



## Divinyl sulfides/sulfones-based D- $\pi$ -A- $\pi$ -D dyes as efficient non-aromatic bridges for $\pi$ -conjugated compounds



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### ABSTRACT

Novel photoactive divinyl sulfides and sulfones have been obtained by a straightforward approach using a Wittig–Horner reaction. These compounds behave as quadrupolar chromophores and show absorption in the UV region and fluorescence emission tailored by the solvent polarity due to an intramolecular charge transfer mechanism in the excited state, confirmed by the large Stokes' shift and the positive solvatochromism exhibited by their fluorescence spectra. In particular, a large Stokes' shift has been achieved for the sulfone containing the carbazole moiety, which behaves like a "push–pull" architecture. These new molecules represent an efficient alternative as stable non-heterocyclic  $\pi$ -conjugated compounds for potential applications as photoactive or two-photon absorption chromophores.

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### 1. Introduction

Due to the rapid growth in the field of organic light emitting diodes (OLEDs), the development of novel and efficient emitters is a very important task. In this context, organic  $\pi$ -conjugated heterocyclic compounds containing a sulfur atom, such as thiophenes or thiazoles, can display a wide variety of optical, electrical and photoelectric properties and have attracted much attention due their potential applications in organic optoelectronics [1–4]. However, the presence of sulfur atoms in organic emitters is limited to heterocycles or as a peripheral substituent in condensed structures [5,6]. The use of vinyl sulfides moieties to connect functional units, as a means of building large  $\pi$ -conjugated structures, had not been reported until Tolbert and co-workers [7] studied ferrocenyl molecular wires in which two ferrocenes are linked by a conjugated chain. These studies validated the use of the sulfur atom as a linker moiety for charge transport in unsaturated chains, allowing the design of efficient conductors for organic electronics based on organochalcogen blocks. Recently, our research group described a

convenient Wittig–Horner based synthetic methodology which enables an easy access to symmetrical and unsymmetrical vinyl organochalcogens [8]. These structures can be easily modified to obtain compounds with diverse characteristics. In this regard, the light-emitting property combined with the hole-transporting capability of arylamine [9,10] and carbazole [11–13] derivatives make them an interesting class of compounds for design of stable  $\pi$ -conjugated organochalcogen-based dyes. The arylamine and carbazole derivatives, in which a benzene ring acts as a linker, are the most common donor units for the molecularly designed dyes, and their properties make these compounds promising candidates for applications in optoelectronic devices [14,15].

On the other hand, the combination of electron donor (D) and electron acceptor (A) units connected by a  $\pi$ -conjugated system ( $\pi$ -bridge) has provided an important role in the photophysics of systems due to the intramolecular charge transfer (ICT) processes [16,17]. Therefore, the bipolar (D- $\pi$ -A structure) and quadrupolar (D- $\pi$ -A- $\pi$ -D or A- $\pi$ -D- $\pi$ -A) molecules have attracted great technological interest and the field is currently an interesting subject of research [18–21], despite the new molecules that have been presented in the literature based on non-aromatic  $\pi$ -conjugate bridges [22–24]. The charge separation in the ground and excited state of these materials provides them with unique optical and electrical properties with potential applications in areas of

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OLED development [25,26], nonlinear optics [27], photovoltaics [28,29] and biochemistry [30,31]. In this regard, divinyl sulfides appear as very interesting precursors for the synthesis of compounds that exhibit ICT, as they can be easily oxidized in a single step to the respective vinyl sulfones, which are excellent electron acceptor groups [32]. Although vinyl sulfones not appear in the literature for applications in optoelectronics,  $\pi$ -conjugated materials based on phenyl sulfones have been recently described; for example, some sulfone-based dyes containing electron-donors moieties were reported exhibiting an ICT mechanism [33,34]. These materials exhibit very interesting properties and have been used in a wide variety of applications, including optical sensors [35,36], photochromic dyes [37,38], photoactive dyes [39] and low molecular weight-based OLEDs [40].

In this paper, we describe the synthesis of novel symmetrical vinyl sulfides containing end-capped electron donor groups, employing bis-[(diphenylphosphinoyl)methyl] sulfide as starting material. Considering the synthesis of compounds which exhibit ICT properties, the quadrupolar (D- $\pi$ -A- $\pi$ -D) vinyl sulfones are readily obtained by oxidation of respective vinyl sulfides. These compounds were characterized and their photophysical and thermal properties were evaluated.

## 2. Experimental

### 2.1. Materials and methods

All solvents were purified according to literature and transferred under argon via syringe. Tetrahydrofuran (THF) was heated under reflux with sodium metal with benzophenone indicators, and distilled immediately before use. Commercial reagents were used without further purification. All reactions were performed in flame-dried glassware. Chromatographic purification of products was accomplished using 230–400 mesh chromatography silica. Thin-layer chromatography (TLC) was performed on 0.20 mm silica gel plates (Whatman Al Sil G/UV). Visualization of the developed chromatogram was performed by UV-365 nm, iodine powder and acid solution of vanillin.

NMR spectra ( $^1\text{H}$  and  $^{13}\text{C}$ ) were recorded on Bruker DPX-200 (200 MHz) and Bruker DPX-400 (400 MHz). Data for  $^1\text{H}$  NMR are reported as follows: multiplicity ( $s$  = singlet,  $d$  = doublet,  $t$  = triplet,  $m$  = multiplet), integration, coupling constant (Hz) and assignment. Data for  $^{13}\text{C}$  NMR are reported in terms of chemical shift (ppm). Elemental analysis was recorded on a Perkin-Elmer CHN 2400. IR spectroscopy was performed on Shimadzu IR Prestige-21 using KBr pellets. Spectroscopic grade solvents (Merck or Aldrich) were used for fluorescence emission and UV-Vis absorption measurements. UV-Vis absorption spectra were performed on a Shimadzu UV-2450 spectrophotometer. Steady-state fluorescence spectra were measured using a Shimadzu spectrofluorometer model RF-5301PC. Spectrum correction was performed to enable measuring a true spectrum by eliminating instrumental response such as wavelength characteristics of the monochromator or a detector using Rhodamine B as an external standard (quantum counter). All experiments were performed at room temperature in a concentration range of  $10^{-6}$ – $10^{-5}$  M. The quantum yield of fluorescence ( $\phi_f$ ) was made at 25 °C in spectroscopic grade solvents using the dilute optical methodology (absorbance intensity lower than 0.05). Quinine sulphate (Riedel) in  $\text{H}_2\text{SO}_4$  1 M ( $\phi_f = 0.55$ ) was used as quantum yield standard [41]. TGA was conducted on a TA Instruments model SDT Q600, under  $\text{N}_2$  atmosphere. Dry samples (1–6 mg) were weighed directly into Platinum high temperature pans (Platinum HT). A heating rate of  $15\text{ }^\circ\text{C min}^{-1}$  was applied. The temperature range was from 20 to 700 °C. The DTG curves (Supporting information) for all compounds were obtained from

the TGA curves and were analyzed by least squares fit of multi-Gaussian functions, and its deconvolution were performed using only the main degradation processes. The Marquard algorithm for multi-functional fits was applied to analyze the overall degradation process by deconvolution into steps of degradation.

### 2.2. Synthesis of bis[(diphenylphosphinoyl)methyl] sulfide (3) [8]

To a solution of (diphenylphosphinoyl)methyl *p*-toluenesulfonate **2** (3.86 g, 10 mmol) in dry DMF (30 mL), under an atmosphere of argon at 0 °C, was added an excess amount of dry  $\text{Na}_2\text{S}$  (0.780 g, 10 mmol) in small portions. The reaction mixture was heated at 60 °C for 90 min and then water (50 mL) was added, and the mixture was extracted with ethyl acetate ( $4 \times 50$  mL). The combined organic layers were washed with water ( $2 \times 100$  mL) and brine (100 mL). The organic layer was dried ( $\text{MgSO}_4$ ), and the solvent was removed under reduced pressure. The solid residue was recrystallized ( $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ , 1:9) to give **3**. Yield: 81%. M.p. 149–152 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.59 (*d*,  $J_{\text{P-H}} = 6.19$  Hz, 4 H), 7.41–7.53 (*m*, 12 H), 7.70–7.79 (*m*, 8 H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 29.77 (*d*,  $J_{\text{P-C}} = 69.40$  Hz), 128.53 (*d*,  $J_{\text{P-C}} = 11.60$  Hz), 131.01 (*d*,  $J_{\text{P-C}} = 9.70$  Hz), 131.39 (*d*,  $J_{\text{P-C}} = 100.05$  Hz), 131.98 (*d*,  $J_{\text{P-C}} = 1.50$  Hz) ppm. IR (KBr):  $\nu$  = 1180 (P=O), 1367, 1436, 2896  $\text{cm}^{-1}$ . MS:  $m/z$  (%) = 462 (6)  $[\text{M}]^+$ , 217 (21), 216 (22), 215 (100), 201 (28), 183 (15), 125 (11), 91 (51), 77 (37), 51 (21), 47 (31).  $\text{C}_{26}\text{H}_{24}\text{O}_2\text{P}_2\text{S}$  (462.48): calcd. C 67.21, H 5.51; found C 67.52, H 5.23.

### 2.3. 4-(Diphenylamino)benzaldehyde (4)

This compound was prepared according to literature [42]. A dry 50 mL two-necked flask was equipped with reflux condenser under a positive argon pressure and cooled with ice-water bath. The flask was charged with dry DMF (3 mL, 39 mmol) and  $\text{POCl}_3$  (2.3 mL, 25 mmol) is then added dropwise. After that, triphenylamine (1.2 g, 5 mmol) in 1,2-dichloroethane (10 mL) was also added dropwise. The reaction was heated at 45 °C for 5 h. After cooling, the mixture was poured into an ice-bath stirring and neutralized with sodium carbonate. The pale yellow solid was collected by filtration and crystallized from ethanol to give **4**. Yield: 82%. M.p.: 129–132 °C [42].  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.00 (*d*,  $J = 8.7$  Hz, 2 H, Ar-H), 7.13–7.17 (*m*, 6 H, Ar-H), 7.30–7.34 (*t*,  $J = 7.5$  Hz, 4 H, Ar-H), 7.66 (*d*,  $J = 8.7$  Hz, 2 H, Ar-H), 9.79 (*s*, 1 H, -CHO).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  (ppm): 119.4, 125.1, 126.3, 129.2, 129.7, 131.2, 146.2, 153.3, 190.3. EI-MS  $\text{C}_{19}\text{H}_{15}\text{NO}^+$   $m/z$  (%): 77 (25), 166 (15); 167 (16); 244 (28); 273 (100).

### 2.4. 4-(Octyl(phenyl)amino)benzaldehyde (5) [43]

A dry 50 mL two-necked flask was equipped with a reflux condenser under argon atmosphere and cooled with ice-water bath. The flask was charged with dry DMF (7.5 mL, 97 mmol) and  $\text{POCl}_3$  (2.41 mL, 26 mmol) is then added dropwise. After that, *N*-octyldiphenylamine (2.5 g, 8.9 mmol) in 1,2-dichloroethane (10 mL) was added dropwise. The reaction was heated at 80 °C for 24 h. After cooling, the mixture was neutralized with sodium carbonate and extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 30$  mL). The organic layer was dried ( $\text{MgSO}_4$ ), and the solvent was removed under reduced pressure. The product was purified on a silica gel column using dichloromethane/hexane (1:10) as eluent to give yellow oil **5**. Yield: 65%.  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 0.83–0.92 (*t*,  $J = 6.7$  Hz, 3 H, - $\text{CH}_3$ ), 1.2–1.45 (*d*, 10 H, - $\text{CH}_2$ -), 1.6–1.8 (*m*, 2 H, - $\text{CH}_2$ -), 3.65–3.77 (*t*,  $J = 7.6$  Hz, 2 H, - $\text{CH}_2$ -), 6.65–6.75 (*d*,  $J = 8.8$  Hz, 2 H, Ar-H), 7.15–7.3 (*m*, 3 H, Ar-H), 7.45–7.53 (*t*,  $J = 7.7$  Hz, 2 H, Ar-H), 7.6–7.7 (*d*,  $J = 8.9$  Hz, 2 H, Ar-H), 9.72 (*s*, 1 H, -CHO).  $^{13}\text{C}$  NMR (200 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  (ppm): 14.1, 22.6, 26.9, 27.2, 29.2, 29.3, 31.8, 52.7,

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