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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.

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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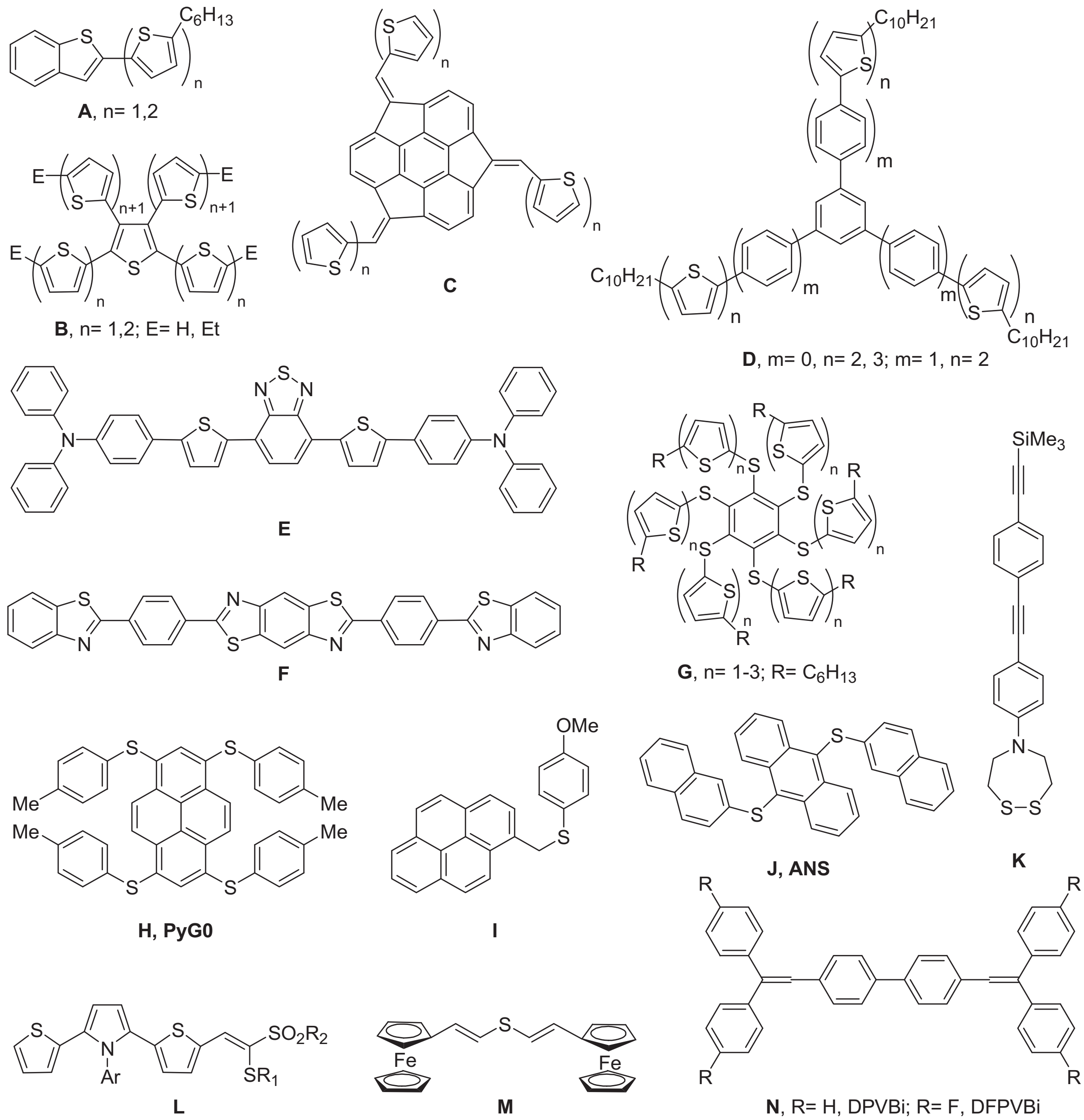

Fig. 1. Chemical structures of some sulfur-containing conjugated heterocycles with potentially useful photophysical and photochemical properties, DPVBi and DFPVBi.

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.