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Monothiatruxene: a new versatile core for functional materials†

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A truxene molecule incorporating a sulfur atom at one of the three bridgehead positions has been prepared through an efficient route, together with its oxidized analogue (featuring an SO2 unit) and brominated derivatives. The photophysical, electrochemical and thermal properties of the compounds are presented: the materials show high thermal stability and the ability to form amorphous glasses. This central monothiatruxene core offers multiple routes to further modifications, thereby opening a way to the synthesis of a variety of novel functional materials beyond the parent truxene.

Fig. 1 Structures of truxene, trithiatruxene and monothiatruxene.
involving introduction of bromine atoms into different positions, and sulfur oxidation.

Selective bromination of the aromatic ring adjacent to the sulfur atom (position 1) has been achieved by ortho-lithiation and subsequent treatment with 1,2-dibromoethane. Di- and tribrominated derivatives were obtained with the use of simple bromination method with the use of bromine in dichloromethane. Non-oxidized intermediates, namely 1-BrTrxS, 7,12-DiBrTrxS and 3,7,12-TrisBrTrxS, were directly subjected to oxidation with hydrogen peroxide. The tribrominated product appeared as a side product of the reaction aiming for the dibromo derivative therefore the final yield is only 10%. Where the aimed 7,12-DiBrTrxSO2 has been obtained in 65% yield. The 1-BrTrxSO2 was obtained in 50% yield, after three steps; ortho-lithiation, reaction with ethylene dibromide and oxidation with hydrogen peroxide. All obtained materials possess good solubility in most common organic solvents even though only ethyl chains were utilized. Detailed reaction descriptions can be found in the ESI.† All the materials were fully characterized by 1H, 13C and 2D NMR spectroscopy and mass spectrometry. Final materials were also characterized by elemental analysis.

The UV-VIS absorption and fluorescence spectra of TrxS and TrxSO2 in dilute dichloromethane solution are presented in Fig. 2. The corresponding spectra in cyclohexane and acetonitrile (less and more polar solvents than CH2Cl2 respectively) were almost identical, showing no significant solvatochromism (Fig. S1†). Both compounds absorb light only in the UV region with λmax 288 nm (ε = 54 800 cm⁻¹ M⁻¹) and 285 nm (ε = 35 000 cm⁻¹ M⁻¹) for TrxS and TrxSO2, respectively, with somewhat weaker absorption peaks at longer wavelength: 350 and 366 nm for TrxS and 357 and 374 nm for TrxSO2. The emission bands appear at only slightly lower energy than the lowest-energy absorption bands: the Stokes shifts are only 550 cm⁻¹ for TrxS and 940 cm⁻¹ for TrxSO2. This contrasts with unsubstituted hexaalkyltruxene, which has a large Stokes shift of 4600 cm⁻¹. Clearly, C3h symmetry-forbidden transitions in truxene become allowed upon introduction of the sulfur atom to the core, accounting for the small Stokes shifts. In Fig. S2,† the mirror image relationship between the absorption and emission bands can be observed for both materials. Oxidation of the sulfur atom leads to a less structured spectral profile and red-shifting of the emission maximum: a red-shift of 830 cm⁻¹ in TrxSO2 compared to TrxS (580 cm⁻¹ in the lowest energy absorption band). The fluorescence quantum yield (Φf) of TrxS is 0.05, while oxidation to TrxSO2 increases this value to 0.14. Table 1 summarizes the photophysical and thermal data.

The oxidation and reduction potentials were obtained from square-wave voltammetry (SWV) experiments using ferrocene as an internal standard (Fig. S3†). Only one oxidation peak of TrxS was recorded at 0.86 V and no reduction. In contrast, TrxSO2 showed only one reduction peak at 2.21 V without oxidation under the same conditions. Both oxidation of TrxS and reduction of TrxSO2 remain unchanged with the scan direction (Fig. S4†). The cyclic voltammetry measurement (Fig. 3) at five different scan rates showed that TrxS can be stably and reversibly oxidized (Fig. 3, S5 and Table S1†). The cathodic/anodic current ratio is about 1, proving the stability of the oxidized species.

![Scheme 1](image1.png) Synthetic route to monothiatruxene.

![Scheme 2](image2.png) Derivatization of monothiatruxene.

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Fig. 2 Absorption and fluorescence spectra of TrxS and TrxSO2 in dichloromethane solution.
Therefore, it may be concluded that this redox couple is reversible. On the other hand, the reversibility of the reduction of the TrxSO₂ could not be evaluated, as can be seen in the Fig. 3, since the process is close to the solvent window and both peaks could not be distinguished clearly.

The differential scanning calorimetry (DSC) showed that both materials are of crystalline nature with melting points of 198 °C for TrxS and 214 °C for TrxSO₂ (see Fig. S6 and S7†). After melting the material and heating it again, TrxS showed a glass transition temperature of 84.5 °C and cold crystallization at 180.6 °C along with again two melting points at 207.8 °C and 213.7 °C. TrxSO₂ showed on the second heating a glass transition at 119.3 °C but no cold crystallization and only a tiny peak representing melting point indicating that the material is mostly amorphous. Additionally, powder diffraction patterns confirmed the crystalline nature of both as-synthesized truxenes (Fig. S8†) in their powder form. Thermogravimetric analysis proved the high thermal stability of TrxS with 5% mass loss at the temperature of 326 °C and for TrxSO₂ 357 °C (Fig. S6 and S7†) which can be attributed to the all-aromatic backbone. Both DSC and TGA show how the introduction of oxygen atoms affects thermal properties where the melting point and glass transition temperature increase. Moreover, the sulfonyl group probably prevents stacking of the rings and leads to a more stable amorphous state. All these indicate that monothiatruxenes are promising candidates for optoelectronic applications.

In conclusion, we designed and synthesized monothiatruxene, its oxidized derivative and their brominated counterparts. The presented work shows that introduction of a sulfur atom to the truxene structure affects its electronic properties while maintaining high thermal stability. Additionally, due to the low symmetry of the molecule and presence of sulfur, a wider range of modifications is possible than that for truxene. Importantly, these materials also show high solubility.

**Author contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Conflicts of interest**

There are no conflicts to declare.

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### Table 1  Electrochemical, photophysical and thermal properties

|        | λ_{abs}a, nm | ε² × 10³ | λ_{em}a, nm | ε² | Stokesshifta, cm⁻¹ | E_{gap}abc, eV | Φ_aabc, % | E_{ox}a, V | E_{red}a, V | T_{g}d, °C | T_m, °C | T_d, °C |
|--------|--------------|----------|-------------|----|---------------------|---------------|----------|-----------|-----------|-----------|--------|--------|
| TrxS   | 288, 299     | 54.8, 51.1 | 374, 391    | 550| 3.38                | 0.05          | +0.86    | --        | 84        | 208       | 214    | 326    |
|        | 350, 366     | 4.5, 5.7  |             |    |                     |               |          |           |           |           |        |        |
| TrxSO₂ | 285, 357, 374| 35, 6.5, 5.2| 387, 400    | 940| 3.42                | 0.14          |          | --        | -2.21     | 119       | 256    | 357    |

* a In dichloromethane solution. b Optical gap, from intersection of Abs and Pl. c In reference to quinine sulfate in 0.1 N H₂SO₄ (Φ = 0.51). d Glass transition temperature (T_g) and melting point (T_m) by DSC. e Decomposition temperature (T_d) by TGA.

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**Fig. 3**  Cyclic voltammetries of TrxS (top) and TrxSO₂ (bottom) at different scan rates.
References

1 W. Wislicenus, *Ber. Dtsch. Chem. Ges.*, 1887, 20(1), 589.
2 F. Goubard and F. Dumur, *RSC Adv.*, 2015, 5(5), 3521.
3 G. Zhang, F. Rominger and M. Mastalerz, *Chem.–Eur. J.*, 2016, 22(9), 3084.
4 Y. Xie, X. Zhang, Y. Xiao, Y. Zhang, F. Zhou, J. Qi and J. Qu, *Chem. Commun.*, 2012, 48(36), 4338.
5 X.-Y. Cao, X.-H. Liu, X.-H. Zhou, Y. Zhang, Y. Jiang, Y. Cao, Y.-X. Cui and J. Pei, *J. Org. Chem.*, 2004, 69(18), 6050.
6 Z. Yang, B. Xu, J. He, L. Xue, Q. Guo, H. Xia and W. Tian, *Org. Electron.*, 2009, 10(5), 954.
7 M. Kimura, S. Kuwano, Y. Sawaki, H. Fujikawa, K. Noda, Y. Taga and K. Takagi, *J. Mater. Chem.*, 2005, 15(25), 2393.
8 Y. M. Sun, K. Xiao, Y. Q. Liu, J. L. Wang, J. Pei, G. Yu and D. B. Zhu, *Adv. Funct. Mater.*, 2005, 15(5), 818.
9 X. R. Zhang, W. Chao, Y. T. Chuai, Y. Ma, R. Hao, D. C. Zou, Y. G. Wei and Y. Wang, *Org. Lett.*, 2006, 8(12), 2563.
10 Z. Lu, C. Li, T. Fang, G. Li and Z. Bo, *J. Mater. Chem. A*, 2013, 1(26), 7657.
11 X. Zong, M. Liang, C. Fan, K. Tang, G. Li, Z. Sun and S. Xue, *J. Phys. Chem. C*, 2012, 116(20), 11241.
12 X. Qian, Y. Z. Zhu, J. Song, X. P. Gao and J. Y. Zheng, *Org. Lett.*, 2013, 15(23), 6034.
13 G. Tsiminis, Y. Wang, P. E. Shaw, A. L. Kanibolotsky, I. F. Perpeichka, M. D. Dawson, P. J. Skabara, G. A. Turnbull and I. D. W. Samuel, *Appl. Phys. Lett.*, 2009, 94(24), 243304.
14 R. Cayuela, H. T. Nguyen, C. Destrade and A. M. Levelut, *Mol. Cryst. Liq. Cryst.*, 1989, 177(1), 81.
15 Y. Kobori, T. Toyooka, H. Mazaki and Y. Satoh, US 5855971, 1996.
16 M. Maciejczyk, K. Górska and M. Pietraszkiewicz, PL 407006, 2014.
17 S. Y. Hyun, Y. H. Yoon and J. H. Song, KR20140000611, 2014.
18 J. Clayden, *Organolithiums: Selectivity for Synthesis*, Pergamon, 2002.
19 V. Pandya, M. Jain, B. V. Chaugule, J. S. Patel, B. M. Parmar, J. K. Joshi and P. R. Patel, *Synth. Commun.*, 2012, 42(4), 497.
20 M.-T. Kao, J.-H. Chen, Y.-Y. Chu, K.-P. Tseng, C.-H. Hsu, K.-T. Wong, C.-W. Chang, C.-P. Hsu and Y.-H. Liu, *Org. Lett.*, 2011, 13(7), 1714.