

Synthesis, structure and photophysical properties of regioisomeric sulfone-bridged pyrene–thienoacenes



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ABSTRACT

Three regioisomeric sulfone-bridged phenyl-pyrene derivatives have been synthesized by post-oxidizing the corresponding sulfide-bridged phenyl-pyrene isomers. The photophysical properties and two crystal structures of these sulfones were investigated and compared with those of their parent compounds. These sulfones display all remarkable solid-state photoluminescence efficiencies as well as good fluorescence quantum yield in solutions.

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1. Introduction

Although sulfur-containing thienoacenes have been extensively developed as active organic semiconductor of organic field-effect transistors (OFETs) during the past decade [1–3], the properties of post-oxidized product of these thienoacenes are seldom investigated. Some sulfur-bridged un-fused aromatic substituted sulf-oxides and sulfones exhibit different emission properties compared to their reduced sulfide counterparts [4–7]. For example, Barbarella et al. found that introduction of thiophene S,S-dioxide into conjugated oligothiophenes could offer better photoluminescence (PL) efficiency [4]. Liu et al. also successfully prepared high PL efficiency polyfluorenes by incorporating dibenzothiophene-S,S-dioxide [5]. Christensen et al. recently reported that the PL efficiency of some symmetrical sulfur-bridged chromophores could be enhanced by oxidizing the sulfur to sulfone [6]. In other cases, the sulfones are reported as less emissive than the reduced sulfides [7,8].

As a part of our continuing work on pyrene–thienoacenes (PTAs) for optoelectronic materials applications [9], we present here the synthesis, crystal structures and light emitting properties of a group of sulfone-bridged phenyl-pyrene (SO₂-PhPy) isomers. The comparisons between sulfide and sulfone bridged phenyl-pyrene derivatives and also between regioisomers are especial key to understand the structure–property relationships (Scheme 1).

2. Experimental

2.1. Materials and instruments

3-Chloroperbenzoic acid (*m*CPBA) was purchased from Acros Ltd. All solvents were freshly distilled before using. ¹H and ¹³C NMR spectra were recorded with a Bruker 400 spectrometer in CDCl₃ with TMS as internal reference. High-Res Mass spectra were recorded using MALDI (DHB matrix) or ESI modes.

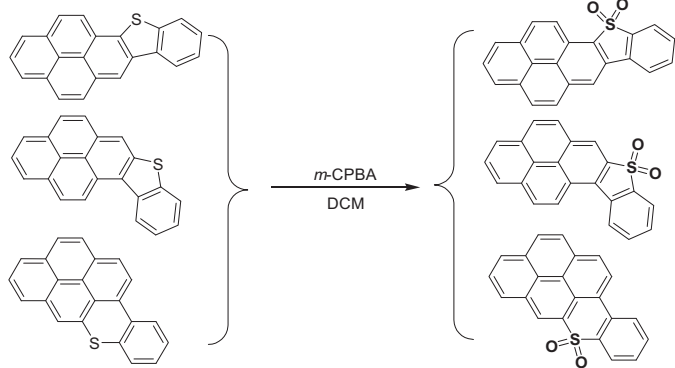
UV–vis absorption spectra and fluorescence emission spectra were recorded on a Shimadzu UV 2550 spectrometer with $C = 5.0 \times 10^{-6} \text{ mol L}^{-1}$ in hexane. For luminescence quantum yield and lifetime measurements, dilute solutions ($C = 2.0\text{--}5.0 \times 10^{-6} \text{ mol L}^{-1}$) of the compounds were carefully degassed via three freeze-pump-thaw cycles to remove dissolved oxygen. Steady state fluorescence emission spectra were recorded on an Edinburgh FLS920 fluorescence spectrometer equipped with a 450W Xe lamp. Reconvolution fits of the fluorescence decay curves were made with F900 analysis software to obtain the lifetime values. To measure the quantum yields of these compounds, pure pyrene and coumarin 307 were used as the reference. The PL efficiencies at solid state were determined using an integrating sphere.

2.2. Crystallography

Suitable single crystals of 2-SO₂-PhPy and 4-SO₂-PhPy were grown from their hexane/DCM solutions. The diffraction data were collected on a Bruker ApexII CCD diffractometer using a graphite mono-chromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 20 °C. The

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Scheme 1. Molecular structures and synthetic approach to isomers of **SO₂-PhPy**.

structures were solved by directed method using the program SHELXL and refined by full-matrix least-squares method on F^2 . All hydrogen atoms were added theoretically. The crystal structures were deposited at the Cambridge Crystallographic Data Centre with a deposition numbers: CCDC 1012348 for **2-SO₂-PhPy** and CCDC 1012349 for **4-SO₂-PhPy**, respectively.

2.3. Theoretical calculations

The ground and excited state calculations of **SO₂-PhPy** were performed with the Gaussian 03 (G03) programs. The ground state geometries of **SO₂-PhPy** molecules were optimized at the DFT/B3LYP level. The original geometries of **2-SO₂-PhPy** and **4-SO₂-PhPy** are based on the molecular structure as determined by X-ray diffraction. Based on the optimized ground state geometries, the single point excited state calculations were performed using time-dependent density functional theory (TD-DFT) with the B3LYP functional.

2.4. General procedure for synthesis of **SO₂-PhPy**

To a solution of **PTA** (0.31 g, 1.0 mmol) in dried DCM (10 mL) at 0 °C was added meta-chloroperoxybenzoic acid (70%, 0.55 g, 2.2 mmol) and the mixture was stirred for 3 h. The reaction mixture was poured over a saturated aqueous solution of sodium bicarbonate (20 mL) and ice and extracted with dichloromethane (3 × 15 mL). The organic layers were combined, dried over anhydrous magnesium sulfate, filtered, and concentrated under vacuum. The crude materials were purified by column chromatography (hexanes: DCM = 2:1) to afford pale yellow solid products.

1-SO₂-PhPy: 86% yield. M.p. 288 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.64 (d, 1H, $J=9.0$ Hz), 8.38 (s, 1H), 8.30 (m, 2H), 8.23 (m, 1H), 8.15 (d, 1H, $J=9.0$ Hz), 8.08 (s, 1H), 8.03 (m, 2H), 7.92 (m, 1H), 7.66 (m, 1H), 7.54 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 139.22, 135.44, 133.99, 132.59, 131.55, 131.04, 130.72, 130.64, 130.45, 129.19, 128.81, 127.60, 127.44, 127.27, 127.22, 126.71, 125.47, 124.35, 122.26, 122.06, 121.85, 116.60. HRMS (ESI): m/z [M+H]⁺ 341.0670, calcd for C₂₂H₁₃O₂S⁺ 341.0636; m/z [M+Na]⁺ 363.0438, calcd for C₂₂H₁₂O₂SNa⁺ 363.0456.

2-SO₂-PhPy: 95% yield. M.p. >320 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.92 (d, 1H, $J=9.2$ Hz), 8.63 (t, 2H, $J=8.0$ Hz), 8.33 (m, 3H), 8.17 (m, 3H), 8.01 (d, 1H, $J=7.6$ Hz), 7.80 (m, 1H), 7.61 (t, 1H, $J=7.6$ Hz). ¹³C NMR (100 MHz, CDCl₃) δ: 138.71, 136.02, 134.18, 133.74, 132.69, 131.90, 130.81, 129.78, 129.50, 127.96, 127.82, 127.66, 127.56, 127.33, 126.68, 125.51, 124.56, 123.27, 122.81, 122.77, 117.63. HRMS (MALDI): m/z [M]⁺ 340.0553, calcd for C₂₂H₁₂O₂S⁺ 340.0549.

4-SO₂-PhPy: 93% yield. M.p. 215 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.18 (s, 1H), 8.83 (d, 1H, $J=8.4$ Hz), 8.48 (d, 1H, $J=7.6$ Hz), 8.42 (m, 3H), 8.35 (d, 1H, $J=8.0$ Hz), 8.18 (m, 3H), 7.81 (m, 1H), 7.66 (t, 1H,

$J=7.2$ Hz). ¹³C NMR (100 MHz, CDCl₃) δ: 135.44, 133.68, 132.98, 132.38, 132.11, 131.14, 129.38, 128.60, 128.49, 128.25, 127.95, 127.34, 127.15, 126.73, 126.55, 125.05, 124.46, 124.30, 123.13, 122.72, 121.85. HRMS (ESI): m/z [M+H]⁺ 341.0620, calcd for C₂₂H₁₃O₂S⁺ 341.0636; m/z [M+Na]⁺ 363.0432, calcd for C₂₂H₁₂O₂SNa⁺ 363.0456.

3. Results and discussion

3.1. Synthesis and structures

Two approaches have been generally applied to synthesize aryl-sulfones: post-oxidation, where the sulfide-bridged system is first synthesized and then oxidized [6]; and the pre-oxidation, where benzothiophene *S,S*-dioxides are first synthesized and then coupled with other reactant to build larger sulfone-bridged structures [10,11]. For example, Nandakumar et al. recently reported the synthesis of substituted dibenzothiophenes *S,S*-dioxides via a Diels–Alder reaction between 1,3-diarylbenzo[*c*]furans and thiophene *S,S*-dioxide derivatives [11]. We chose to synthesize **PTAs** via acid-induced cyclization reaction of aromatic methyl sulfoxides [9], then oxidize them by excess meta-chloroperoxybenzoic acid (*m*CPBA) to generate the sulfone compounds in high yield. All of the regioisomers were fully characterized by ¹H NMR, ¹³C{H} NMR, and HR-MS, and they all exhibit good thermal and oxidative stability in air. The melting points of **SO₂-PhPy** are generally 30–50 °C higher than those of the corresponding **PTAs**.

The structures of **2-SO₂-PhPy** and **4-SO₂-PhPy** were confirmed by single-crystal X-ray diffraction. Both of **2-SO₂-PhPy** and **4-SO₂-PhPy** are crystallized in *P*-1 space group and with very similar unit cell parameters and cell size even half equivalent of dichloromethane was co-crystallized in crystal of **4-SO₂-PhPy**.

As shown in Fig. 1(a) and (b), the molecular structure of **2-SO₂-PhPy** still keep in nearly perfect co-planar manner. The dihedral angle between the phenyl and pyrenyl is only 0.75°. The bond length of S–C bonds and C–C bonds, which connect phenyl and pyrenyl in **2-SO₂-PhPy**, show little difference comparing with those of **2-S-PTA**.

4-SO₂-PhPy, however displays a butterfly-like structure, which is different from the planar structure of **4-S-PTA** and **2-SO₂-PhPy**, with a dihedral angle of 16.28° between pyrenyl and phenyl. The sulfur-containing 6-member ring in this molecule is not planar, although the bond length of S–C bonds and CC bond connecting phenyl and pyrenyl are still quite similar with those of **4-S-PTA**.

3.2. UV–vis absorption and fluorescence emission

The photophysical properties of **SO₂-PhPys** were examined, and some key data are summarized in Table 1. Generally, the absorption

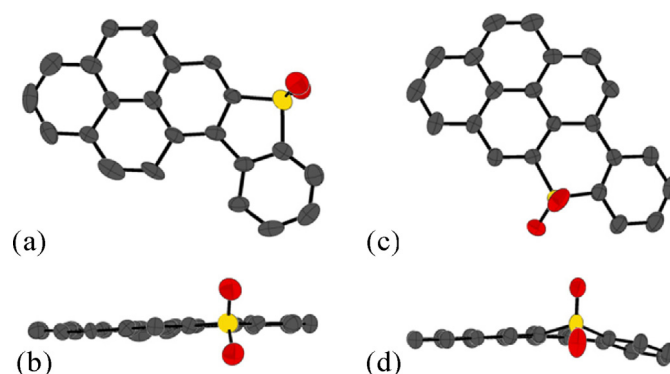


Fig. 1. Crystal structure of **2-SO₂-PhPy** (a) top view (b) side view; and **4-SO₂-PhPy** (c) top view (d) side view. H atoms are omitted for clarity.

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