid (0.95 g, yield 62.5%). ^{1}H NMR (300Hz, $CDCl_3$) δ 7.50(6H, m), 7.79-7.93(12H, m), 8.32(3H, s), 9.66(3H, s). ^{13}C NMR (150Hz, $CDCl_3$) δ 125.39, 127.01, 127.31, 127.88, 128.81, 129.07, 133.49, 133.71, 136.87, 161.15, 177.70. MS (ESI): m/z 746.1(M^+). Anal. Calcd. for $C_{36}H_{24}MoS_6$: C, 58.04; H, 3.25. Found: C, 58.47; H, 2.99. (%).

S2 Density Functional Theory calculation methods

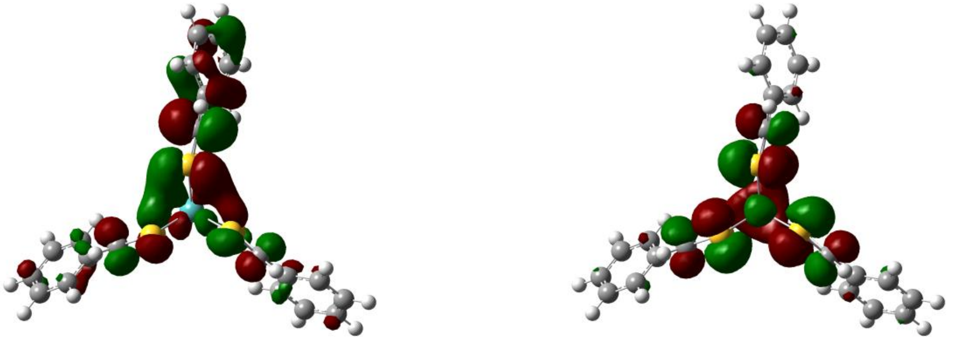
Ground-state geometries of two compounds were optimized at B3LYP/6-31g(d) (with Lanl2dz pseudopotential basis set for Mo) level. Then the time dependent density functional theory (TDDFT) was used to calculate the electron transitions at B3LYP level with Lanl2dz pseudopotential basis set for Mo and 6-311+g(d) for all other atoms. All the calculations were carried out using Gaussian 09 grogram.

Table **S1.** Calculated major transition wavelengths and oscillator strengths for compound **1**

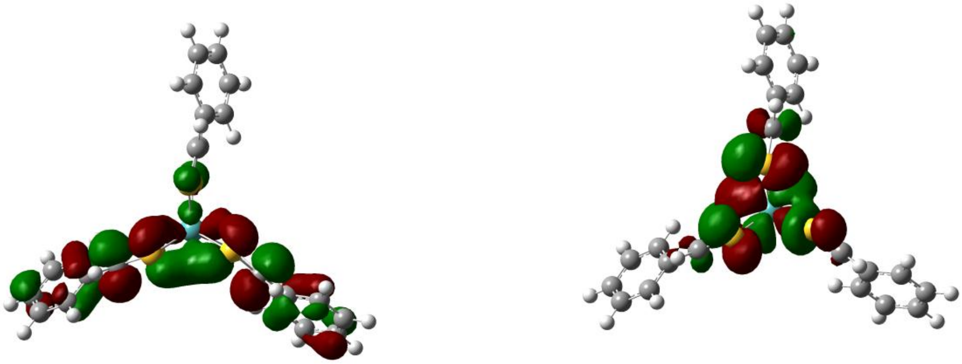
No.	Wavelength (nm)	Osc. Strength	Major contributions
1	803.57	0.0004	H-2->LUMO (88%)
2	707.14	0.1602	H-2->L+1 (21%), HOMO->LUMO (68%)
3	706.38	0.1654	H-2->L+2 (20%), H-1->LUMO (69%)
4	616.71	0.152	H-2->L+1 (59%), HOMO->LUMO (23%)
5	614.69	0.1487	H-2->L+2 (60%), H-1->LUMO (22%)
9	433.05	0.1368	H-1->L+1 (38%), HOMO->L+2 (43%)
10	432.81	0.1351	H-1->L+2 (39%), HOMO->L+1 (41%)

Table **S2.** Calculated major transition wavelengths and oscillator strengths for compound **2**

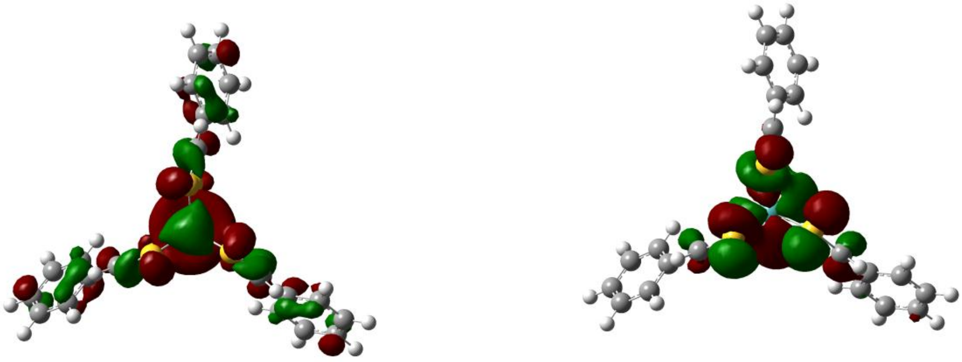
No.	Wavelength (nm)	Osc. Strength	Major contributions
1	818.97	0.0003	H-5->LUMO (43%), H-2->LUMO (45%)
2	721.38	0.2451	HOMO->LUMO (70%)
3	720.75	0.2404	H-1->LUMO (69%)
4	629.36	0.1748	H-5->L+1 (26%), H-5->L+2 (10%), H-2->L+1 (20%), H-1->LUMO (20%)
5	628.53	0.1726	H-5->L+1 (10%), H-5->L+2 (26%), H-2->L+2 (20%), HOMO->LUMO (19%)
11	430.62	0.1301	H-3->LUMO (15%), H-1->L+2 (30%), HOMO->L+1 (29%)
12	430.45	0.1294	H-4->LUMO (15%), H-1->L+1 (30%), HOMO->L+2 (30%)



HOMO LUMO

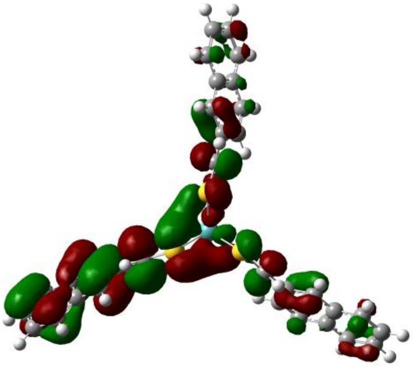


HOMO-1 LUMO+1

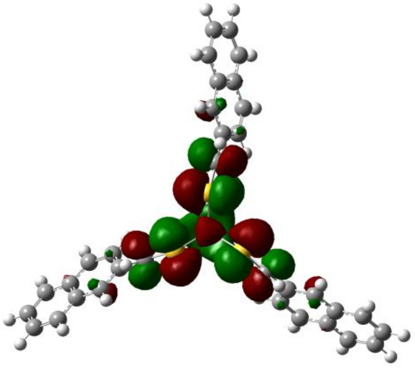


HOMO-2 LUMO+2

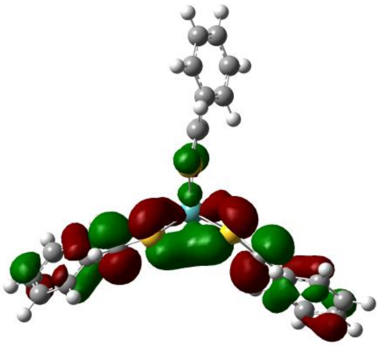
Figure **S1.** Molecular orbitals involved in the major transitions of compound **1**.



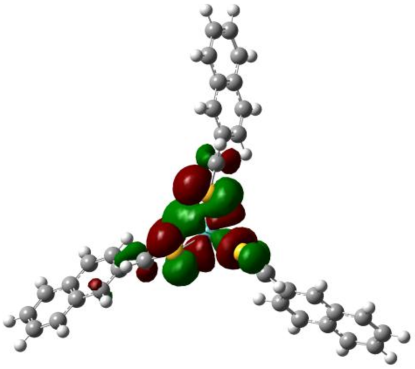
HOMO



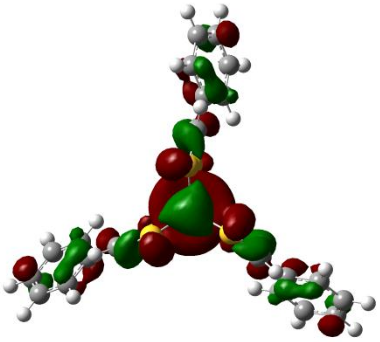
LUMO



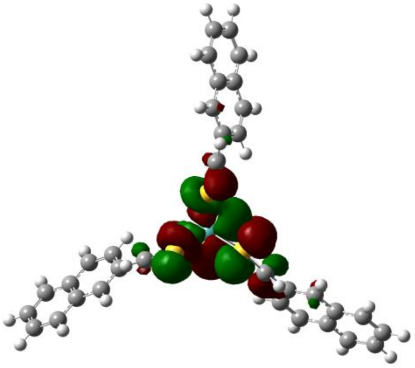
HOMO-1



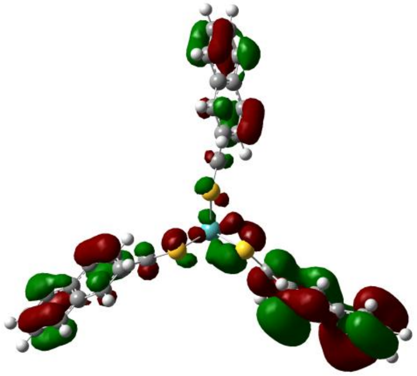
LUMO+1



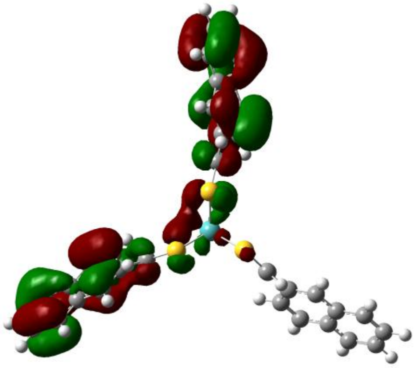
HOMO-2



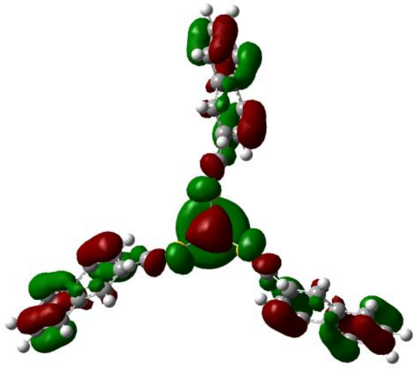
LUMO+2



HOMO-3



HOMO-4



HOMO-5

Figure **S2.** Molecular orbitals involved in the major transitions of compound **2**.

S3 Z-scan method

Third-order nonlinear optical absorption responses were determined by fs-pulsed open Z-scan measurement. The solutions used for the Z-scans were contained in 1 mm glass cuvettes. The excitation light used for all nonlinear optical measurements was generated by a non-collinear optical parametric amplifier (OPA, TOPAS-C, Spectra-Physics) that provides output pulses ~100 fs in the 1100-2800 nm spectral region. The OPA was pumped by regenerative Ti:Sapphire amplifier (Spitfire, Spectra-Physics) that produces ~100 fs pulses with a repetition rate of 1 kHz. The excitation energy on the sample was varied between ~400 μJ and 1200 μJ.

The NLA coefficient β can be obtained from the normalized the open- aperture z-scans of the samples, from which σ_2 can be calculated through the following equation:

$$s_2 = \frac{b h n}{N_A C} \qquad (1)$$

Where N_A is Avogadro‘s number, C is the concentration of the sample, and *hv* is the photon energy.

2PA measurements on **1** and **2** in solution were performed in the wavelength range of ~1.55 μm to 1.26 μm. No detectable signal was found at 1.55 μm while sizable 2PA cross sections were observed near 1.3 μm.

References

S1 S. Boyde, C. D. Garner, J. A. Joule and D. J. Rowe, J. Chem. Soc., Chem. Commun., 1987, 800.

S2 M. Sheik-Bahae, A. A. Said, T.-H. Wei, D. Hagan, E. W and Van Stryland, IEEE J. Quantum Elect., 1990, 26, 760.

S3 D. Beijonne, J. L. Brédas, M. Cha, W. E. Torruellas, G. I. Stegeman, J. W. Hofstraat, W. H. G. Horsthuis and G. R. Möhlmann, J. Chem. Phys., 1995, 103, 7834.