

Synthesis and Characterization of Two Tritylthio-Derivatives: 1-Bromo-3-Tritylthiopropene and 2-(Tritylthio)-Ethanethiol

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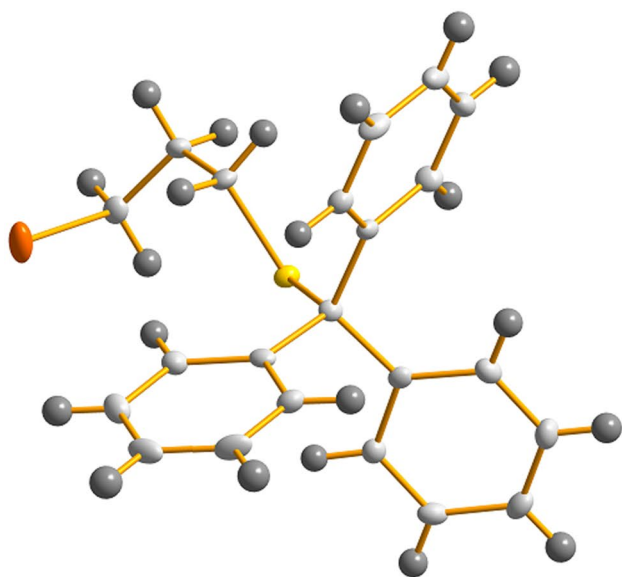
Abstract Two tritylthio-based compounds were synthesized: 1-bromo-3-tritylthiopropene **1** and 2-(tritylthio)-ethanethiol **2**. They were characterized by infrared, NMR, UV–Vis absorption and fluorescence spectroscopy and single-crystal X-ray diffraction. The crystals of both compounds crystallize in the monoclinic space group $P2_1/c$. The unit cell dimensions of **1** are $a = 7.4072(9) \text{ \AA}$, $b = 9.6924(11) \text{ \AA}$, $c = 25.652(3) \text{ \AA}$, $\beta = 90.023(2)^\circ$, and $V = 1841.7(4) \text{ \AA}^3$, and of **2** are $a = 15.3532(8) \text{ \AA}$, $b = 14.1552(7) \text{ \AA}$, $c = 7.8249(4) \text{ \AA}$, $\beta = 94.5239(8)^\circ$, and $V = 1695.27(15) \text{ \AA}^3$. The packing structures of **1** and **2** are supported by weak π – π and hydrogen bond interactions. Both **1** and **2** have absorption maxima at 257 nm, and emission maxima at 314 nm and 313 nm, respectively. The compounds differ by the presence of the S–H stretching vibration at $\sim 2550 \text{ cm}^{-1}$ in **2** and its absence in **1**, as observed in the infrared spectra.

Graphical Abstract Thermal ellipsoid plots of compounds **1** and **2**, with thermal ellipsoids at 50% probability.

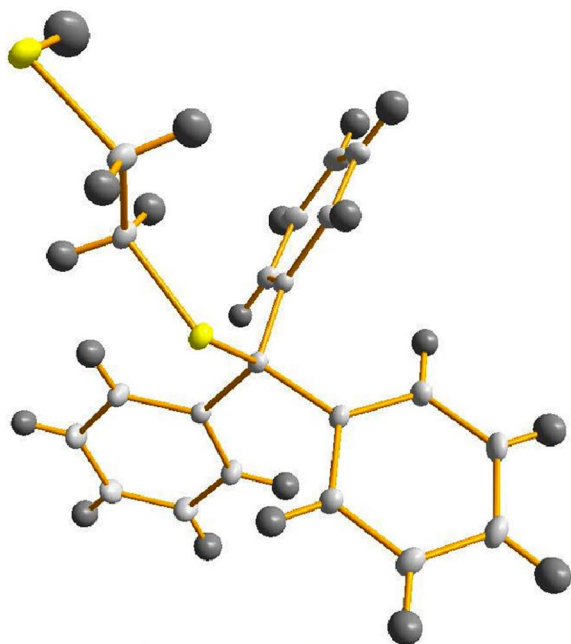
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1-bromo-3-tritylthiopropane



2-(tritylthio)-ethanethiol

Keywords Tritylthio-derivatives · UV–Vis absorption · Fluorescence and infrared spectroscopy · X-ray diffraction · NMR

Introduction

The use of thiol head groups as surface capping agents of nanoparticles (NPs) is common practice [1–8]. They lower

the surface energy of NPs and stabilize them [3]. Thiol-containing compounds can also be used as a sulfur source, which is especially important in crystal-bound thiol NPs [3]. Furthermore, Hollingsworth and co-workers have shown that the concentration of thiols used during the surface capping can either enhance or diminish the photoluminescence quantum yield of CdSe/ZnS core/shell NPs [9]. Compared to free thiols, less reactive thioethers compounds such as dendritic thioethers have been used to stabilize and control the size of gold NPs [10]. As a result of the critical role that these sulfur-containing compounds play in NP chemistry, it is important to understand the structural and photophysical properties of thiol building blocks such as tritylthio-alkyl groups. To address this, we synthesized 1-bromo-3-tritylthiopropane, **1**, following a procedure reported by Jagadish and co-workers, and substituted the alkyl-bromide to generate 2-(tritylthio)-ethanethiol, **2** [4, 11]. We avoided the use of thiiranes in the synthesis of **2** by modifying a procedure developed by Chan and co-workers [12]. We then characterized these two compounds by a combination of FT-IR, NMR, UV–Vis absorption and fluorescence spectroscopy, as well as single-crystal X-ray diffraction.

Experimental

All the chemicals used were of analytical grade, and the solvents were dried by standard methods and degassed with nitrogen prior to use. Unless otherwise noted, the reactions were run under a nitrogen atmosphere.

Syntheses

Synthesis of 1-Bromo-3-Tritylthiopropane **1**

5.432 g (19.7 mmol) of triphenyl-methyl-mercaptan and 8.0 mL (78.9 mmol) of 1,3-dibromopropane were dispersed in 150 mL of acetonitrile and 20.915 g (151 mmol) of anhydrous potassium carbonate was added while stirring. After stirring at room temperature overnight, the mixture was filtered and the filtrate evaporated under reduced pressure to yield a yellow oil that was recrystallized from hexanes to yield **1** as a white powder (5.458 g, 70%). TLC (SiO₂, hexane/ethyl acetate, 1:1): R_f = 0.91. ¹H NMR (CDCl₃, 400 MHz): δ = 7.42 (d, J = 7.4 Hz, 6H, *o*-aryl-*H*), 7.29 (t, J = 7.5 Hz, 6H, *m*-aryl-*H*), 7.22 (t, J = 7.1 Hz, 3H, *p*-aryl-*H*), 3.33 (t, J = 6.6 Hz, 2H, *BrCH*₂), 2.33 (t, J = 7.0 Hz, 2H, *SCH*₂), and 1.81 (p, J = 6.7 Hz, 2H, *CH*₂*CH*₂*CH*₂) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 144.73, 129.59, 127.93, 126.70, 32.29, 31.65 and 30.30 ppm.

Synthesis of 2-(Tritylthio)-Ethanethiol 2

1.8 mL (21.4 mmol) of 1,2-ethanedithiol was added to a 10 mL 50% mixture of trifluoroacetic acid/dichloromethane. 0.250 g (0.63 mmol) of **1** was added and the mixture stirred at room temperature overnight. The solvent was removed by vacuum transfer and the concentrated oil redissolved in chloroform (50 mL), followed by washing with water (3×25 mL) and brine (3×50 mL). The organic phase was dried over magnesium sulfate, filtered and concentrated under reduced pressure to yield a pale-yellow oil that was purified by flash chromatography in 1:1 Hex/EtOAc to give **2** as a clear oil (0.111 g, 52%). TLC (SiO_2 , hexane/ethyl acetate, 1:1): $R_f = 0.91$. ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.42$ (d, $J = 7.8$ Hz, 6H, *o*-aryl-H), 7.29 (t, $J = 7.5$ Hz, 6H, *m*-aryl-H), 7.22 (m, 3H, *p*-aryl-H), 2.47 (t, 2H, SCH_2), 2.27 (q, $J = 7.8$ Hz, 2H, CH_2SH), 1.42 (t, $J = 8.3$ Hz, 1H, SH) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 144.69$, 129.57, 127.94, 126.75, 36.09 and 23.89 ppm.

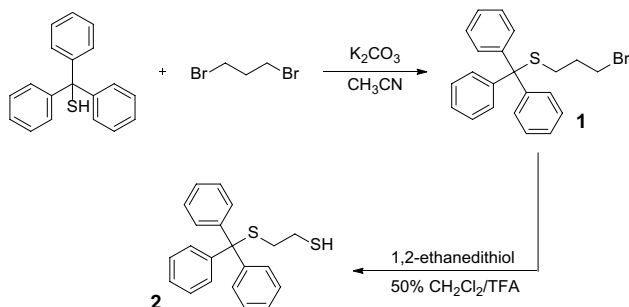
Spectroscopy

FT-IR

The infrared spectra of the compounds were recorded using a Nicolet 6700 FT-IR instrument in the range $3500\text{--}590\text{ cm}^{-1}$ at 4 cm^{-1} resolution with 32 scans in ATR mode. Before each acquisition, a background spectrum was acquired to correct for CO_2 and H_2O interference.

NMR

^1H and ^{13}C NMR spectra were recorded using a Varian NMR instrument operating at 400 MHz, while using deuterated chloroform (CDCl_3) as solvent and tetramethylsilane (TMS) as a reference.



Scheme 1 Syntheses of **1** and **2**

UV–Vis Absorption and Fluorescence

1.0×10^{-4} M stock solutions of each compound were prepared by dissolving the appropriate amount in spectroscopic grade acetonitrile, and transferring the required amount into a 1.0 cm pathlength cuvette. Following this, the absorption spectrum of each compound was acquired on a Perkin Elmer Lambda 35 UV–Vis spectrometer at 480 nm/min in the range 600–200 nm at room temperature. The excitation and emission spectra were recorded on a Horiba Jobin Yvon Nanolog fluorimeter equipped with a 450 W (Ushio) xenon lamp. The excitation/emission slits were set at 5/1 nm, with integration time of 1.0 s and 1 nm increments. The instrument was set to the front face mode at a 22.5° angle in order to record the emission spectra at 77 K (frozen solution) and at a 90° angle for measurements at $25.0 \pm 0.1^\circ\text{C}$.

Single-Crystal X-Ray Diffraction

Both compounds yielded X-ray quality single crystals after recrystallization from acetonitrile. A suitable crystal was mounted on a glass fiber and placed in the low-temperature nitrogen stream of a Bruker SMART CCD area detector diffractometer. A full sphere of data was collected using graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) source. Multi-scan absorption corrections were applied using SADABS [13]. The structures were solved by direct methods and refined by least square methods on F^2 using the SHELXTL program package [14]. The hydrogen atoms were geometrically added and all the non-hydrogen atoms refined anisotropically. The structures were deposited with

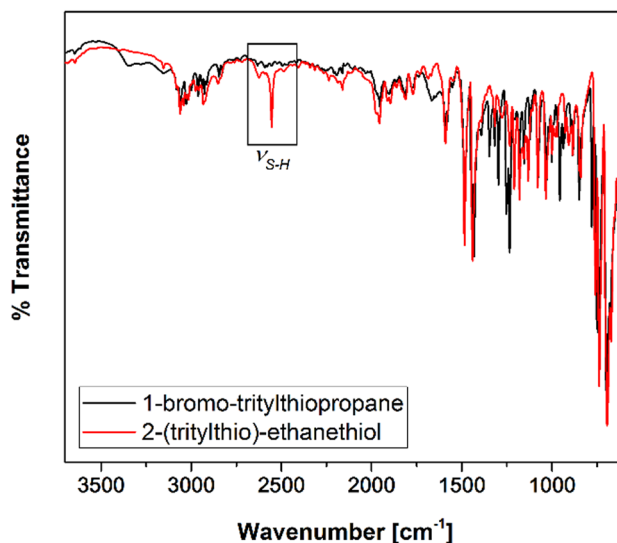


Fig. 1 FT-IR spectra of **1** and **2** with the S-H stretch region highlighted

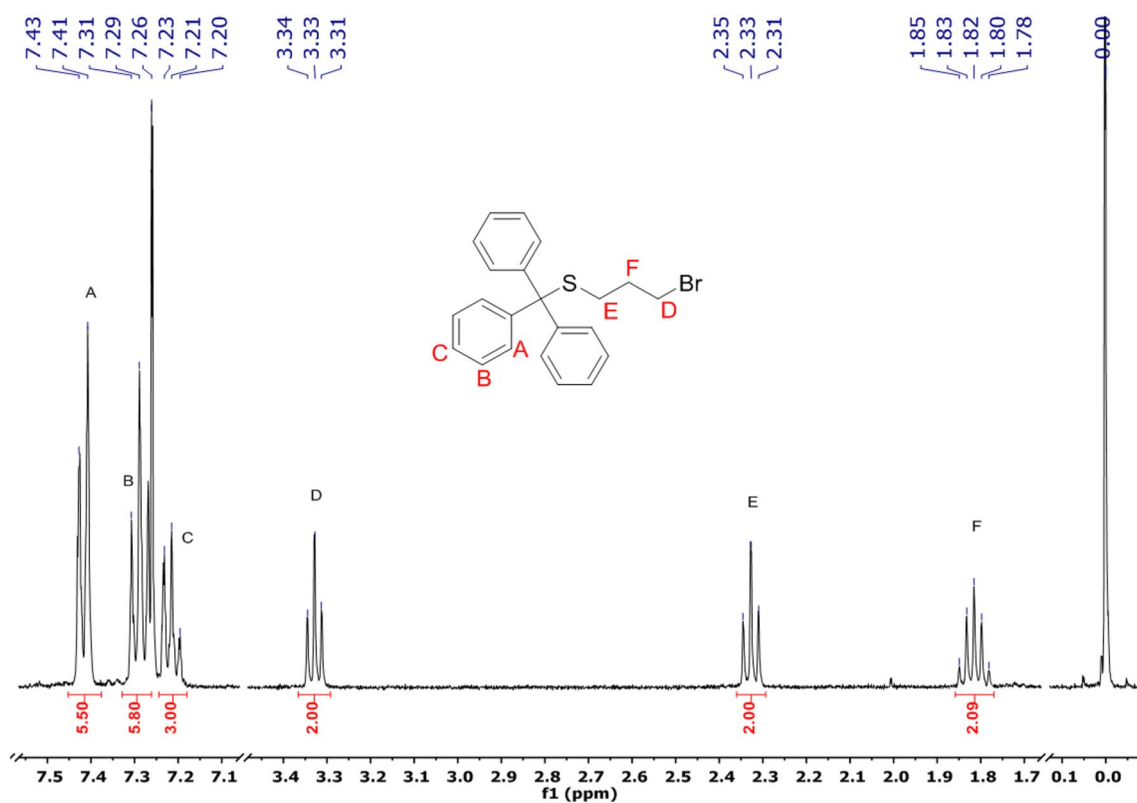


Fig. 2 ¹H NMR spectrum of **1** in CDCl₃

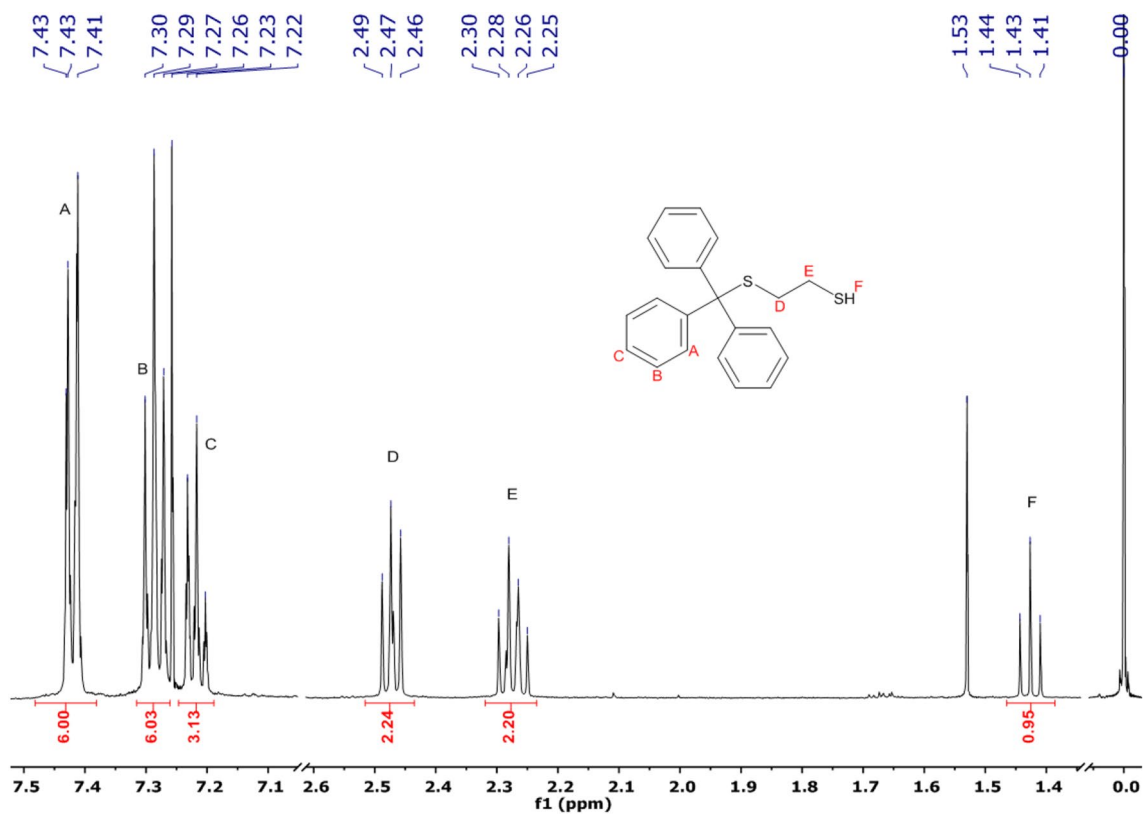


Fig. 3 ¹H NMR spectrum of **2** in CDCl₃

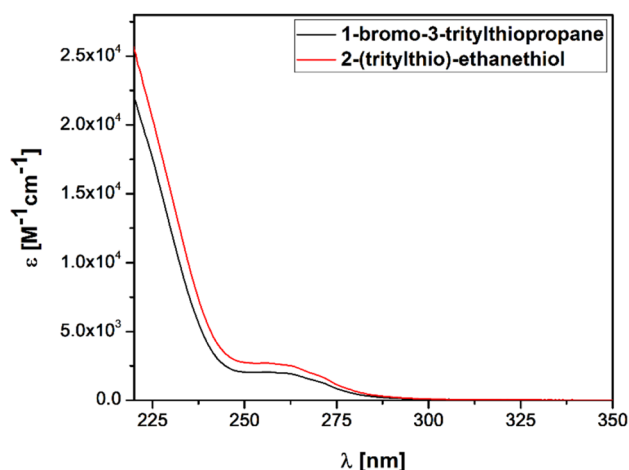


Fig. 4 UV-Vis absorption spectra of **1** (black) and **2** (red) in acetonitrile

the Cambridge Crystallographic Database and their reference numbers are CCDC 1430109 for **1** and 1430110 for **2**.

Results and Discussion

Compounds **1** and **2** were synthesized by modified literature procedures [4, 11] as shown in Scheme 1. While previously isolated as oils, they were obtained in pure crystalline form, which enabled characterization by single crystal X-ray diffraction (vide infra). The FT-IR spectra of **1** and **2** show bands in the ranges 3100–2800 cm^{-1} and 2000–1630 cm^{-1} that correspond to aliphatic and aromatic C–H vibrations, as well as combination modes, respectively (Fig. 1). The vibrational bands in the range 1500–1400 cm^{-1} and those at 1592 cm^{-1} correspond to aromatic C–C and C=C vibrations, respectively. In general, the FT-IR spectra of **1** and **2**

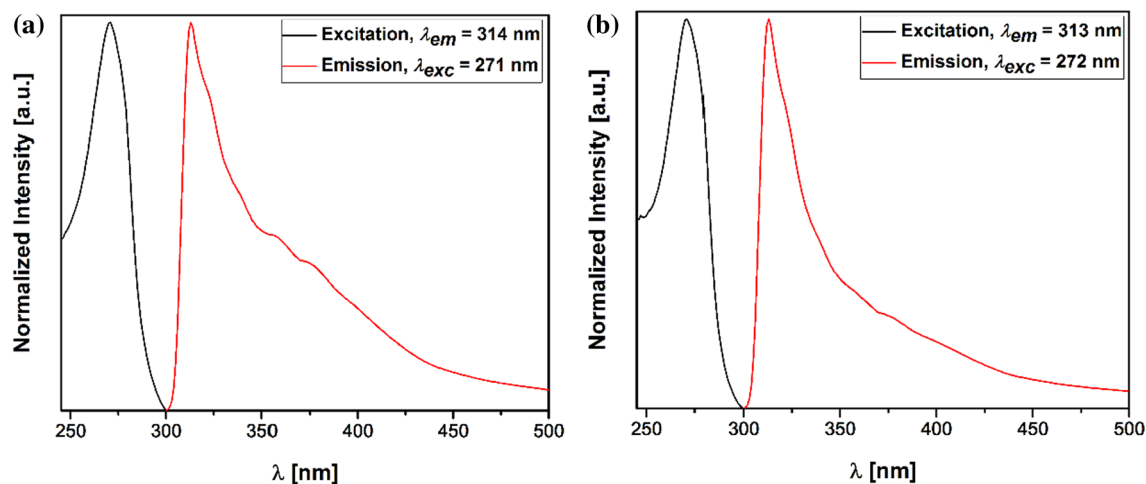


Fig. 5 Normalized excitation (black) and emission (red) spectra of **a 1** and **b 2** in acetonitrile

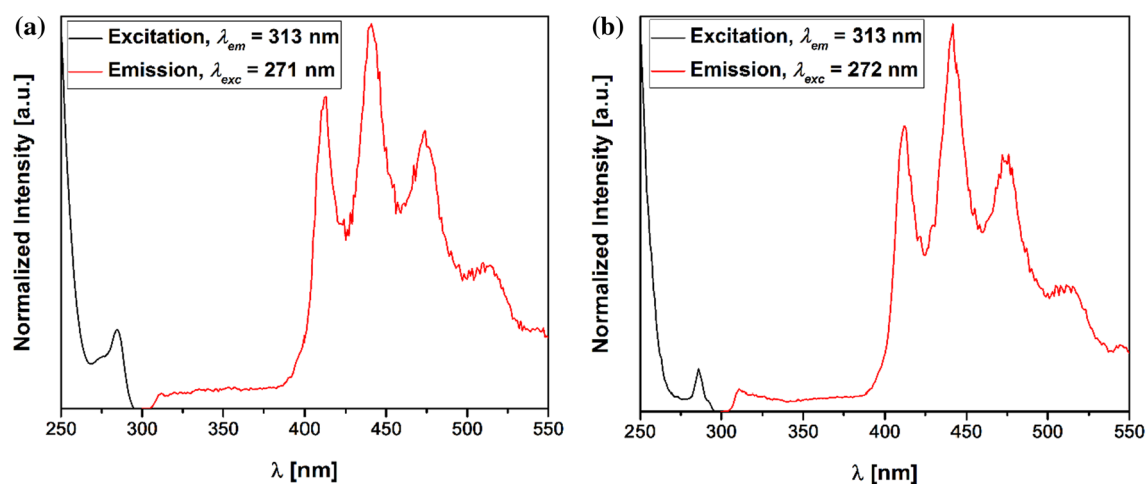


Fig. 6 Low temperature (77 K) phosphorescence excitation and emission spectra of **a 1** and **b 2** in acetonitrile

Table 1 Crystallographic data and structure refinement of **1** and **2**

Compound	1	2
Formula	C ₂₂ H ₂₁ BrS	C ₂₁ H ₂₀ S ₂
M/g mol ⁻¹	397.35	336.49
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	7.4072 (9)	15.3532 (8)
<i>b</i> /Å	9.6924 (11)	14.1552 (7)
<i>c</i> /Å	25.652 (3)	7.8249 (4)
α /deg	90	90
β /deg	90.023 (2)	94.5239 (8)
γ /deg	90	90
<i>V</i> /Å ³	1841.7 (4)	1695.27 (15)
<i>T</i> /K	100	100
<i>Z</i>	4	4
<i>D_c</i> /g cm ⁻³	1.433	1.318
μ (Mo–K α)/mm ⁻¹	2.345	0.311
Independent reflections,	5097	5868
<i>R</i> _{int} [<i>F</i> _o ≥ σ (<i>F</i> _o)]	0.0567	0.0392
Reflections collected	5174	6114
GoF on <i>F</i> ²	1.096	1.020
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.0412 (4080) 0.1335 (5097)	0.0324 (5121), 0.0921 (5868)
Largest diff. peak and hole/e	1.07, −1.18	0.54, −0.27

are indistinguishable, as the C–Br band of **1** appears in the fingerprint region. In contrast, a band at ~ 2550 cm⁻¹, which corresponds to the S–H stretch is absent in the spectrum of **1**, but present in the spectrum of **2**. This assignment is consistent with literature values [6, 15].

The ¹H NMR spectra of **1** and **2** show very similar aromatic peaks in the 7.40–7.20 ppm region (Figs. 2, 3). However, there is a significant upfield shift of the proton

resonance at 3.33 ppm in **1** to 2.47 ppm in **2**, which is explained by the additional shielding of these protons by the two sulfur atoms. The resonance from the thiol (S–H) proton of **2** appears as a triplet at 1.43 ppm (Fig. 3). Similarly, the ¹³C NMR spectra of **1** and **2** showed no significant differences in the aromatic region (Figs. S1, S2).

Both **1** and **2** display absorption maxima attributed to π – π^* transitions at 257 nm and excitation maxima at 271 and 272 nm, respectively (Figs. 4, 5a, b) [16]. The molar extinction coefficient, ϵ , of **2** at 257 nm (2700 M⁻¹cm⁻¹) is larger than that of **1** at 257 nm (2100 M⁻¹cm⁻¹), as supported by the relatively intense absorption spectrum of **2** compared to that of **1** (Fig. 4).

Each compound displays emission bands with maxima that are mirror images of the excitation/absorption spectra and thus due to $\pi^* \rightarrow \pi$ transitions at 314 nm for **1** and 313 nm for **2** (Fig. 5a, b). 77 K time-resolved emission spectra show phosphorescence in the range 400–600 nm with resolved vibrational fine-structure (Fig. 6). The measured energy gap, $\Delta\nu$, between the peaks of each phosphorescence spectrum was determined to be 1587.5 ± 8.5 cm⁻¹, and is attributed to the aromatic C=C vibrations in the compounds. These vibrations were also observed in the FT-IR spectra of **1** and **2** at 1592 cm⁻¹ (Fig. 1).

Both compounds crystallize in the monoclinic *P*2₁/*c* space group with four molecules in the unit cell. Details of the crystallographic data and refinement for **1** and **2** are given in Table 1. The asymmetric units of **1** and **2** are shown in Fig. 7. They display simple structures, with the expected propeller shape of the trityl functional group for **1** and chain-like structure of the alkyl groups. The trityl–C–S distances are 1.862 and 1.871 Å and the C–Br and C–SH distances are 1.962 Å and 1.817 Å in **1** and **2**, respectively. The latter two are in good agreement with literature values of 1.966 Å for C–Br and 1.808 Å for C–SH, respectively [17]. The packing

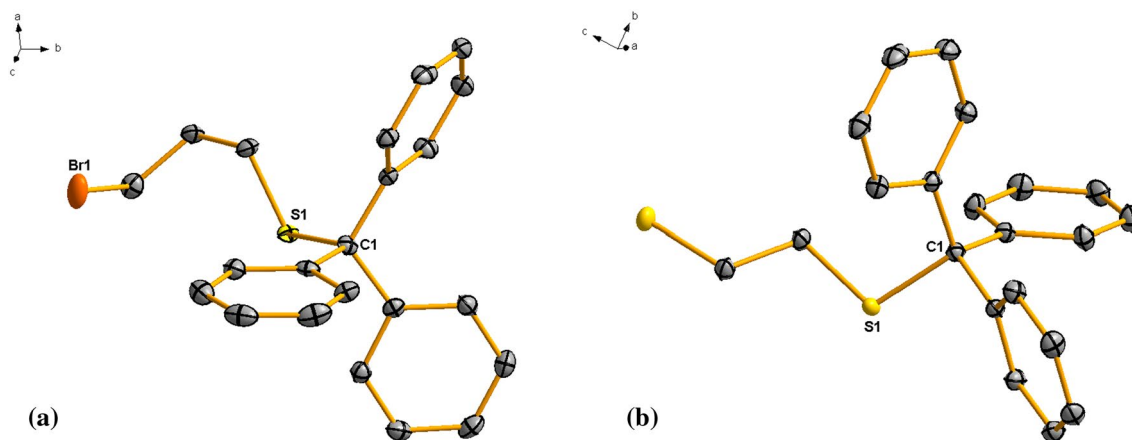


Fig. 7 Thermal ellipsoid plots of the asymmetric units of **a 1** and **b 2**, with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity

structure of both compounds displays an alternating arrangement of neighboring molecules in a zig-zag pattern (Fig. 8a, b). The packing of **1** is supported by intermolecular C–H \cdots π interactions (Fig. 9a), [18–20] with C–H \cdots π distances of 2.684–3.387 Å. **1** also shows a weak intramolecular hydrogen bond between a phenyl ring of the trityl functional group and the bromine atom, with a C–H \cdots Br distance of 3.066 Å, [20] as shown in Fig. 9b. Despite the presence of the phenyl rings, only extremely weak π – π stacking is observed, as the planes spanned by phenyl rings on adjacent molecules

intersect at an angle of $\sim 10^\circ$, while the centroid-to-centroid distance is long at 6.152 Å. The packing of **2**, on the other hand, is supported by weak π – π stacking interactions of two neighboring molecules, as shown in Fig. 10. The distance between the parallel planes spanned by the phenyl rings is 3.3 Å and the centroid-to-centroid distance is 5.2 Å [21].

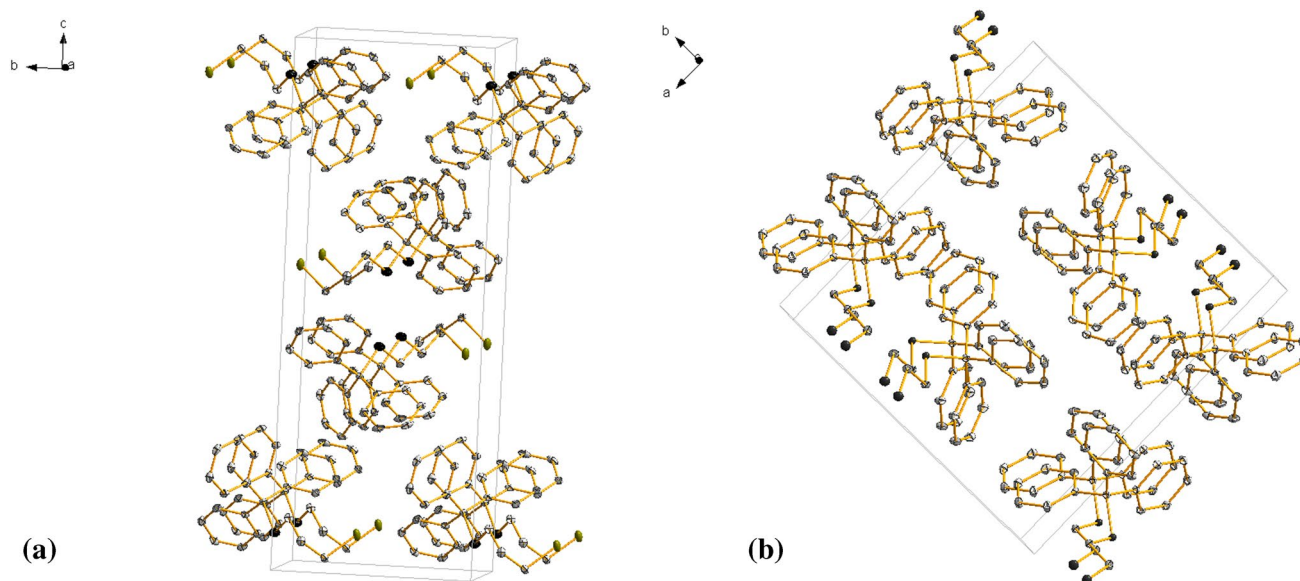


Fig. 8 Packing structures of **a** **1** along the *a* axis and **b** **2** along the *c* axis, with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity

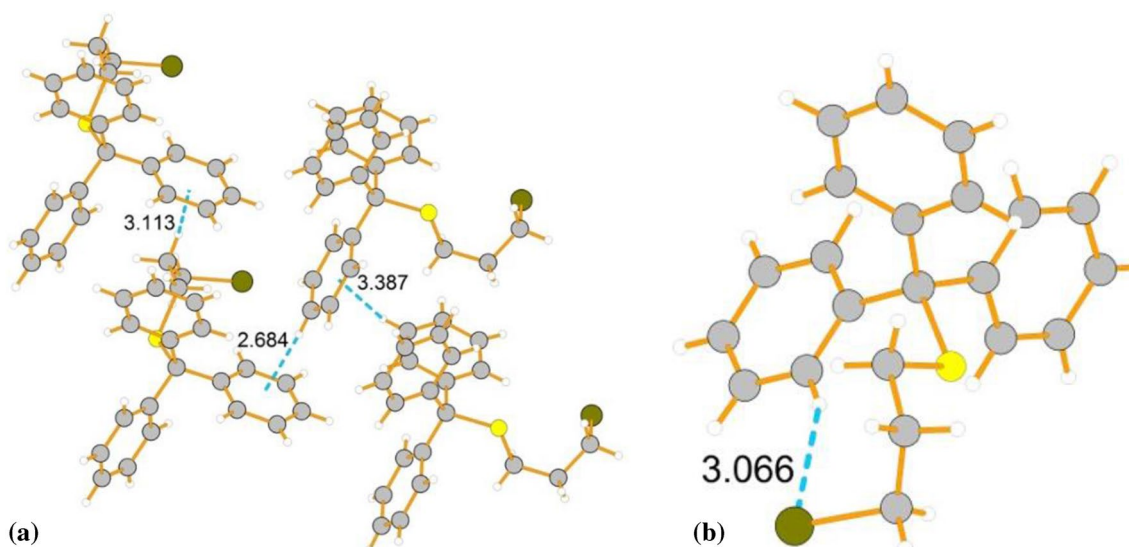


Fig. 9 Ball-and-stick plot of **1** showing the **a** intermolecular C–H \cdots π and **b** intramolecular C–H \cdots Br interactions and relevant distances in Å

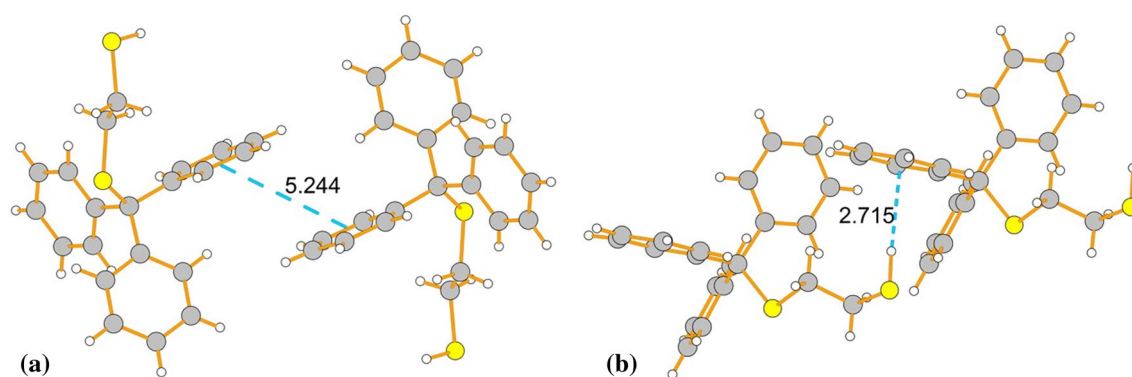


Fig. 10 Ball-and-stick plot of **2** showing **a** the π - π interaction with an interplanar distance of 3.3 Å and a centroid-to-centroid distance of 5.244 Å and **b** the S-H $\cdots\pi$ interaction with distance 2.715 Å

Conclusion

Two tritylthio-containing compounds were synthesized. **2** was synthesized for the first time without the use of thiiranes. Both compounds were characterized by FT-IR, NMR, UV-Vis absorption and fluorescence spectroscopy. Since they were, for the first time, obtained as solids, characterization by single-crystal X-ray diffraction was possible. They both belong to the monoclinic space group $P2_1/c$ with simple packing structures supported by weak π - π and hydrogen bond interactions. Both compounds absorb and emit in the UV, due to π - π^* transitions, with vibrationally resolved phosphorescence spectra.

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