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Synthesis, structure and theoretical investigation into a homoleptic tris(dithiolene) tungsten



SPECTROCHIMICA ACTA

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HIGHLIGHTS

- A new homoleptic dithiolene tungsten complex was successfully synthesized.
- Spectroscopic analysis and X-ray single crystal study confirm the structure and geometry.
- HOMO and LUMO comes from separate moieties of the complex.
- The optical properties showed a slight blue shift in several low dielectric solvents.

G R A P H I C A L A B S T R A C T



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ABSTRACT

A new homoleptic dithiolene tungsten complex, tris-{1,2-bis(3,5-dimethoxyphenyl)-1,2-ethylenodithiolene-S,S'}tungsten, was successfully synthesized via a reaction of the thiophosphate ester and sodium tungstate. The thiophosphate ester was prepared from 3,5-dimethoxybenzaldehyde via benzoin condensation to produce the intermediate 1,2-bis-(3,5-dimethoxyphenyl)-2-hydroxy-ethanone compound, followed by a reaction of the intermediate with phosphorus pentasulfide. FTIR, UV–Vis spectroscopy, ¹H NMR and ¹³C NMR and elemental analysis confirmed the product as tris{1,2-bis-(3,5-dimethoxyphenyl)-1,2-ethylenodithiolene-S,S'}tungsten with the molecular formula of C₅₄H₅₄O₁₂S₆W. Crystals of the product adopted a monoclinic system with space group of *P*2(1)/n, where *a* = 12.756(2) Å, *b* = 21.560(3) Å, *c* = 24.980(4) Å and β = 103.998(3)°. Three thioester ligands were attached to the tungsten as bidentate chelates to form a distorted octahedral geometry. Density functional theory calculations were performed to investigate the molecular properties in a generalized-gradient approximation framework system using Perdew–Burke–Ernzerhof functions and a double numeric plus polarization basis set. The HOMO was concentrated on the phenyl ligands, while the LUMO was found along the W(S₂C₂)₃ rings. The theoretical optical properties showed a slight blue shift in several low dielectric solvents. The solvatochromism effect was insignificant for high polar solvents.

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Introduction

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Since the early 1960s, investigation into the synthesis, structure and molecular properties of metal complexes with dithiolene ligands has attracted a number of researchers [1-8]. The dithiolene

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ligand can bond easily to various metals such as nickel (Ni) [7], tungsten (W) [8,9], molybdenum (Mo) [10,11], cobalt (Co) [1,12] and platinum (Pt) [13], to form complex molecules with unique optical, magnetic and conductive properties. The complexes have been considered for a wide variety of applications, such as enzyme cofactors [8,14], opto-electronic devices [15,16], building block materials [17], dye sensitizers for solar cells [18] and photocatalysts for water splitting [19–22].

Dithiolene is known as a bidentate ligand. The metal-ligand complex forms a 1,2-dithiolene chelate which has the possibility to become a resonance structure [23]. Electron delocalization occurring on the dithiolene ring involves a thienyl radical monoanion as shown in Fig. 1. The oxidation state of the metal and the ligands in dithiolene complexes are highly variable and difficult to define. In addition, the dithiolene is often a non-innocent ligand that depends on the system [24.25]. The majority of non-innocent ligands are redox-active and are capable of acting as donors or acceptors depending on the redox state [26].

The bidentate dithiolene ligand can form mono-, bis- or tris-(1,2-dithiolenes) metal complexes. Molecular geometry of a dithiolene complex depends on the variation and number of bidentate ligands attached to the metal center. Dithiolene complexes are classified into three categories: (i) homoleptic dithiolene complexes, in which only 1,2-dithiolene is coordinated to the metal center forming bis(dithiolene) complexes with a square-planar geometry or tris-(dithiolene) complexes with either trigonal prismatic or octahedral geometries; (ii) heteroleptic dithiolene complexes, in which a dithiolene and other inorganic ligands are attached to the metal center, such as $[(P \land P)M(dithiolene)]$ $(M = Pt, P \land P = diphosphine)$ and $[oxo-M(dithiolene)_2]$ (M = Mo,W) complexes with square-planar geometries; and (iii) organometallic dithiolene complexes, in which a dithiolene and organic ligands with metal-carbon bonds are incorporated [27].

The most common homoleptic dithiolene complex is bis-(1,2diphenyl-1,2-dithiolene) nickel (II), which is made from the reaction of NiS₂ with diphenylacetylene [28]. Other homoleptic bisor tris-dithiolenes complexes are generally synthesized from the reaction of metal halides and dithiolate [29], and also via oxodithiolenes from the photoreaction of metal carbonyls with dithiolate [30]. An alternative route is through thiophosphate esters by the reaction of α -hydroxyketones with phosphorus pentasulfide, which is mostly used for the preparation of dithiolene complexes in large scale [28].

In this work, a new tris(dithiolene) compound called tris{1,2bis(3,5-dimethoxyphenyl)-1,2-ethylenodithiolenic-S,S'}tungsten abbreviated MTDT was synthesized from 3,5-dimethoxybenzaldehyde in three steps: (i) benzoin condensation to produce an intermediate 1,2-bis-(3,5-dimethoxyphenyl)-2-hydroxy-ethanone; (ii) thioester formation to give 1,2-dithiophosphate; and (iii) reaction of 1,2-dithiophosphate with a tungsten salt to produce MTDT [10,11]. The non-innocent behavior of the dithiolene ligands was examined using structural geometry and density functional theory (DFT) calculations. The DFT calculations were performed on the molecular configuration found in the X-ray crystal structure which was then optimized until no imaginary frequencies to be found. Frontier molecular orbitals, optical characteristics and

solvatochromism of MTDT were studied by time-dependent density functional theory (TDDFT) on the optimized molecular structure. Furthermore, the effects of ligand substitution on the structure, spectra and molecular orbital (MO) energy properties were also investigated. For the purpose of comparison, all OCH₃ groups were removed from the phenyl rings of the original X-ray crystal structure, and the structure was then optimized using the same calculation parameters.

Experiments

Materials and instruments

Chemicals: 3,5-dimethoxybenzaldehyde, triethylbenzylammonium chloride, tetrabuthylammonium iodide, potassium hydroxide, phosphorus pentasulfide and all organic solvents were obtained from Merck. Hydrochloric acid and hydrazine monohydrate were obtained from Aldrich. IR spectra were recorded on a Spectrum One (Perkin Elmer) in the form of KBr disk for solid material and ATR for liquid. ¹H and ¹³C NMR spectrum were obtained using a Varian JEOL ECP 400 MHz in CDCl₃ or deuterated acetone. Electronic absorption spectra were recorded using a Lambda 35 UV/Vis spectrophotometer. Elemental analyzes were performed on a Fisons EA 1108 Elemental Analyzer. Electrochemical experiments were performed on a Voltalab PGZ402 Radiometer. The crystal structure was determined using a Bruker AXS Smart APEX with a CCD detector and a SHELXTL suite program.

Preparation of MTDT

Benzoin condensation (I)

3,5-Dimethoxybenzaldehyde (3.32 g) was dissolved in 12.5 ml DMF followed by the addition of tetrabutylammonium iodide (0.63 g) and KCN (0.251 g). The resulting mixture was stirred for 18 h under nitrogen. The reaction was quenched by adding 75 ml of cold water. A white precipitate was formed, filtered and recrystallized from hot ethanol to give a white flaky benzoin (I). Yield 60%; melting point: 102–103 °C; ¹H NMR δ(ppm) 3.80; 3.81; 2.86; 6.04; 6.37; 6.62 7.16; 4.93; 13 C NMR δ (ppm) 100.36; 162.16; 107.61; 142.89; 77.09; 200.10; 137.28; 106.56; 161.90; 106.22; 55.68; 56.00; IR spectrum (v/cm⁻¹) 3843 (OH); 3098 (C-H); 850 and 1672 (C=O); 1165 (C-O-C); UV/Vis spectrum $(\lambda_{\text{max}}/\text{nm})$ (acetone solution) 342. Elemental CHNSO analysis (%): C 65.06, H 6.02, O 29.92, and the theoretical values were C: 63.48; H: 5.87; O: 30.65.

Thioester synthesis (II)

Benzoin I (30 g) and phosphorus pentasulfide (45 g) were dissolved in 250 ml of dry dioxane. The mixture was refluxed for 3-4 h in an inert atmosphere. Hydrogen sulfide produced from the reaction was trapped using lead acetate. The mixture was cooled to room temperature before filtering. The filtrate was concentrated *in vacuo* to give a dark red oil, yield 37.5%. ¹H NMR δ (ppm) 3.56; 6.37; 7.27 and ¹³C NMR δ(ppm) 56.44; 66.92; 77.25; 107.56; 160.56. IR spectrum (v/cm⁻¹) 1254 (P=O), 1081 and 958 (P-O



ene-1,2-dithiolate

thienyl radical monoanion

 α -dithione

209

Fig. 1. Several oxidation states of a dithiolene ligand.

and P–O–P), 870 (P=S). UV spectrum (λ_{max}/nm) (acetone solution) 300.

MTDT synthesis

Thioester II (5 g) was added to a mixture of sodium tungstate (9 g) in 40 ml HCl 1 M. The mixture was refluxed for 2 h under nitrogen. A dark-green solution was obtained, cooled and then concentrated by evaporation. The product was extracted with benzene (250 ml). The dithiolene complex was extracted by hydrazine 95% (80 ml), washed and neutralized by HCl 1 M. Yield 39%. Melting point: 220.4–221.6 °C, ¹H NMR δ (ppm) 2.84; 3.67; 6.47; ¹³C δ (ppm) 55.85; 101.90; 108.98; 144.70; 162.62; 171.71. IR spectrum (ν /cm⁻¹) 2933 (C–H); 1678 (C–C); 1592 and 1155 (C–S); 1298 (C–O–C). UV/Vis spectrum (λ_{max} /nm) as acetone solution 330; 412; 659. Elemental CHNS Analysis (%): C 51.02 (52.15); H 4.25 (4.84), S 15.12 (13.77).

Cyclic voltammetry

Voltammograms of the samples were recorded on a computercontrolled Voltalab PGZ402 potentiostat. The cell consisted of a platinum disk as working electrode, a platinum wire as an auxiliary electrode and an Ag/AgCl reference electrode. The redox potentials of the dithiolene complex (0.1 mM) were determined in CH_2Cl_2 containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) electrolyte under nitrogen.

Single crystal X-ray crystallography

Single crystals of MTDT were obtained by recrystallization using vapor diffusion of diethyl ether into an acetone solution of MTDT. The crystallographic data of the complex given in Table 1 was collected using a SMART diffractometer [31]. Cell refinement and data reduction were carried out with SAINT [31]. Data analysis was performed with the SHELXS97 program [32].

Computational details

The isolated-molecule DFT calculations were carried out using the DMol³ code in Materials Studio 5.5 from Accelrys, which

Table 1

Crystal and structure refinement parameters for MTDT.

Identification code	
Empirical formula	C ₅₄ H ₅₄ O ₁₂ S ₆ W
Formula weight	1271.18
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 12.756(2) Å
	b = 21.560(3) Å
	c = 24.980(4) Å
	$\beta = 103.998(3)^{\circ}$
Volume	6666.0(18) Å ³
Z, calculated density	4, 1.583 Mg/m ³
Absorption coefficient	2.463 mm^{-1}
F(000)	3220
Crystal size	$0.49\times0.24\times0.21~mm$
Theta range for data collection	1.26–25.00°
Limiting indices	$-13 \leqslant h \leqslant 15, -25 \leqslant k \leqslant 23, -29 \leqslant l \leqslant 29$
Reflections collected/unique	34,059/11,716 [<i>R</i> (int) = 0.0741]
Completeness to theta = 25.00	99.8%
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	11,716/0/655
Goodness-of-fit on F ²	1.051
Final R indices [I > 2sigma(I)]	$R1 = 0.0687, wR_2 = 0.1905$
R indices (all data)	$R1 = 0.1287, wR_2 = 0.2230$
Largest diff. peak and hole	2.443 and –1.147 (e Å ⁻³)

utilized the framework of a generalized-gradient approximation (GGA) system [33]. The starting atomic coordinates were taken from the final X-ray refinement cycle. Geometry of the molecule was fully optimized in a double numeric plus polarization (DNP) basis set using Perdew–Burke–Ernzerhof (PBE) functions [34].

The geometrical optimization was an iterative procedure in which the coordinates of the atoms were adjusted until the energy of the structure was brought to a stationary value. The stationary value of the minimum energy was determined by analysis of the vibrational frequencies at the ground state geometry of the complex. The absence of imaginary eigenvalues confirmed the validity of the molecular geometry, from which further properties can be calculated [35]. The self-consistent field (SCF) method was used for calculating the electronic structure with the core treatment to DFT Semi-core Pseudopots (DSPP) [36] and spin-unrestricted Hartree-Folk (URHF) mode. TDDFT calculations were conducted on the ground state in spin-restricted. The effect of a solvent when calculating optical properties was determined using the conductor-like screening model (COSMO) approach.

Results and discussion

Synthesis

The synthetic route proposed by Schrauzer et al. was modified and used to synthesize the tungsten complex of tris(dithiolene) starting from 3,5-dimethoxybenzaldehyde in three steps, as shown in Fig. 2 [37,38]. First, an intermediate 1,2-bis-(3,5-dimethoxyphenyl)-2-hydroxy-ethanone was synthesized from 3,5-dimethoxybenzaldehyde using a similar method to traditional benzoin condensation reaction, but at room temperature. The synthesis used tertiarybutylammonium iodide as an electrolyte and DMF as the solvent. The desired product was obtained as white crystals with the melting point of 102–103 °C.

The thiolation of the benzoin was exothermic and was accompanied by the evolution of H_2S . An excessive amount of P_2S_{10} was used and the unreacted P_2S_{10} was recrystallized and eliminated upon cooling. The resulting solution contained thioesters of the corresponding dithiols and was stable during storage.

Preparation of the metal complex involved mixing the metal salt solution in HCl (1 M) with the ligand and the resulting mixture was refluxed. In addition to acting as a solvent, the HCl also hydrolyzed the thioester into the corresponding thiols. The unreacted thioester was guite difficult to separate from the desired complex. Purification was carried out by addition of hydrazine, and the resulting compound was purified by silica gel column chromatography using benzene as the elutant. The melting point of the dark green crystals was 220.4–221.6 °C, and the reported melting point of a similar compound was 250 °C [21]. Micro elemental analysis for CHNS confirmed the empirical formula of MTDT as C₅₄H₅₄O₁₂S₆₋ W. The IR spectrum for this complex showed stretching frequencies of C=S and C-O-C at 1592 cm^{-1} and 1297 cm^{-1} , respectively. The ¹³C NMR spectrum exhibited six signals corresponding to the four carbon atoms in the benzene ring at δ 101.90 ppm, 108.98 ppm, 144.70 ppm and 163.62 ppm, and the two carbon atoms of the ethylene moiety at δ 171.71 ppm. The signal for the methoxy carbon was recorded at δ 55.07 ppm. The ¹H spectrum using the CDCl₃ solution exhibited the OCH₃ protons as a singlet at δ 2.84 ppm and two aromatic proton signals at around δ 6.46 ppm.

Crystal structure

The crystallographic data showed the compound adopting a monoclinic system with space group of $P2_1/n$, where



Fig. 2. A schematic diagram showing the synthetic route of MTDT.

a = 12.756(2) Å, *b* = 21.560(3) Å, *c* = 24.980(4) Å, β = 103.998(3)°, *Z* = 4 with a density of 1.583 Mg/m³ and *V* = 6666.0(18) Å³. The crystal system and atomic displacement parameters are shown in Table 1.

Fig. 3 shows the X-ray structure of MTDT with the numbering scheme. Three thioester ligands were chelated to the central tungsten W1 atom to form a distorted octahedral geometry. The angles of the W1 atoms were between 80.15° and 137.02°. The W-S bond lengths were between 2.352(3) and 2.367(3) Å, which are considered to be in normal range [39]. The C-S bond lengths were 1.710(10) and 1.745(10) Å. The chelated thioesters formed three 5-membered (WS_2C_2) rings. The presence of OCH₃ groups in each phenyl ring forced the ligands to be twisted around the thiolate back-bone resulting in a non-planar arrangement. Some of OCH₃ groups were found to be disordered due to the position of the OCH₃ on some phenyl rings which were not in the appropriate orientation. However, the disorder had no effect on the distorted octahedron of the tungsten dithiolate backbone. The tungsten atom remained in oxidation state of VI in the neutral complex molecule. The W-S bond lengths which were formed by coordinated ion



Fig. 3. X-ray crystallographic structure of MTDT with 50% probability ellipsoid. Hydrogen atoms were omitted for clarity.

bonding of S atoms confirmed the central W atom to be in that oxidation state.

Optimized geometry

The selected bond lengths and angles of the optimized structure of MTDT calculated by PBE on DNP basis set, listed in Table 2, are in good agreement with the experimental values. The calculation was run after the disordered carbon atoms from the X-ray data were resolved. The total energy changes during the optimization have been calculated, which are between -20669.16 Hartrees and -20670.26 Hartrees.

Fig. 4 shows a comparison of the X-ray structure and the optimized structure from the top-view. Both the X-ray structure and the theoretical calculation resulted in a similar geometry, which was between a distorted octahedron and a trigonal prism. The changes were observed from simultaneous rotation of OCH₃ groups in some phenyl rings twisted angularly around the thiolate ligands. Most of the calculated bond lengths were found to be longer than the experimental data, and only a few were shorter. However, the calculated results were considered to be in the normal range [39]. The S-W-S angles in two five-member (WS₂C₂) rings calculated were found to be narrower than for the X-ray crystal data. Nevertheless, not all of the S-W-S angles between the rings became larger. Some of them became narrower than the X-ray single crystal. Some main torsion angles became larger, while some others became smaller. Overall, the calculations resulted in a molecular structure with more uniform bond lengths and angles compared to the crystal data parameters.

In the neutral complex molecule, the tungsten atom would be expected to have an octahedral geometry and had an oxidation state of VI. However, because dithiolene ligands often exhibit non-innocent behavior, the VI oxidation state cannot be assured. The C–S and C–C bond lengths are two parameters that can be used to determine the complex oxidation state. Significant departure from the normal bond length of C-S and C-C would be an indication of ligand reduction or oxidation. X-ray crystallography and DFT data can be used to determine the non-innocent behavior of the dithiolene ligands in this system. The C–C bond lengths in the WS₂C₂ rings in the crystal structure are typical for C–C double bond lengths, and all C-S bond lengths are similar and within the normal (1.733–1750 Å) [39]. Furthermore, the bond lengths did not change during the optimized structure calculation process, suggesting the ligands adopted a dithiolate state. This assumption is supported by cyclic voltammetry (CV) results, as shown in Fig. 5. The complex shows a reversible redox couple, with oxidation and reduction peaks at -0.106 and -0.197 volts, respectively. The peak

Table 2
Selected bond lengths (A°), bond angles (°) and torsion angles of MTDT from X-ray single crystal analyzes and optimized calculated

bond length (A*)W1-S12.352 (3)2.3872.394W1-S22.366 (3)2.3932.331W1-S32.366 (3)2.3932.447W1-S42.360 (3)2.3922.394W1-S52.362 (3)2.3922.394S1-C91.737 (11)1.7371.736S2-C101.732 (11)1.7371.735S3-C191.707 (10)1.7341.735S4-C281.727 (11)1.7341.735S5-C371.737 (10)1.7341.735S5-C461.747 (10)1.7331.735C9-C101.367 (14)1.3921.392C37-C461.350 (13)1.3911.392C37-C461.352 (15)1.3911.391Bond angle (*)181.4180.92S4-W1-S381.46 (9)81.1281.41S6-W1-S481.25 (10)81.0680.79S1-W1-S581.12 (10)81.6680.79S1-W1-S581.16 (10)13.2813.41S6-W1-S41.354 (11)16.6313.565S1-W1-S513.416 (10)13.2813.41S6-W1-S41.356 (11)13.2813.41S7-W1-S513.16 (10)13.2813.41S7-W1-S41.356 (11)13.3813.565S1-W1-S513.56 (10)13.0813.565S1-W1-S41.356 (11)13.3813.565S2-W1-S41.350 (10)13.30613.518S6-W1-S31.356 (10)13.306 <th>Parameter</th> <th>MTDT X-ray</th> <th>MTDT optimized PBE/DNP basis set</th> <th>MTDT w/o methoxy optimized PBE/DNP basis set</th>	Parameter	MTDT X-ray	MTDT optimized PBE/DNP basis set	MTDT w/o methoxy optimized PBE/DNP basis set
W1-51 2.352 (3) 2.388 2.394 W1-52 2.366 (3) 2.393 2.355 W1-53 2.366 (3) 2.393 2.447 W1-54 2.360 (3) 2.392 2.394 W1-55 2.352 (3) 2.382 2.466 W1-56 2.354 (3) 2.392 2.394 S2-C10 1.737 (11) 1.732 1.736 S2-C10 1.737 (10) 1.734 1.735 S4-C28 1.707 (10) 1.734 1.735 S5-G37 1.737 (10) 1.733 1.391 S6-C46 1.747 (10) 1.733 1.392 C19-C10 1.356 (14) 1.392 1.392 C37-C46 1.362 (15) 1.391 1.391 S1-W1-S2 81.46 (9) 81.12 81.41 S6-W1-S5 81.25 (10) 81.06 80.79 S1-W1-S5 81.70 82.96 83.37 S1-W1-S5 134.16 (10) 132.8 134.04 S2-W1-S5 135.16 (10) 133.28 134.04 S2-W1-S5 135.05 (10) 133	Bond length (A°)			
W1-S2 2.363 (a) 2.387 2.355 W1-S3 2.366 (a) 2.393 2.331 W1-S4 2.360 (a) 2.393 2.447 W1-S5 2.362 (a) 2.382 2.466 W1-S6 2.354 (a) 2.392 2.394 S1-C9 1.737 (11) 1.737 1.736 S2-C10 1.732 (11) 1.737 1.735 S4-C28 1.727 (10) 1.734 1.735 S5-C37 1.737 (10) 1.733 1.735 S6-C46 1.747 (10) 1.733 1.735 C9-C10 1.367 (14) 1.392 1.392 C37-C46 1.360 (13) 1.391 1.391 Bond angle (*) I I.391 1.391 S4-W1-S5 81.25 (10) 81.06 80.79 S1-W1-S4 81.78 81.72 81.41 S6-W1-S5 81.78 (10) 82.96 83.37 S1-W1-S4 135.45 (11) 136.33 135.65 S1-W1-S5 81.78 (10) <td>W1-S1</td> <td>2.352 (3)</td> <td>2.388</td> <td>2.394</td>	W1-S1	2.352 (3)	2.388	2.394
W1-S3 2366 (3) 2393 2.331 W1-S4 2.360 (3) 2.393 2.447 W1-S5 2.352 (3) 2.382 2.466 W1-S6 2.354 (3) 2.392 2.394 S1-C9 1.737 (11) 1.732 1.735 S2-C10 1.732 (11) 1.732 1.735 S4-C28 1.727 (11) 1.734 1.735 S5-C37 1.737 (10) 1.734 1.735 S6-C46 1.747 (10) 1.733 1.735 C9-C10 1.367 (14) 1.392 1.392 C19-C28 1.350 (13) 1.391 1.392 C19-C28 1.350 (13) 1.391 1.392 C37-C46 1.362 (15) 1.391 1.392 S4-W1-S3 81.46 (9) 81.12 81.41 S6-W1-S5 81.25 (10) 81.09 80.79 S1-W1-S4 81.345 (11) 136.33 135.65 S1-W1-S5 81.27 (10) 83.08 82.45 S2-W1-S4 81.30	W1-S2	2.363 (3)	2.387	2.355
W1-S4 2360 2.393 2.447 W1-S5 2.362 2.362 2.466 W1-S6 2.354 3.2392 2.394 S1-C9 1.737 1.736 S2-C10 1.732 1.735 S3-C19 1.707 1.734 S4-C28 1.727 1.737 S5-C37 1.737 1.735 S5-C37 1.737 1.734 S6-C46 1.747 10 1.735 1.735 C9-C10 1.367 1.391 C19-C28 1.350 1.391 S1-W1-S2 8.141 8.101 80.428 8.121 8.131 S6-W1-S5 81.25 81.09 S1-W1-S3 81.46 8.102 S1-W1-S4 13545 81.26 S1-W1-S5 8.178 81.69 S1-W1-S5 8.121 81.41 S2-W1-S5 8.2110 8.3098 S2-W1-S5 8.2110 8.3098 S2-W1-S4 81.80 13.91 S2-W1-S5 13.555 13.552 S2-W1-S4 81.80 13.91 S2-W1-S5 13.556 10 S3-W1-S5 13.556 10 S3-W1-S5 13.556 10 S3-W1-S5 13.556 10 S4-W1-S5 8.126 13.518 S6-W1-S4 13.04 13.515 S6-W1-S5 13.556 13.515 S6-W1-S4 13.04 13.515 S6-W1-S4 13.04 13.515 S6-W1-S5 13.569 83.31 <td>W1-S3</td> <td>2.366 (3)</td> <td>2.393</td> <td>2.331</td>	W1-S3	2.366 (3)	2.393	2.331
W1-S5 2.362 (3) 2.382 2.466 W1-S6 2.354 (3) 2.392 2.394 S1-C9 1.737 (11) 1.737 1.736 S2-C10 1.732 (11) 1.732 1.735 S3-C19 1.707 (10) 1.734 1.735 S4-C28 1.727 (11) 1.734 1.735 S5-C37 1.737 (10) 1.734 1.735 S6-C46 1.747 (10) 1.733 1.735 C9-C10 1.367 (14) 1.392 1.392 C19-C28 1.350 (13) 1.391 1.392 C37-C46 1.362 (15) 1.391 1.392 C37-C46 1.362 (15) 1.391 1.392 S6-W1-S2 81.41 (10) 81.01 80.92 S4-W1-S3 81.46 (9) 81.12 81.41 S6-W1-S5 81.25 (10) 81.06 80.79 S1-W1-S4 135.45 (11) 136.33 135.65 S1-W1-S5 134.16 (10) 133.28 134.04 S2-W1-S4	W1-S4	2.360 (3)	2.393	2.447
W1-S62.354 (3)2.3922.394 $S1-C9$ 1.737 (11)1.7371.736 $S2-C10$ 1.732 (11)1.7321.735 $S3-C19$ 1.707 (10)1.7341.735 $S4-C28$ 1.727 (11)1.7341.735 $S5-C37$ 1.737 (10)1.7341.735 $S6-C46$ 1.747 (10)1.7331.735 $C9-C10$ 1.367 (14)1.3921.392 $C19-C28$ 1.360 (13)1.3911.391 $C37-C46$ 1.362 (15)1.3911.391Bond angle (°)181.0180.92 $S4-W1-S3$ 81.46 (9)81.1281.41 $S6-W1-S5$ 81.25 (10)81.0680.79 $S1-W1-S6$ 80.13 (10)81.4981.91 $S1-W1-S4$ 135.45 (11)136.33135.65 $S1-W1-S4$ 81.80 (10)81.4781.31 $S2-W1-S4$ 81.80 (10)81.4781.31 $S2-W1-S5$ 83.21 (10)83.0882.45 $S2-W1-S4$ 135.05 (10)133.06135.18 $S6-W1-S3$ 81.68 (10)81.69182.21 $S6-W1-S3$ 81.68 (10)81.69182.21 $S6-W1-S5$ 83.51 (0)135.15136.07 $S4-W1-S5$ 83.51 (9)83.3182.78	W1-S5	2.362 (3)	2.382	2.466
SI-C9 1.737 (11) 1.737 1.736 $S2-C10$ 1.732 (11) 1.732 1.735 $S3-C19$ 1.707 (10) 1.734 1.735 $S4-C28$ 1.727 (11) 1.734 1.735 $S5-C37$ 1.737 (10) 1.734 1.735 $S6-C46$ 1.747 (10) 1.733 1.735 $C9-C10$ 1.367 (14) 1.392 1.392 $C19-C28$ 1.360 (13) 1.391 1.392 $C37-C46$ 1.362 (15) 1.391 1.391 Bond angle (°) $S1.12$ 81.41 $S6-W1-S5$ 81.25 (10) 81.06 80.79 $S1-W1-S2$ 81.41 (10) 81.49 81.91 $S1-W1-S4$ 81.51 81.66 80.79 $S1-W1-S5$ 81.25 (10) 81.49 81.91 $S1-W1-S4$ 135.65 (11) 136.33 135.65 $S1-W1-S4$ 135.16 (10) 132.28 134.04 $S2-W1-S6$ $135.31(10)$ 81.47 81.31 $S2-W1-S6$ $135.33(10)$ 137.10 135.62 $S2-W1-S6$ $135.33(10)$ 137.10 135.62 $S2-W1-S6$ $135.05(10)$ 133.06 135.18 $S6-W1-S3$ $81.68(10)$ 81.691 82.21 $S6-W1-S5$ $83.51(9)$ 83.31 82.78	W1-S6	2.354 (3)	2.392	2.394
S2-C10 $1.732 (11)$ 1.732 1.735 S3-C19 $1.707 (10)$ 1.734 1.735 S5-C37 $1.737 (10)$ 1.734 1.735 S5-C46 $1.747 (10)$ 1.733 1.735 C9-C10 $1.367 (14)$ 1.392 1.392 C19-C28 $1.350 (13)$ 1.391 1.392 C37-C46 $1.362 (15)$ 1.391 1.391 Bond angle (°) S S S S1-W1-S2 $81.41 (10)$ 81.01 80.92 S4-W1-S3 $81.25 (10)$ 81.06 80.79 S1-W1-S4 $81.25 (10)$ 81.06 80.79 S1-W1-S5 $81.25 (10)$ 81.06 83.37 S1-W1-S4 $135.45 (11)$ 136.33 135.65 S1-W1-S4 $135.45 (11)$ 136.33 135.65 S1-W1-S4 $135.45 (10)$ 81.08 82.45 S2-W1-S5 $83.21 (10)$ 83.098 82.45 S2-W1-S5 $135.05 (10)$ 133.06 135.33 S5-W1-S3 $135.05 (10)$ 133.06 135.18 S6-W1-S3 $81.68 (10)$ 81.691 82.21 S6-W1-S5 83.59 83.31 82.78	S1-C9	1.737 (11)	1.737	1.736
S3-C191.707 (10)1.7341.735S4-C281.727 (11)1.7341.735S5-C371.737 (10)1.7341.734S6-C461.747 (10)1.7331.735C9-C101.367 (14)1.3921.392C19-C281.350 (13)1.3911.392C37-C461.362 (15)1.3911.391Bond angle (°)181.0180.92S4-W1-S281.41 (10)81.0180.92S4-W1-S381.46 (9)81.1281.41S6-W1-S581.25 (10)81.0680.79S1-W1-S680.13 (10)81.4981.91S1-W1-S381.78 (10)82.9683.37S1-W1-S4135.45 (11)136.33135.65S1-W1-S5134.16 (10)133.28134.04S2-W1-S481.80 (10)81.4781.31S2-W1-S583.21 (10)83.09882.45S2-W1-S5135.05 (10)133.98135.33S5-W1-S3135.65 (10)133.98135.33S5-W1-S3135.65 (10)133.98135.33S5-W1-S3135.65 (10)133.06135.18S6-W1-S381.68 (10)81.69182.21S6-W1-S4137.04 (10)135.15136.07S4-W1-S583.56 (9)83.3182.78	S2-C10	1.732 (11)	1.732	1.735
S4-C28 $1.727 (11)$ 1.734 1.735 $S5-C37$ $1.737 (10)$ 1.734 1.734 $S6-C46$ $1.747 (10)$ 1.733 1.735 $C9-C10$ $1.367 (14)$ 1.392 1.392 $C19-C28$ $1.350 (13)$ 1.391 1.392 $C37-C46$ $1.362 (15)$ 1.391 1.391 Bond angle (°) $S1-W1-S2$ $81.41 (10)$ 81.01 $S1-W1-S2$ $81.41 (10)$ 81.01 80.92 $S4-W1-S3$ $81.46 (9)$ 81.12 81.41 $S6-W1-S5$ $81.25 (10)$ 81.06 80.79 $S1-W1-S6$ $80.13 (10)$ 81.49 81.91 $S1-W1-S6$ $80.13 (10)$ 81.47 81.31 $S2-W1-S4$ $81.80 (10)$ 83.098 82.45 $S2-W1-S5$ $83.21 (10)$ 83.098 82.45 $S2-W1-S5$ $135.05 (10)$ 133.06 135.18 $S6-W1-S3$ $135.65 (10)$ 133.06 135.18 $S6-W1-S3$ $81.68 (10)$ 81.691 82.21 $S6-W1-S5$ $83.85 (9)$ 83.31 82.78	S3-C19	1.707 (10)	1.734	1.735
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	S4-C28	1.727 (11)	1.734	1.735
S6-C46 $1.747 (10)$ 1.733 1.735 $C9-C10$ $1.367 (14)$ 1.392 1.392 $C19-C28$ $1.350 (13)$ 1.391 1.392 $C37-C46$ $1.362 (15)$ 1.391 1.391 Bond angle (°)SI-W1-S2 $81.41 (10)$ 81.01 80.92 S4-W1-S3 $81.46 (9)$ 81.12 81.41 S6-W1-S5 $81.25 (10)$ 81.06 80.79 SI-W1-S6 $80.13 (10)$ 81.49 81.91 SI-W1-S3 $81.78 (10)$ 82.96 83.37 SI-W1-S3 $81.78 (10)$ 82.96 83.37 SI-W1-S5 $134.16 (10)$ 133.28 134.04 S2-W1-S4 $81.80 (10)$ 81.47 81.31 S2-W1-S5 $83.21 (10)$ 83.098 82.45 S2-W1-S5 $83.21 (10)$ 133.06 135.18 S5-W1-S3 $135.05 (10)$ 133.06 135.18 S6-W1-S3 $81.68 (10)$ 81.691 82.21 S6-W1-S3 $81.68 (10)$ 81.691 82.78	S5-C37	1.737 (10)	1.734	1.734
C9-C10 $1.367 (14)$ 1.392 1.392 C19-C28 $1.350 (13)$ 1.391 1.392 C37-C46 $1.362 (15)$ 1.391 1.391 Bond angle (°) 81.01 80.92 S4-W1-S3 $81.46 (9)$ 81.12 81.41 S6-W1-S5 $81.25 (10)$ 81.06 80.79 S1-W1-S6 $80.13 (10)$ 81.49 81.91 S1-W1-S6 $80.13 (10)$ 82.96 83.37 S1-W1-S5 $135.45 (11)$ 136.633 135.65 S1-W1-S5 $134.16 (10)$ 133.28 134.04 S2-W1-S4 $81.80 (10)$ 81.47 81.31 S2-W1-S4 $81.50 (10)$ 133.08 82.45 S2-W1-S6 $135.05 (10)$ 133.08 135.62 S2-W1-S3 $135.05 (10)$ 133.06 135.18 S6-W1-S3 $81.68 (10)$ 81.691 82.21 S6-W1-S5 $83.85 (9)$ 83.31 82.78	S6-C46	1.747 (10)	1.733	1.735
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C9–C10	1.367 (14)	1.392	1.392
C37-C461.362 (15)1.3911.391Bond angle (°) $S1-W1-S2$ 81.41 (10)81.0180.92S4-W1-S381.46 (9)81.1281.41S6-W1-S581.25 (10)81.0680.79S1-W1-S680.13 (10)81.4981.91S1-W1-S681.78 (10)82.9683.37S1-W1-S4135.45 (11)136.33135.65S1-W1-S5134.16 (10)133.28134.04S2-W1-S481.80 (10)81.4781.31S2-W1-S583.21 (10)83.09882.45S2-W1-S6135.33 (10)137.10135.62S2-W1-S3135.05 (10)133.06135.18S6-W1-S381.68 (10)81.69182.21S6-W1-S481.68 (10)83.3182.78	C19–C28	1.350 (13)	1.391	1.392
Bond angle (°) $S1-W1-S2$ 81.41 (10) 81.01 80.92 $S4-W1-S3$ 81.46 (9) 81.12 81.41 $S6-W1-S5$ 81.25 (10) 81.06 80.79 $S1-W1-S6$ 80.13 (10) 81.49 81.91 $S1-W1-S3$ 81.78 (10) 82.96 83.37 $S1-W1-S4$ 135.45 (11) 136.33 135.65 $S1-W1-S5$ 134.16 (10) 133.28 134.04 $S2-W1-S4$ 81.80 (10) 81.47 81.31 $S2-W1-S5$ 83.21 (10) 83.098 82.45 $S2-W1-S6$ 135.33 (10) 137.10 135.62 $S2-W1-S3$ 135.05 (10) 133.06 135.18 $S6-W1-S3$ 81.68 (10) 81.691 82.21 $S6-W1-S4$ 137.04 (10) 135.15 136.07 $S4-W1-S5$ 83.85 (9) 83.31 82.78	C37—C46	1.362 (15)	1.391	1.391
S1-W1-S2 $81.41 (10)$ 81.01 80.92 $S4-W1-S3$ $81.46 (9)$ 81.12 81.41 $S6-W1-S5$ $81.25 (10)$ 81.06 80.79 $S1-W1-S6$ $80.13 (10)$ 81.49 81.91 $S1-W1-S6$ $80.13 (10)$ 82.96 83.37 $S1-W1-S3$ $81.78 (10)$ 82.96 83.37 $S1-W1-S4$ $135.45 (11)$ 136.33 135.65 $S1-W1-S5$ $134.16 (10)$ 133.28 134.04 $S2-W1-S4$ $81.80 (10)$ 81.47 81.31 $S2-W1-S5$ $83.21 (10)$ 83.098 82.45 $S2-W1-S6$ $135.33 (10)$ 137.10 135.62 $S2-W1-S3$ $135.05 (10)$ 133.06 135.18 $S6-W1-S3$ $81.68 (10)$ 81.691 82.21 $S6-W1-S4$ $137.04 (10)$ 135.15 136.07 $S4-W1-S5$ $83.85 (9)$ 83.31 82.78	Bond angle (°)			
S4-W1-S3 81.46 (9) 81.12 81.41 $S6-W1-S5$ 81.25 (10) 81.06 80.79 $S1-W1-S6$ 80.13 (10) 81.49 81.91 $S1-W1-S3$ 81.78 (10) 82.96 83.37 $S1-W1-S4$ 135.45 (11) 136.33 135.65 $S1-W1-S5$ 134.16 (10) 133.28 134.04 $S2-W1-S4$ 81.80 (10) 81.47 81.31 $S2-W1-S5$ 83.21 (10) 83.098 82.45 $S2-W1-S6$ 135.33 (10) 137.10 135.62 $S2-W1-S3$ 135.05 (10) 133.06 135.18 $S6-W1-S3$ 81.68 (10) 81.691 82.21 $S6-W1-S4$ 137.04 (10) 135.15 136.07 $S4-W1-S5$ 83.85 (9) 83.31 82.78	S1-W1-S2	81.41 (10)	81.01	80.92
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	S4-W1-S3	81.46 (9)	81.12	81.41
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	S6-W1-S5	81.25 (10)	81.06	80.79
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	S1-W1-S6	80.13 (10)	81.49	81.91
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	S1-W1-S3	81.78 (10)	82.96	83.37
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	S1-W1-S4	135.45 (11)	136.33	135.65
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	S1-W1-S5	134.16 (10)	133.28	134.04
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	S2-W1-S4	81.80 (10)	81.47	81.31
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	S2-W1-S5	83.21 (10)	83.098	82.45
S2-W1-S3 135.05 (10) 133.98 135.33 S5-W1-S3 135.65 (10) 133.06 135.18 S6-W1-S3 81.68 (10) 81.691 82.21 S6-W1-S4 137.04 (10) 135.15 136.07 S4-W1-S5 83.85 (9) 83.31 82.78	S2-W1-S6	135.33 (10)	137.10	135.62
S5-W1-S3 135.65 (10) 133.06 135.18 S6-W1-S3 81.68 (10) 81.691 82.21 S6-W1-S4 137.04 (10) 135.15 136.07 S4-W1-S5 83.85 (9) 83.31 82.78	S2-W1-S3	135.05 (10)	133.98	135.33
S6-W1-S3 81.68 (10) 81.691 82.21 S6-W1-S4 137.04 (10) 135.15 136.07 S4-W1-S5 83.85 (9) 83.31 82.78	S5-W1-S3	135.65 (10)	133.06	135.18
S6-W1-S4 137.04 (10) 135.15 136.07 S4-W1-S5 83.85 (9) 83.31 82.78	S6-W1-S3	81.68 (10)	81.691	82.21
S4-W1-S5 83.85 (9) 83.31 82.78	S6-W1-S4	137.04 (10)	135.15	136.07
	S4-W1-S5	83.85 (9)	83.31	82.78



Fig. 4. Comparison of X-ray crystallographic structure (A) and calculated optimized structure of MTDT (B) from a top-view.

separation of the oxidation–reduction wave for the complex was 92 mV, which is a normal value for a process involving one electron in polar solvent. The characteristics of the CV fit the profile of being a formal reduction of W(VI) to W(V) [40,41].

Orbital configuration

The HOMO/LUMO configurations and frontier molecular orbital energies of MTDT are depicted in Fig. 6. According to the calculations, there are 343 molecular orbitals of MTDT complex with 644 total electrons, in which there are 322 occupied and 21 unoccupied molecular orbitals. Fig. 6 shows that the HOMO and the LUMO involved a separate component on the molecule. The HOMO was concentrated on the 3,5-dimethoxyphenyl groups of one of the three bidentate dithiolene ligands, while the LUMO was concentrated along the WS_2C_2 rings. The fact that the LUMO comes from WS_2C_2 rings are supported by the CV of the compound, which showed that the formal reduction potential of the complex comes from W metal center (Fig. 6) with no contribution of the ligands.

The HOMO and LUMO orbital energies were -0.1970 and -0.1606 Hartrees, which were equivalent to -5.362 eV and -4.370 eV, respectively. The band gap energy of the molecule is therefore, 0.992 eV. The next highest energy level, HOMO-1 and HOMO-2 as well as LUMO + 1 and LUMO + 2 were also examined. HOMO-1 and HOMO-2 were located on 3,5-dimethoxyphenyl rings of the ligands, which were corresponding to -0.1995 and -0.1998 Hartrees, respectively. These orbitals were located on the other two 3,5-dimethoxyphenyl groups of the ligands. Meanwhile, the LUMO-1 to LUMO + 2 were located along the WS₂C₂ rings, with energy levels of -0.184 and -0.1162 Hartrees,



Fig. 5. The CV of MTDT collected in DCM/TBA(PF_6) with scan rate 10 mV s^{-1} at 20 $^\circ\text{C}$ versus Fc*/Fc internal standard.



Fig. 6. The HOMO and LUMO orbital energies of MTDT.

respectively. The molecular orbital configuration clearly shows that the main charge transfer band in the MTDT complex is due to a charge transfer from the 3,5-dimethoxyphenyl group to the WS_2C_2 ring, which is corresponding to the ligand-to-metal charge transfer (LMCT) and ligand to ligand charge transfer (LLCT).

Optical properties

The nature of absorption spectra were investigated via TD-DFT calculations using PBE on a DNP basis set. Conductor-like screening model (COSMO) continuum solvation models were used to evaluate the influence of solvent polarity on the absorption spectra [42]. The calculated absorption spectra of MTDT *in vacuo* and in various solvents are shown in Fig. 7, and were compared with the experimental spectrum (Fig. 8). The solvatochromism effects were calculated for different dielectric solvents such as benzene (Fig. 7B), acetone (Fig. 7C), methanol (Fig. 7D) and dimethylsulfoxide (Fig. 7E). All of the optical calculations were performed on the optimized geometry structure of MTDT. The spectra are slightly different with the solvent effect shifting.



Fig. 7. Optical spectra of MTDT, (A) calculated *in vacuo*, (B) calculated in benzene, (C) calculated in acetone, (D) calculated in methanol and (E) calculated in dimethylsulfoxide.



Fig. 8. Experimental spectrum of MTDT in acetone.

In vacuo (Fig. 7A), there were several absorption peaks in the visible region with the highest oscillator strength peak was at approximately 800 nm corresponding to the transition of HOMO-1 to LUMO. This represents ligand-to-metal charge transfer (LMCT). The lowest energy absorption peak appeared at 1050 nm and was attributed to the transition of an electron from HOMO to LUMO. The small absorption peak at approximately 650–700 nm are supposed to be d-d transition in visible spectrum.

The solvatochromism calculation of MTDT in benzene with dielectric constant, K = 2.284, resulted in a slightly different absorption spectrum compared to in vacuo. The absorption spectra in benzene gave a broad peak of approximately 800-900 nm, due to the similar intensity of three peaks in overlapping positions. A new peak appeared at 950 nm, and the lowest energy absorption peak was found at 1100 nm. All peaks in benzene were shifted approximately 50 nm compared with in vacuo. Furthermore, the calculated spectrum in acetone (K = 20.7) showed the lowest energy absorption peak, which was also at 1100 nm. However, pattern of the absorption between 800 and 900 nm was slightly different when calculated in vacuo and in benzene, where the broad peak was split into two peaks. Moreover, the calculations in methanol (K = 32.63) and dimethylsulfoxide (K = 46.7) also gave similar spectra. These spectra were similar with the spectrum in acetone with blue shifts at approximately 100 nm. The highest oscillator strength peak appeared at 920 nm, while the lowest energy absorption peak was at 1200 nm. The COSMO optical calculations of MTDT in various solvents showed that the absorption spectra gradually blue shifted with the increase of the solvent dielectric constant. The solvation effect was only found in solvents with lower dielectric constants than methanol, and no absorption changes were found in solvents with dielectric constants higher than methanol.

Table 3 is the experimental absorption of MTDT and similar molecules from the literature [43]. The strong LMCT peaks appear at 600 nm and are shifted approximately 100 nm to higher energy compared to the calculated result. The lowest energy absorption indicated by the calculation at approximately 1100 nm could not be observed due to instrument limitations.

Ligand substitution effect

To study the effect of ligand substitution on the structure, spectra and molecular orbital (MO) energy properties of MTDT, the OCH₃ groups on the phenyl rings of the ligands were removed, and the structure was optimized using the same calculation parameters. Removal of the OCH₃ groups did not affect the original structure geometry. Only a small effect on the phenyl ring orientation was observed, as seen from the torsion angles. The effect was

Table 3

Experimental electronic absorption data of MTDT and similar molecules in acetonewater (70:30) mixed solvent.

Metal (M)	R′	R	$L \rightarrow M \lambda_{max} (nm)/\epsilon$ (M ⁻¹ cm ⁻¹)	$\begin{array}{l} L \rightarrow M \; \lambda_{max} \; (nm) / \varepsilon \\ (M^{-1} \; cm^{-1}) \end{array}$
W	o,o- CH₃OPh	o,o- CH₃OPh	660 (25,000)	412 (12,600)
W ^a	Ph	p- CH₃OPh	685 (18,500)	413 (10,250)
W ^a	Ph	Ph	654 (28,100)	416 (22,500)
W ^a	p- CH₃OPh	p- CH₃OPh	679 (16,600)	405 (7000)

^a Ref. [43]



found on the frontier orbital molecule configuration and the optical properties only.

Fig. 9 shows the HOMO and LUMO of MTDT without OCH₃ groups. The LUMO was found along the WS_2C_2 rings and was unchanged relative to the original crystal structure. The HOMO configuration was different from the HOMO of the original MTDT and was found at the WS_2C_2 rings and a part of phenyl rings of the ligand. The calculations showed that the OCH₃ groups in the MTDT acted as electron donors. The effect on the theoretical optical spectrum of MTDT without OCH₃ groups is shown in Fig. 10. The maximum absorption was at approximately 800 nm, narrower than the MTDT spectrum area.

Conclusion

A tris{1,2-bis(3,5-dimethoxylphenyl)-1,2-ethylenodithiolenic-S,S'}tungsten complex (MTDT) was successfully synthesized and



Fig. 9. The HOMO and LUMO orbital energies of MTDT without OCH_3 groups.



Fig. 10. Optical spectrum calculated of MTDT without OCH₃ groups in vacuo.

fully characterized. The X-ray crystallographic structure and the DFT calculations of the optimized structure showed the molecular geometry of MTDT to be in between distorted octahedral and trigonal prismatic geometries. The ligand was in the 1,2-dithiolate form, and the tungsten metal center remained in a VI oxidation state. DFT calculations on the optimized geometry of MTDT exhibited that the HOMO orbital was concentrated on the dimethoxyphenyl moiety of the ligand, and the LUMO orbital was concentrated at the WS₂C₂ rings. Thus, the dithiolene ligands in this system were acting as electron acceptors. The electronic transition calculations showed the molecule to have a good absorption response extending to the near-infrared region in high solvent dielectric constants.

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