Synthesis and photophysical characterization of novel π-conjugated vinyl sulfides

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ABSTRACT

The synthesis and photophysical properties of a series of π-conjugated vinyl sulfides are described. These compounds exhibited their absorption maxima in the range of 350–366 nm, while the emission spectra displayed peaks in the zone of 421–441 nm; both of them were influenced, although in different degrees, by the extent of the conjugated system. Red-shifted absorption and emission were observed when the π-conjugation was extended, clearly indicating that the sulfur atom participates as a bridge within these highly conjugated structures. Therefore, this preliminary investigation suggests that vinyl sulfide-based π-conjugated materials are promising compounds for the development of novel and efficient organic emitters.

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1. Introduction

Luminescent compounds are attracting considerable attention in the fields of biochemistry and materials science [1]. The development of polyconjugated fluorescent organic compounds has been extensively investigated in recent years due to their variety of optical, electrical and photoelectric properties, and their potential applications in organic optoelectronics, molecular electronics and manufacturing of organic light-emitting devices (OLEDs).

The OLEDs are a class of highly advanced electronic devices which have great quantum efficiencies and are now being commercially available in handheld apparatus and all-size full-color displays, where they act as successful replacements of the old cathode ray tubes and the most modern liquid crystal displays [2]. Therefore, new photoactive materials are continually being developed for application in high-efficiency organic devices and the development of simple synthetic routes to wavelength-tunable fluorophores, with potential applications in electronic and photonic devices, is of great interest [3].

So far, the fluorophores that have demonstrated suitability in this area have a large and effective π-conjugated system, as the most relevant common feature (Fig. 1). In many of these compounds, the π-conjugated system embodies a sulfur derivative, mainly thiophene-based (A–E) [4], but heterocycles such as benzothiadiazoles (E) [5], benzothiazoles (F) [6] and others [7] have also been described.

The frequent use of these heterocycles as π-bridges for design of efficient conjugated structures stems from their excellent optical and electronic properties, as well as thermal and environmental stabilities, intrinsic electron-rich nature, and ability to furnish derivatives under relatively simple conditions [8].

Opposite to the ubiquity of sulfur-containing heterocycles, the presence of non-heterocyclic sulfur atoms in organic emitters has been essentially limited. They were placed as linkers [9] between aromatic structures (G–M), such as in the pyrene derivatives PyG0 (H) and (I), a precursor of visual chemosensors for peroxides [10], and in the substituted anthracene ANS (J). Alternatively, thioester [11] or disulfide (K) [12] moieties have been used as peripheral structural elements to connect molecular wires or just to anchor various probes to gold particles.

It has been demonstrated that the incorporation of sulfur to the anthracene core drastically changes the photo- and electronic properties of the resulting molecules, suggesting that the lone pair of electrons of sulfur participate in the photo-induced electron transfer to the excited state of the aromatic tricycle [13]. On the other hand, Yanai and co-workers [14] synthesized a thioketene

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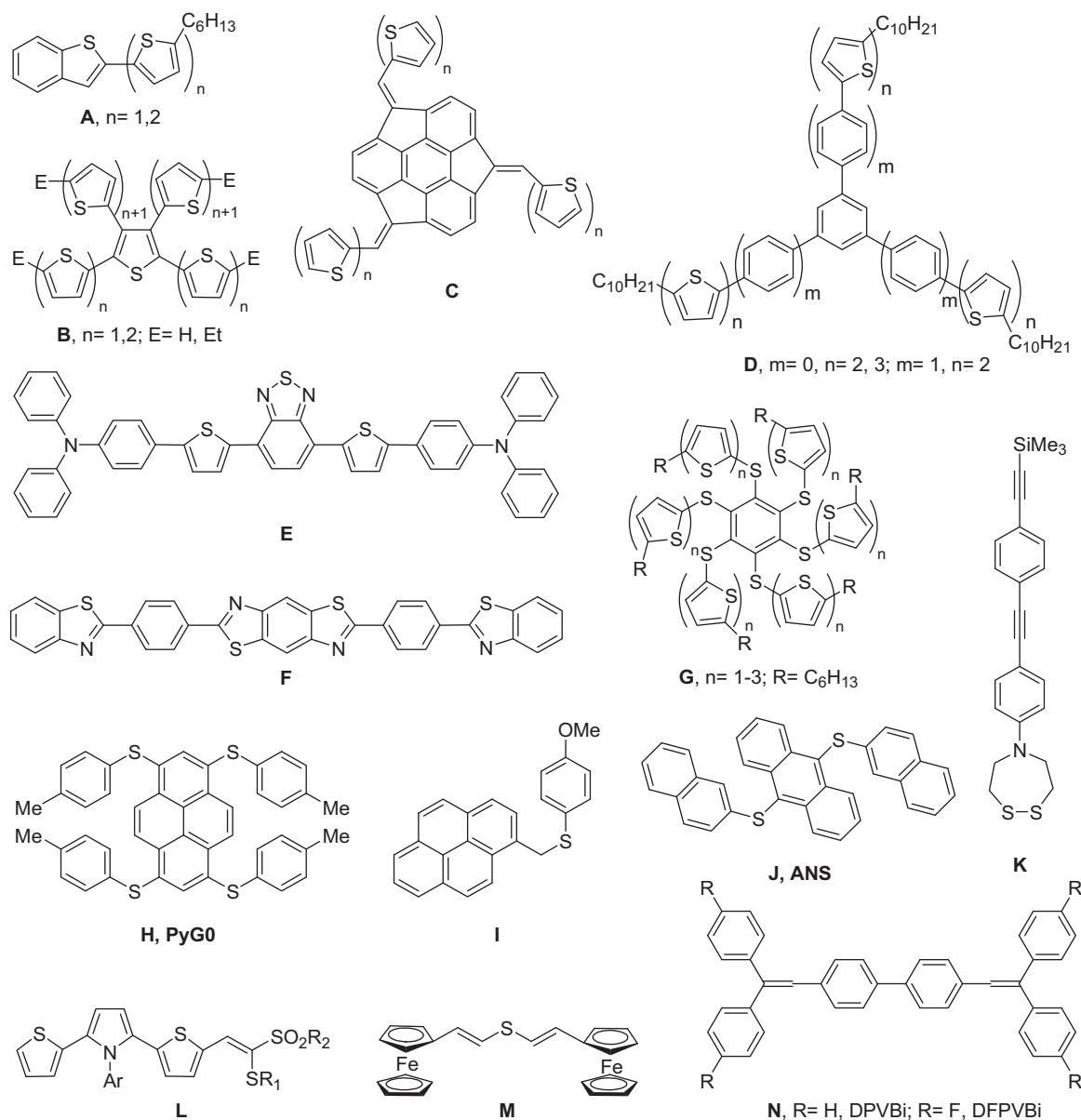 E-mail address: silveira@quimica.ufsm.br (C.C. Silveira).

Fig. 1. Chemical structures of some sulfur-containing conjugated heterocycles with potentially useful photophysical and photochemical properties, DPVBi and DFPVBi.

acetal-type dopant (**L**), and other investigations [15] validated the use of sulfur as a group electrically equivalent to a double bond for charge transport in unsaturated chains (**M**).

Furthermore, it has been envisioned that the association of aromatic rings, sulfur atoms and double bonds in which the delocalization of p-electrons through the sulfur bridge is possible, may endow the resulting molecules with an array of remarkable characteristics, such as light refractivity and nonlinear optical properties [16]. These precedents support the hypothesis that non-heterocyclic organochalcogen moieties can be potentially useful structural motifs for the design of efficient π-systems for organic electronics.

We have recently reported a facile and convenient Horner–Wittig-based synthetic approach to the preparation of (diphenylphosphinoyl)methyl vinyl sulfides as well as symmetrically and unsymmetrically substituted divinyl sulfides and cyclic sulfides [17], from the easily available bis[(diphenylphosphinoyl) methyl]sulfide [18].

Based on the outstanding properties of sulfur-containing derivatives related above, as well as on our previous experience on the synthesis of vinyl chalcogen compounds, we were interested in the preparation of novel organochalcogen derivatives for potential applications in optoelectronic devices. Therefore, herein we report the synthesis, characterization and photoluminiscent properties of novel π-conjugated vinyl sulfides (**3**), employing aromatic dialdehydes (**2**) as central cores, through the use of a Wittig–Horner based approach, as shown in Scheme 1.

2. Materials and methods

2.1. Reagents

The solvents for chemical reactions were purified according to the literature and transferred under argon, via syringe. The fluorescence and UV–vis measurements were carried out in spectroscopic grade solvents. Commercial reagents were used without further purification. All the reactions were performed in flame-dried glassware.
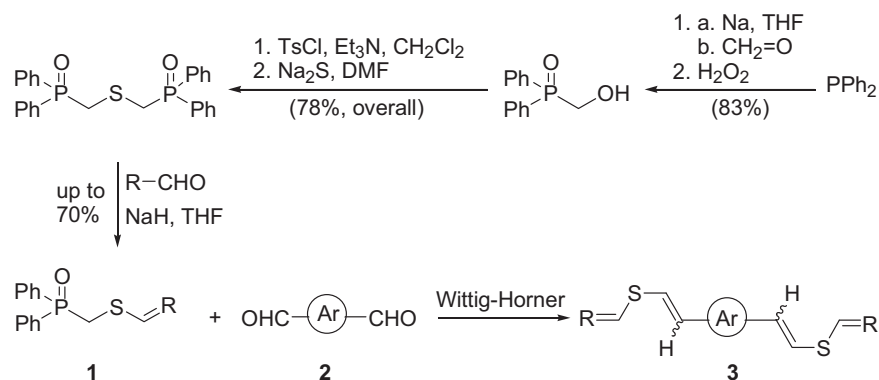
Scheme 1. Preparation of **1** [17,18] and proposed synthetic strategy toward the vinylic sulfides **3** (Ar = aryl).

2.2. Structural characterization methodology

The melting points were measured on an MQAPF-301 (Microquímica) instrument and are reported uncorrected. NMR spectra (^{1}H and ^{13}C) were recorded on Bruker DPX-200 and Bruker DPX-400 spectrometers (200 and 400 MHz for ^{1}H, respectively). Chemical shift data are reported in ppm downfield from TMS, employed as internal standard. Coupling constants (J) are informed in Hertz. Elemental analyses were recorded on a Perkin-Elmer CHN 2400 analyzer. Low-resolution mass spectra were run on a Shimadzu QP2010 *Plus* CG-MS instrument. High-resolution mass spectral data were obtained in a Bruker microTOF-Q IIT instrument. Infrared spectra were acquired on a Shimadzu Prestige-21 spectrometer, with the samples prepared as KBr pellets.

2.3. Photophysical characterization methodology

UV–vis absorption spectra were taken in a Cary 50 Bio UV/Visible spectrophotometer, employing the pure solvent as reference. Steady state fluorescence spectra were measured in a Varian Cary Eclipse fluorescence spectrophotometer. The fluorescence quantum yields (Φ_F) of the synthesized compounds were determined in CH_2Cl_2 solutions ($\eta_D^{20} = 1.4242$), relative to quinine in 0.1 M H_2SO_4 ($\eta_D^{20} = 1.3576$; $\Phi_F = 0.55$ at 20 °C) [19], employing the following equation: $\Phi_{Fs} = \Phi_{Fr} \times (I_s \times OD_r \times \eta_s^2)/(I_r \times OD_s \times \eta_r^2)$, where I, OD and η are the integrated emission intensities of the solutions (s = sample; r = reference), their corresponding optical densities of the respective solutions and the refractive index of the solvents used, respectively. All the experiments were performed at room temperature with samples in the concentration range of 10^{-6} to 10^{-5} M.

2.4. Synthesis

2.4.1. Synthesis of the (diphenylphosphinoyl)methyl ethenyl sulfides (*1a–g*)

A stirred solution of bis[(diphenylphosphinoyl)methyl] sulfide (462 mg, 1 mmol) in THF (10 mL) was treated with NaH (dry 95%; 2 mmol) at room temperature. After 20 min, the appropriate carbonyl compound (1.1 mmol) was added and the system was stirred for 24 h at 60 °C (oil bath temperature). The reaction was quenched with saturated aqueous NH$_4$Cl solution (20 mL) and the mixture was extracted with CH$_2$Cl$_2$ (3× 20 mL). The combined organic layers were dried (MgSO$_4$), filtered and concentrated under reduced pressure. The residue was purified by column chromatography (CH$_2$Cl$_2$:hexanes:EtOAc, 1:5:4) to give the desired products.

2.4.2. Synthesis of the 1,4-bis(((methyl)thio)ethenyl)benzenes **3a–g**

A solution of *n*BuLi in hexanes (4 mmol) was added dropwise to a stirred solution of the corresponding (diphenylphosphinoyl)methyl ethenyl sulfide (**1**, 2.2 mmol) in THF (15 mL) at room temperature. After 20 min, terephthalaldehyde (**2**, 1.0 mmol) was added and the solution was stirred under reflux for 3–5 h. Then, saturated aqueous NH$_4$Cl solution (20 mL) was added and the mixture was extracted with EtOAc (2× 20 mL). The organic layer was dried (MgSO$_4$), filtered and concentrated under reduced pressure. The residue was purified by column chromatography, eluting with hexanes.

2.4.2.1. 1,4-bis(2-((Cyclopentylidenemethyl)thio)ethenyl)benzene (**3a**). Yield: 74%. Yellow solid, m.p.: 68–72 °C. *E,E/Z,E*: >20/1. IR (KBr): ν 2951, 2862, 1589, 1408, 934, 810 and 768 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.67–1.77 (m, 8 H), 2.30–2.41 (m, 8 H), 5.97 (t, *J* = 2.2, 2 H), 6.42 (d, *J* = 15.5, 2 H), 6.73 (d, *J* = 15.5, 2 H) and 7.20 (s, 4 H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 26.2, 26.7, 31.0, 34.3, 109.4, 124.0, 125.7, 126.1, 136.6 and 150.1. GC–MS: *m/z* (rel. int., %) = 354 (M$^+$, 98), 229 (66), 199 (11), 197 (14), 191 (12), 185 (11), 173 (17), 161 (18), 147 (49), 129 (28), 125 (100) and 115 (36). Anal. Calcd. for C$_{22}$H$_{26}$S$_2$: C, 74.52; H, 7.39. Found: C, 74.62; H, 8.01.

2.4.2.2. 1,4-bis(2-((Cyclohexylidenemethyl)thio)ethenyl)benzene (**3b**). Yield: 76%. Yellow solid, m.p.: 67–75 °C. *E,E/Z,E*: 4/1. IR (KBr): ν = 2924, 2851, 1589, 1443, 988, 934, 845 and 775 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ (*E,E*-**3b**) = 1.51–1.63 (m, 12 H), 2.20–2.35 (m, 8 H), 5.82 (s, 2 H), 6.42 (d, *J* = 15.4, 2 H), 6.72 (d, *J* = 15.4, 2 H) and 7.20 (s, 4 H). ^{13}C NMR (100 MHz, CDCl$_3$): δ (*E,E*-**3b**) = 26.3, 27.3, 28.2, 30.5, 36.6, 110.9, 124.2, 125.8, 126.2, 135.6 and 147.2. GC–MS: *m/z* (rel. int., %) = 382 (M$^+$, 46), 281 (14), 207 (31), 147 (26), 139 (100), 129 (13) and 73 (32). Anal. Calcd. for C$_{24}$H$_{30}$S$_2$: C, 75.34; H, 7.90. Found: C, 74.79; H, 8.07.

2.4.2.3. 1,4-bis(2-((Cycloheptylidenemethyl)thio)ethenyl)benzene (**3c**). Yield: 80%. Yellow solid, m.p.: 60–65 °C. *E,E/Z,E*: 7/1. IR (KBr): ν = 2920, 2847, 1586, 1443, 937, 845 and 787 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ (*E,E*-**3c**) = 1.49–1.69 (m, 16 H), 2.35–2.42 (m, 8 H), 5.89 (s, 2 H), 6.43 (d, *J* = 15.5, 2 H), 6.73 (d, *J* = 15.5, 2 H) and 7.20 (s, 4 H). ^{13}C NMR (100 MHz, CDCl$_3$): δ (*E,E*-**3c**) = 26.6, 28.9, 29.2, 29.9, 32.2, 37.5, 114.4, 124.0, 125.7, 126.4, 135.6 and 147.4. GC–MS: *m/z* (rel. int., %) = 410 (M$^+$, 28), 281 (14), 253 (10), 207 (28), 154 (14), 153 (100), 147 (22), 135 (14) and 117 (13). Anal. Calcd. for C$_{26}$H$_{34}$S$_2$: C, 76.04; H, 8.34. Found: C, 77.21; H, 9.04.

2.4.2.4. 1,4-bis(2-((Cyclooctylidenemethyl)thio)ethenyl)benzene (**3d**). Yield: 73%. Yellow solid, mp 52–60 °C. *E,E/Z,E*: 2.5/1. IR (KBr): ν = 2920, 2847, 1589, 1443, 937, 841 and 787 cm^{-1}. ^{1}H NMR

(400 MHz, CDCl$_3$): δ (E,E-**3d**) = 1.45–1.55 (m, 12H), 1.64–1.72 (m, 8H), 2.30–2.37 (m, 8H), 5.92 (s, 2H), 6.43 (d, J = 15.5, 2H), 6.73 (d, J = 15.5, 2H) and 7.21 (s, 4H). ^{13}C NMR (100 MHz, CDCl$_3$): δ (E,E-**3d**) = 25.9, 26.2, 26.3, 26.6, 27.2, 31.1, 37.3, 114.5, 124.1, 125.8, 126.3, 135.6 and 147.9. GC–MS: m/z (rel. int., %) = 438 (M$^+$, 68), 168 (13), 167 (100), 147 (19), 129 (10), 117 (16), 115 (12), 97 (51) and 81 (30). HRMS: found m/z 439.2487; C$_{28}$H$_{38}$S$_2$ [(M+H)$^+$] requires m/z 439.2448.

2.4.2.5. 1,4-bis(2-(((4-Methylcyclohexylidene)methyl)thio)ethenyl) benzene (3e). Yield: 86%. Yellow solid, m.p.: 37–55 °C. E,E/Z,E: 6/1. IR (KBr): ν = 2920, 2847, 1589, 1454, 1288, 1227, 937, 837 and 771 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ (E,E-**3e**) = 0.92 (d, J = 6.6, 6H), 0.96–1.09 (m, 4H), 1.50–1.61 (m, 2H), 1.75–1.82 (m, 4H), 1.85–1.93 (m, 2H), 2.11–2.20 (m, 2H), 2.29–2.39 (m, 2H), 2.75–2.81 (m, 2H), 5.83 (s, 2H), 6.42 (d, J = 15.4, 2H), 6.71 (d, J = 15.4, 2H) and 7.20 (s, 4H). ^{13}C NMR (100 MHz, CDCl$_3$): δ (E,E-**3e**) = 21.8, 29.8, 32.3, 35.3, 35.9, 36.3, 111.0, 124.2, 125.7, 126.1, 135.6 and 146.6. GC–MS: m/z (rel. int., %) = 410 (M$^+$, 52), 257 (14), 154 (12), 153 (100), 145 (14), 129 (11), 117 (12) and 97 (22). Anal. Calcd. for C$_{26}$H$_{34}$S$_2$: C, 76.04; H, 8.34. Found: C, 76.09; H, 8.79.

2.4.2.6. 1,4-bis(2-(((4-(tert-Butyl)cyclohexylidene)methyl)thio) ethenyl)benzene (3f). Yield: 73%. Yellow solid, m.p.: 60–69 °C. E,E/Z,E: 6/1. IR (KBr): ν = 2943, 2859, 1589, 1366, 937, 841 and 775 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ (E,E-**3f**) = 0.86 (s, 18H), 1.00–1.25 (m, 6H), 1.78–1.92 (m, 6H), 2.06–2.16 (m, 2H), 2.41–2.46 (m, 2H), 2.85–2.89 (m, 2H), 5.81 (s, 2H), 6.42 (d, J = 15.4, 2H), 6.73 (d, J = 15.4, 2H) and 7.21 (s, 4H). ^{13}C NMR (100 MHz, CDCl$_3$): δ (E,E-**3f**) = 27.6, 28.0, 28.9, 30.4, 32.4, 36.5, 48.0, 110.5, 124.2, 125.8, 126.1, 135.6 and 147.1. GC–MS: m/z (rel. int., %) = 494 (M$^+$, 64), 299 (12), 196 (15), 195 (100), 161 (10), 147 (16), 117 (26), 105 (12), 97 (29) and 57 (96). Anal. Calcd. for C$_{32}$H$_{46}$S$_2$: C, 77.67; H, 9.37. Found: C, 77.65; H, 9.93.

2.4.2.7. 1,4-bis(2-((2,2-Diphenylethenyl)thio)ethenyl)benzene (3g). Yield: 57%. Yellow solid, m.p.: 97–107 °C. E,E/Z,E: 4/1. IR (KBr): ν = 3024, 1597, 1493, 1439, 930, 772, 752 and 698 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ (E,E-**3g**) = 6.57 (d, J = 15.5, 2H), 6.83 (s, 2H), 6.85 (d, J = 15.5, 2H) and 7.21–7.42 (m, 24H). ^{13}C NMR (100 MHz, CDCl$_3$): δ (E,E-**3g**) = 122.1, 123.7, 126.1, 127.1, 128.3, 128.4, 129.7, 135.6, 139.0 and 141.2. GC–MS: m/z (rel. int., %) = 550 (M$^+$, 33), 223 (13), 205 (21), 192 (43), 191 (28), 178 (42) and 165 (31). Anal. Calcd. for C$_{38}$H$_{30}$S$_2$: C, 82.87; H, 5.49. Found: C, 82.38; H, 5.73.

2.4.3. Synthesis of the 4,4-bis(((methyl)thio)ethenyl)biphenyl derivatives 5a–g

NaOMe (4 mmol) was added to a stirred solution of the corresponding (diphenylphosphinoyl) methyl ethenyl sulfide (**1**, 2.2 mmol) in THF (20 mL) at room temperature. After 20 min, the system was treated with [1,1′-biphenyl]-4,4′-dicarbaldehyde (**4**, 1 mmol) and the solution was stirred under reflux for 3–5 h. A saturated aqueous solution of NH$_4$Cl (20 mL) was added and the mixture was extracted with EtOAc (2× 20 mL). The combined organic layers were dried (MgSO$_4$), filtered and concentrated under reduced pressure. The residue was purified by column chromatography, eluting with hexanes.

2.4.3.1. 4,4′-bis(2-((Cyclopentylidenemethyl)thio)ethenyl)biphenyl (5a). Yield: 68%. Yellow solid, m.p.: 115–120 °C. E,E/Z,E: >20/1. IR (KBr): ν = 2951, 2862, 1589, 934, 822 and 783 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.66–1.78 (m, 8H), 2.31–2.43 (m, 8H), 6.00 (t, J = 2.0, 2H), 6.48 (d, J = 15.5, 2H), 6.79 (d, J = 15.5, 2H), 7.34 (d, J = 8.3, 4H) and 7.52 (d, J = 8.3, 4H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 26.2, 26.7, 31.0, 34.3, 109.3, 124.5, 125.9, 125.9, 126.9, 136.0, 138.8 and 150.2. GC–MS: m/z (rel. int., %) = 430 (M$^+$, 98), 306 (19), 305 (70),

233 (13), 193 (15), 125 (100), 81 (16) and 79 (32). Anal. Calcd. for C$_{28}$H$_{30}$S$_2$: C, 78.09; H, 7.02. Found: C, 78.34; H, 7.58.

2.4.3.2. 4,4′-bis(2-((Cyclohexylidenemethyl)thio)ethenyl)biphenyl (5b). Yield: 80%. Yellow solid, m.p.: 120–130 °C. E,E/Z,E: 10/1. IR (KBr): ν = 2924, 2847, 1589, 1443, 934, 817 and 783 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ (E,E-**5b**) = 1.57–1.59 (m, 12H), 2.23–2.25 (m, 4H), 2.32–2.35 (m, 4H), 5.84 (s, 2H), 6.48 (d, J = 15.4, 2H), 6.78 (d, J = 15.4, 2H), 7.34 (d, J = 8.2, 4H) and 7.52 (d, J = 8.2, 4H). ^{13}C NMR (100 MHz, CDCl$_3$): δ (E,E-**5b**) = 26.3, 27.2, 28.3, 30.5, 36.6, 110.8, 124.7, 125.9, 125.9, 126.9, 136.0, 138.8 and 147.3. GC–MS: m/z (rel. int., %) = 458 (M$^+$, 28), 169 (35), 147 (24), 139 (100), 97 (28) and 79 (34). Anal. Calcd. for C$_{30}$H$_{34}$S$_2$: C, 78.55; H, 7.47. Found: C, 78.51; H, 7.49.

2.4.3.3. 4,4′-bis(2-((Cycloheptylidenemethyl)thio)ethenyl)biphenyl (5c). Yield: 77%. Yellow solid, m.p.: 113–120 °C. E,E/Z,E: 6/1. IR (KBr): ν = 2920, 2847, 1589, 1492, 930, 830 and 779 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ (E,E-**5c**) = 1.42–1.74 (m, 16H), 2.33–2.40 (m, 8H), 5.91 (s, 2H), 6.50 (d, J = 15.5, 2H), 6.79 (d, J = 15.5, 2H), 7.33 (d, J = 8.2, 4H) and 7.51 (d, J = 8.2, 4H). ^{13}C NMR (100 MHz, CDCl$_3$): δ (E,E-**5b**) = 26.7, 28.9, 29.2, 29.9, 32.2, 37.5, 114.3, 124.5, 125.9, 126.2, 126.9, 136.0, 138.9 and 147.5. GC–MS: m/z (rel. int., %) = 486 (M$^+$, 100), 333 (17), 234 (13), 193 (16), 155 (12), 154 (25), 97 (51) and 79 (20). Anal. Calcd. for C$_{32}$H$_{38}$S$_2$: C, 78.96; H, 7.87. Found: C, 78.99; H, 8.01.

2.4.3.4. 4,4′-bis(2-((Cyclooctylidenemethyl)thio)ethenyl)biphenyl (5d). Yield: 80%. Yellow solid, m.p.: 120–129 °C. E,E/Z,E: 6/1. IR (KBr): ν = 2920, 2847, 1589, 1443, 934, 833 and 779 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ (E,E-**5d**) = 1.44–1.59 (m, 12H), 1.63–1.76 (m, 8H), 2.30–2.37 (m, 8H), 5.94 (s, 2H), 6.49 (d, J = 15.5, 2H), 6.78 (d, J = 15.5, 2H), 7.33 (d, J = 8.3, 4H) and 7.51 (d, J = 8.3, 4H). ^{13}C NMR (100 MHz, CDCl$_3$): δ (E,E-**5d**) = 25.9, 26.2, 26.3, 26.6, 27.2, 31.1, 37.3, 114.5, 124.6, 125.9, 126.1, 126.9, 136.0, 138.9 and 147.9. GC–MS: m/z (%) = 514 (M$^+$, 54), 168 (12), 167 (100), 97 (38), 81 (21) and 79 (11). Anal. Calcd. for C$_{34}$H$_{42}$S$_2$: C, 79.32; H, 8.22. Found: C, 79.24; H, 8.31.

2.4.3.5. 4,4′-bis(2-((4-Methylcyclohexylidenemethyl)thio)ethenyl) biphenyl (5e). Yield: 78%. Yellow solid, m.p.: 110–120 °C. E,E/Z,E: 5/1. IR (KBr): ν = 2916, 2847, 1589, 1493, 1439, 933, 833 and 783 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ (E,E-**5e**) = 0.92 (d, J = 6.6, 6H), 0.95–1.12 (m, 4H), 1.50–1.64 (m, 2H), 1.78–1.81 (m, 4H), 1.86–1.94 (m, 2H), 2.12–2.20 (m, 2H), 2.37–2.40 (m, 2H), 2.77–2.81 (m, 2H), 5.85 (s, 2H), 6.48 (d, J = 15.5, 2H), 6.78 (d, J = 15.5, 2H), 7.33 (d, J = 8.3, 4H) and 7.51 (d, J = 8.3, 4H). ^{13}C NMR (100 MHz, CDCl$_3$): δ (E,E-**5e**) = 21.8, 29.8, 32.3, 35.3, 35.9, 36.3, 111.0, 124.7, 125.9, 125.9, 126.9, 136.0, 138.8 and 146.7. GC–MS: m/z (rel. int., %) = 486 (M$^+$, 100), 333 (28), 193 (16), 155 (10), 154 (22), 107 (13), 97 (45), 91 (13), 81 (16) and 79 (17). Anal. Calcd. for C$_{32}$H$_{38}$S$_2$: C, 78.96; H, 7.87. Found: C, 79.01; H, 8.10.

2.4.3.6. 4,4′-bis(2-((4-(tert-Butyl)cyclohexylidenemethyl)thio) ethenyl)biphenyl (5f). Yield: 80%. Yellow solid, m.p.: 147–155 °C. E,E/Z,E: 12/1. IR (KBr): ν = 2944, 1591, 1365, 933, 819 and 782 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ (E,E-**5f**) = 0.87 (s, 18H), 1.02–1.25 (m, 6H), 1.79–1.92 (m, 6H), 2.09–2.19 (m, 2H), 2.43–2.47 (m, 2H), 2.86–2.90 (m, 2H), 5.84 (s, 2H), 6.49 (d, J = 15.4, 2H), 6.79 (d, J = 15.4, 2H), 7.34 (d, J = 8.4, 4H) and 7.52 (d, J = 8.4, 4H). ^{13}C NMR (100 MHz, CDCl$_3$): δ (E,E-**5f**) = 27.6, 28.0, 28.9, 30.4, 32.5, 36.5, 48.0, 110.5, 124.7, 125.9, 125.9, 126.9, 136.0, 138.9 and 147.2. GC–MS: m/z (%) = 570 (M$^+$, 100), 375 (21), 196 (21), 193 (18), 149 (20), 111 (12), 97 (41), 91 (13) and 81 (16). Anal. Calcd. for C$_{38}$H$_{50}$S$_2$: C, 79.94; H, 8.83. Found: C, 79.95; H, 8.85.

Table 1
Optimization of the reaction conditions for the olefination of **2** toward the 1,4-bis(((methyl)thio)ethenyl)benzene derivative **3f**.
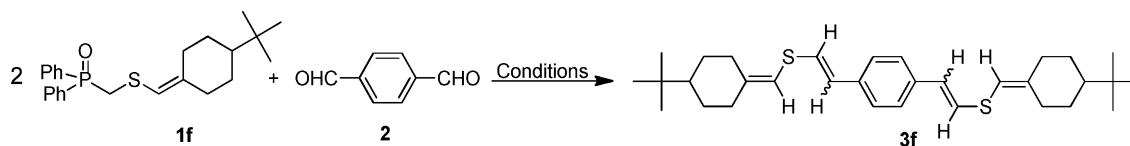
Entry No.	Base[a]	Temperature	Time (h)	E,E/Z,E ratio[b]	Yield (%)[c]
1	NaH	r.t.	24	1.5:1	78
2	NaH	Reflux	5	2.3:1	72
3	NaOMe	r.t.	24	1.3:1	45
4	NaOMe	Reflux	5	3.7:1	57
5	nBuLi	r.t.	24	2.5:1	70
6	nBuLi	Reflux	3	6:1	73

[a] Excess base (2 equiv.) was employed.
[b] Determined by ^{1}H NMR.
[c] Isolated yields.

2.4.3.7. 4,4′-bis(2-((2,2-Diphenylethenyl)thio)ethenyl)biphenyl (5g).
Yield: 80%. Yellow solid, m.p.: 147–154 °C. *E,E/Z,E*: >20/1. IR
(KBr): ν = 3024, 1597, 1493, 934, 822, 752 and 698 cm^{-1}. ^{1}H NMR
(400 MHz, CDCl$_3$): δ = 6.62 (d, *J* = 15.5, 2H), 6.83 (s, 2H), 6.88 (d,
J = 15.5, 2H) and 7.19–7.53 (m, 28H). ^{13}C NMR (100 MHz, CDCl$_3$):
δ = 122.1, 123.9, 126.2, 127.0, 127.1, 128.3, 128.4, 129.6, 135.6,
139.0, 139.2 and 141.2. GC–MS: *m/z* (rel. int., %) = 626 (M$^+$, 1), 391
(23), 390 (71), 279 (11), 223 (22), 211 (17), 210 (22), 199 (51), 192
(100), 178 (90), 165 (54), 152 (26) and 121 (31). Anal. Calcd. for
C$_{44}$H$_{34}$S$_2$: C, 84.30; H, 5.47. Found: C, 84.11; H, 5.96.

3. Results and discussion

3.1. Compound synthesis and characterization

The Wittig–Horner olefination entails the reaction between an
ylide precursor and a carbonyl component. Accordingly, a series of
starting diphenylphosphinoyl derivatives (**1a–g**) were synthesized,
as ylide precursors, employing our previously reported procedure
[17a,18]. On the other hand, the symmetric dialdehydes terephtha-
laldehyde (**2**) and [1,1′-biphenyl]-4,4′-dicarbaldehyde (**4**), which
embody the aromatic cores of the proposed products, were used
as the starting carbonyl components. Compound **4** was included as
starting material on account that biphenyl derivatives have been
previously prepared as new materials for use in organic blue-light-
emitting diodes [20].

In order to optimize the proposed Wittig–Horner olefination
toward the expected 1,4-bis(((methyl)thio)ethenyl)benzenes (**3**),
the model reaction between the phosphinoyl derivative **1f** and
dialdehyde **2** was studied in THF. Modifications were performed
in the reaction temperature and time, employing NaH, NaOMe and
*n*BuLi as bases.

As shown in Table 1, except for NaH, the yields were better when
the reaction was carried out under reflux. In addition, these con-
ditions allowed to attain improved stereoselectivities (entries 1, 3
and 5 vs. entries 2, 4 and 6, respectively), always being the *E,E* iso-
mer the most favored one. NaOMe afforded only moderate yields
(<60%) and stereoselectivity (*E,E/Z,E* up to 3.7).

On the other hand, the use of *n*BuLi under reflux proved to be the
most efficient conditions (Entry 6); despite giving chemical yields
essentially similar to those furnished by NaH (Table 1, Entries 1
and 2), these afforded improved product stereoselectivity (*E,E/Z,E*
diasteromer ratio = 6:1) under shorter reaction times. Therefore,
these optimized conditions were chosen for the synthesis **3a–g**
(Scheme 2), with the results exhibited in Table 3.

Next, the reaction was also optimized for the use of the biphenyl
derivative **4**, with the results contained in Table 2. It was observed

that, unlike the reaction of **1f** with **2**, the use of dialdehyde **4**
afforded no product after 24 h, at room temperature, when NaH
was employed as the base (Table 2, Entry 1). However, addition of
HMPA to the reaction furnished 72% of the expected product in a
E,E/Z,E isomer ratio of 1.2:1 (Table 2, Entry 2). Inclusion of the addi-
tive could be omitted by carrying out the reaction under reflux,
which gave the anticipated bis vinyl sulfide **5f** in 82% yield after
5 h, in a 5:1 *E,E/Z,E* isomer ratio (Entry 3).

Changing the base to potassium *tert*-butoxide favored the
formation of the *Z,E* isomer, but did not improve the reaction per-
formance (Entry 4), and the vinyl sulfide was obtained in 60%
yield (*E,E/Z,E* isomer ratio = 0.5:1). Finally, using NaOMe as base,
at room temperature, furnished 72% of the product (*E,E/Z,E* isomer
ratio = 5:1), after 24 h (Entry 5).

Not unexpectedly, however, when the transformation was car-
ried out under reflux the diastereoselectivity increased and the
E,E/Z,E isomer ratio raised to 12:1 (Table 2, Entry 6). Notewor-
thy, the transformation took place in 3 h and 80% yield. Therefore,
the latter reaction conditions were used for the synthesis of the
biphenyl derivatives **5a–g**, as shown in Scheme 2 and Table 3.

The optimized conditions of the Wittig–Horner reaction with
dialdehydes **2** and **4** were employed to synthesize a small library of
symmetrically substituted compounds the bis vinyl sulfides **3a–g**
and **5a–g** (Scheme 2), which were obtained in good to excellent
yields, as summarized in Table 3. Interestingly, the *E,E* isomers
were obtained exclusively when the five-membered ring-derived
reagent **1a** was employed. In addition, the remaining examples
exhibited a clear preference for the *E,E* isomers, in agreement with
the selectivity observed for other Horner–Wittig reactions [21].

The structures of the vinyl sulfide derivatives were confirmed
after rigorous IR, ^{1}H and ^{13}C NMR analysis, as well as by their
HRMS and elemental analysis data. The magnitudes of the observed
coupling constants between the adjacent vinylic protons was
employed to infer the stereochemistry of the double bonds, while
the areas under the curves were used to estimate the corresponding
stereoisomeric ratios. The presence of minor amounts of geomet-
ric isomers accompanying the major *E,E*-product resulted in wide
melting point ranges of the compounds [22a].

Interestingly, compound **5g** can be regarded as a vinylogous
of 4,4′-bis(2,2′-diphenylvinyl)-biphenyl (DPVBi) and related com-
pounds (Fig. 1), which act as blue light emitters [22b,c].

3.2. Photophysical characterization

The optical properties of the synthesized vinyl sulfides, includ-
ing their UV/vis spectra and fluorescence emission characteristics,
were studied in dilute CH$_2$Cl$_2$ solutions, at room temperature.
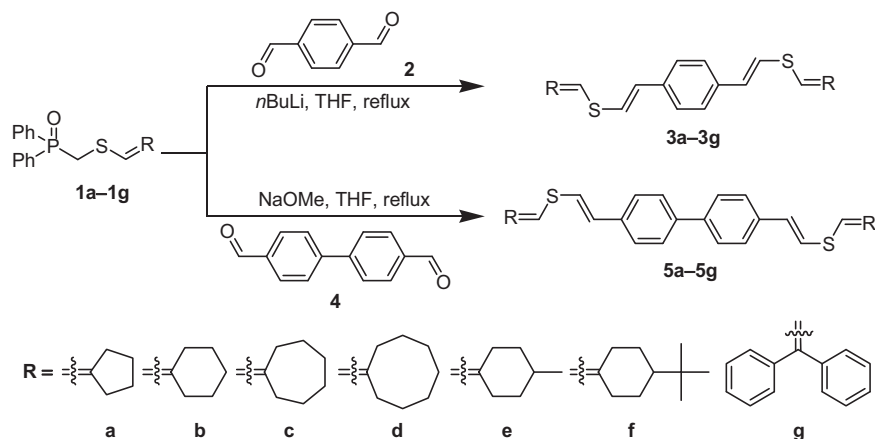
Scheme 2. Wittig–Horner synthesis of the proposed bis vinyl sulfides **3a–g** and **5a–g**.

The absorbance (λ_{max}) and emission (λ_{em}) maxima, Stokes' shifts ($\Delta\lambda_{ST}$), fluorescence quantum yields (Φ_F) and values of their molar extinction coefficient (ε_{max}) are summarized in Table 4.

Fig. 2 shows the normalized excitation spectra of the sulfides **3a–g** and **5a–g**. Both series of compounds exhibited single absorption bands with quite similar characteristics. Except for compounds **3g** and **5g**, which are red-shifted when compared to the other sulfides (λ_{max} = 366 and 365 nm, respectively), the absorption peaks were in the range of 350–355 nm, which can be assigned to the typical $^1\pi{-}\pi^*$ transitions of the whole molecule. Compared to the cycloalkyl-terminated sulfides, their diphenyl end-capped congeners **3g** and **5g** also exhibited the largest extinction coefficients, suggesting the presence of larger and more effective π-conjugated systems, extended through the "sulfur bridge".

The bathochromic shift experienced by compounds **3a–g** with regards to the spectrum of 1,4-diethenylbenzene [λ_{max}: 228, 236 and 279 nm (sh)] [23] clearly evidenced that the sulfur bridge extends the conjugation of the system.

Dale [24] has shown that when the wavelength maxima (λ_{max}) of the main band of chain molecules consisting of alternating benzene rings and ethylenic bonds is plotted against the number of chromophoric units (benzene ring = 2; ethylenic bond = 1), they follow a pattern; this can be fit by an exponential curve of the form $\lambda_{max} = A \times (1 - e^{-bx})$, where x is the number of chromophoric units. Interestingly, interpolation of λ_{max} of compounds **3a–f** in the curve suggests the presence of an absorbing system with approximately eight chromophoric units, consisting with the assignment of a chromophoric unit to each one of the sulfur atoms (S = 1). For

3g, the same plot predicted ten chromophoric units, underestimating the actual number. This may be a consequence of steric interactions between hydrogens supported on adjacent rings of the 1,1′-ethene-1,1′-diyldibenzene system.

On the other hand, the plot predicted approximately eight chromophoric units, for **5a–f** and ten for **5g**, underestimating in all cases the actual number. In the former case (**5a–f**), this may be a consequence of the twisted structure of the biphenyl fragment, resulting from a balance between *ortho* hydrogen–hydrogen steric repulsion and the electronic conjugation of the two phenyl rings, which ends up furnishing a less effective π-conjugation of the whole system [25]. However, in the case of **5g**, steric interactions between hydrogens supported on adjacent rings of the 1,1′-ethene-1,1′-diyldibenzene system, may also be contributing to the observed behavior.

Next, the photoluminescence properties of the sulfides **3** and **5** were investigated. Fig. 3 shows their normalized emission spectra revealed that, when excited at their absorption maxima, the compounds exhibit emission spectral profiles which mirror the corresponding excitation spectra and display maxima in the violet/blue region (421–441 nm), with a full width at half-maximum averaging 85 nm and Stokes' shift values between 4259 and 5498 cm^{-1} (0.53–0.68 eV). The latter are in the same range as those reported for oligothiophenes (∼0.6 eV) [26], which were attributed to significant differences in their geometries of the ground and excited states [27].

The single and strong fluorescence band present in the fluorescence spectra indicated that the emission takes place from the

Table 2
Optimization of the reaction conditions with dialdehyde **4**, for the synthesis of the 4,4′-bis(((methyl) thio)ethenyl)biphenyl derivative **5f**.

Entry No.	Base[a]	Solvent	Temperature	Time (h)	E,E/Z,E ratio[c]	Yield (%)[d]
1	NaH	THF	r.t.	24	–	0
2	NaH	THF[b]	r.t.	24	1.2:1	72
3	NaH	THF	Reflux	5	5:1	82
4	KOtBu	PhMe	r.t.	1	0.5:1	60
5	NaOMe	THF	r.t.	24	5:1	72
6	NaOMe	THF	Reflux	3	12:1	80
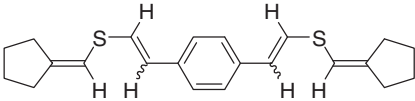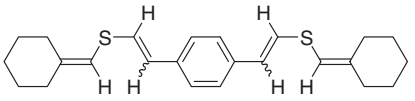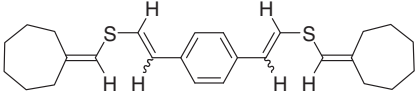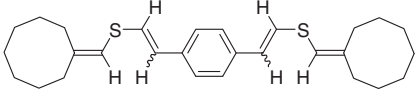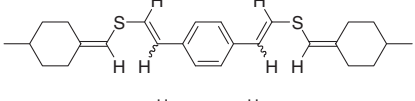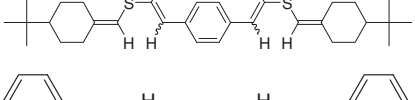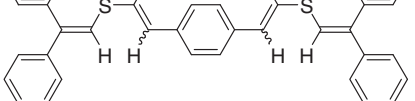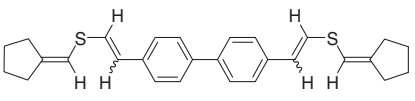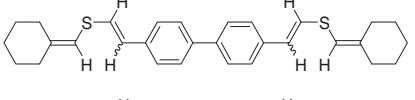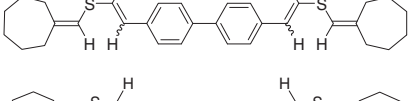
[a] Excess base (2 equiv.) was employed.
[b] HMPA (1 mL) was added to the reaction system.
[c] Determined by ^{1}H NMR.
[d] Isolated yields.

Table 3
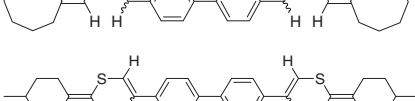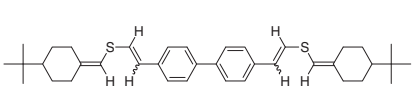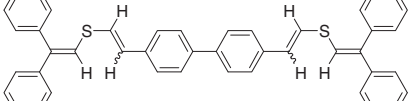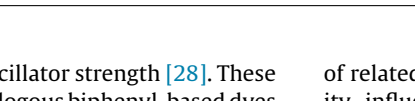Synthesis of 1,4-bis(((methyl)thio)ethynyl)benzenes derivatives **3a–g** and the related 4,4′-bis(((methyl)thio)ethynyl)biphenyls **5a–g**.

Entry No.	Product No.	Product structure	Time (h)	$E,E/E,Z$ ratio[a]	Yield (%)
1	**3a**		5	>20:1	74
2	**3b**		5	4:1	76
3	**3c**		4	7:1	80
4	**3d**		4	2.5:1	60
5	**3e**		3	6:1	72
6	**3f**		3	6:1	73
7	**3g**		5	4:1	57
8	**5a**		4	>20:1	68
9	**5b**		4	10:1	80
10	**5c**		5	6:1	77
11	**5d**		4	6:1	80
12	**5e**		3	5:1	78
13	**5f**		3	12:1	80
14	**5g**		4	>20:1	80

^a Determined by ^{1}H NMR.

lowest excited state with the largest oscillator strength [28]. These sulfides displayed a trend similar to analogous biphenyl-based dyes previously reported in literature; the small red-shifted absorption and fluorescence emission maxima observed among these series of related compounds is due to an increase in the electron mobility, influenced by the end-capping group, generally, an electron donating group [29–32]. From the onset of the absorption peaks ($\lambda_{onset} = 390$–400 nm), the optical band gap E_g ($E_g = 1240/\lambda_{onset}$)

Table 4
Photophysical properties of compounds **3a–g** and **5a–g**, in CH_2Cl_2.

Compd. No.	UV–vis absorption		Fluorescence data		
	λ_{max} (nm)	ε_{max} (10^4 M^{-1} cm^{-1})	λ_{em} (nm)	$\Delta\lambda_{ST}$ (cm^{-1})	Φ_F (λ_{ex} = 347 nm)[a]
3a	350	5.10	424	4987	0.021
3b	350	4.33	421	4818	0.048
3c	353	3.43	422	4632	0.109
3d	355	0.81	424	4584	0.018
3e	350	4.98	427	5152	0.027
3f	351	2.77	422	4793	0.031
3g	366	4.90	435	4259	0.058
5a	352	4.79	431	5368	0.182
5b	351	6.52	433	5180	0.238
5c	353	5.15	434	5368	0.176
5d	352	2.55	437	5498	0.122
5e	353	6.36	432	5180	0.283
5f	350	3.75	432	5423	0.233
5g	365	7.10	441	4722	0.143

[a] Values were computed with the samples in CH_2Cl_2 (η_D^{20} = 1.4242) with reference to a solution of quinine in 0.1 M H_2SO_4 (η_D^{20} = 1.3576); the experimental error was ±0.004 [19].
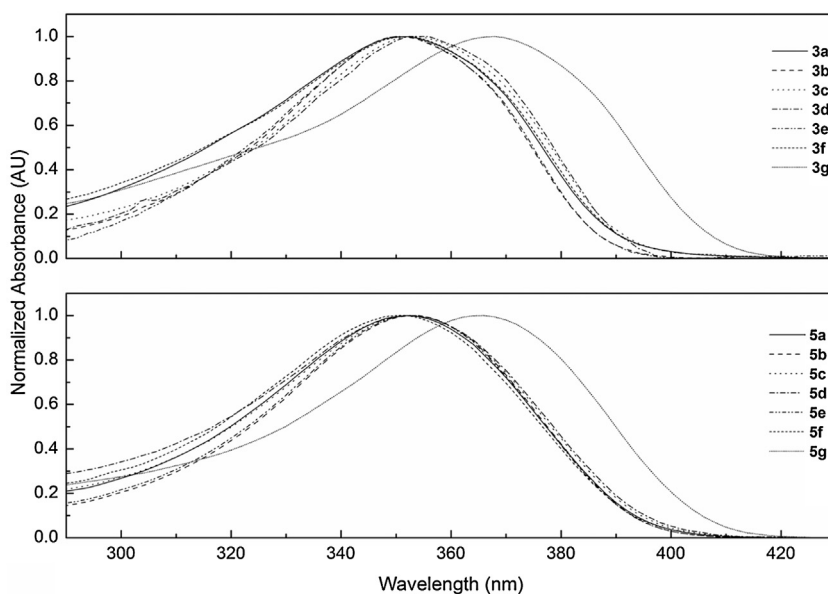

Fig. 2. Overlapped, normalized UV/vis absorption spectra of vinyl sulfides **3a–g** (top) and **5a–g** (bottom) in CH_2Cl_2, at 25 °C.
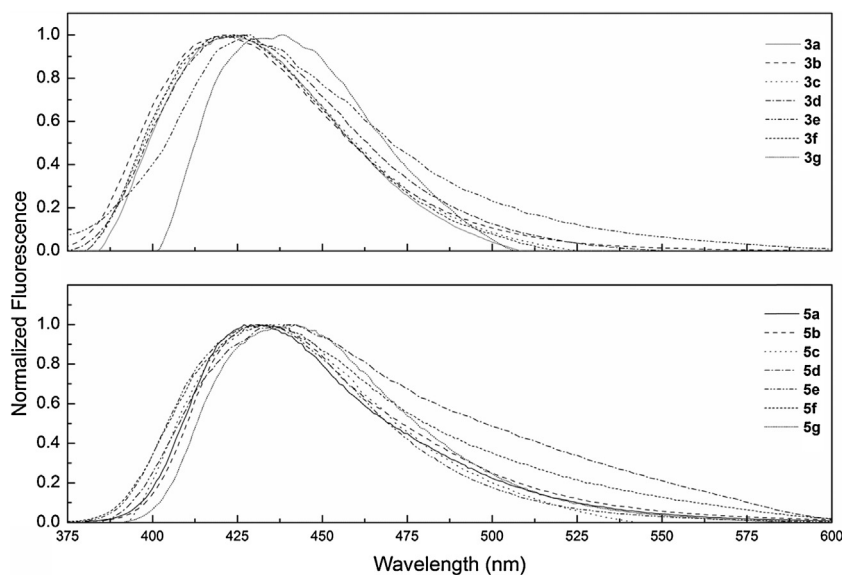

Fig. 3. Normalized, overlapped emission spectra of vinyl sulfides **3a–g** and **5a–g** in CH_2Cl_2, at 25 °C.

was determined to be in the range 3.10–3.18 eV, which nears its properties to those of the semiconductors ($E_g < 3$ eV).

Unlike the structure-λ_{max} effect noticed in the absorption spectra, it was detected that the end-capping group has weak influence on the emission maxima of the sulfides especially among the biphenyl derivatives (λ_{em} = 421–435 nm for **3a–g** and λ_{em} = 432–441 nm for **5a–g**). This may be suggesting that the predominant effect observed is the electron transfer between the sulfur atom and the core biphenyl unit. The emission wavelengths of the terephthaldehyde-derived compounds **3a–f**, end-capped with alicyclic moieties, were approximately 10 nm blue-shifted relative to those of compounds **5a–f**, probably reflecting the more extended π-conjugation in the latter, due to the presence of an extra aromatic ring. Interestingly, however, the emission maxima of sulfides **3g** and **5g** were essentially similar (λ_{em} = 435 and 441 nm, respectively).

Comparison of the fluorescence quantum yields among the series compounds **3a–g** and **5a–g** revealed that the latter group, carrying a biphenyl core, exhibited considerably higher values of Φ_F. On the other hand, establishing a relationship between the length of the conjugated systems and the corresponding Φ_F values of the compounds was not possible. However, despite 9–14 nm red-shifted emission maxima were observed when the spectra of **3g** and **5g** were compared with those of their congeners, only in the case of **3g** was detected an increase in the quantum yield of emission with regards to the related **3a–f**.

Since the chromophores are centrosymmetric, only weak solvatochromism is to be expected. Accordingly, all compounds demonstrated to be only marginally solvatochromic, both in absorption and emission. The maxima of the spectral bands were shifted around 10–20 nm when the excitation and emission of compounds **3f** and **5f** were recorded in three different solvents (CH_2Cl_2, EtOAc and DMSO).

However, that the dipolar moment of the solvents does not play relevant roles in the photophysics of these dyes in the ground and excited states could also be a result of the structures of these series of vinyl sulfides; at this preliminary stage, these have been prepared without highly electron donor or acceptor groups, which could favor the formation of polarized structures.

4. Conclusions

In summary, we have successfully prepared a series of novel vinyl sulfide derivatives and investigated their excitation and emission properties. The syntheses proceeded in good yields, through the Wittig–Horner reaction of dialdehydes and (diphenylphosphinoyl)methyl vinyl sulfides. The absorption spectra of the bis vinyl sulfides exhibited maxima in the range 350–366 nm, while their emission spectra displayed peaks in the zone of 421–441 nm; both of them were influenced, although in different degrees, by the extent of the conjugated system. The red-shifted absorption and emission observed when the π-conjugation was more extended (sulfides **3g** and **5g**) clearly indicate that the sulfur atom participates as a bridge within these highly conjugated structures. Therefore, this preliminary investigation suggests that vinyl sulfide-based π-conjugated materials may be suitable alternatives to double bond conjugated systems. Further investigations on these compounds are currently in progress and their results will be disclosed in due time.

Acknowledgments

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