



# Molecular asterisks with a persulfurated benzene core are among the strongest organic phosphorescent emitters in the solid state



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## ABSTRACT

A series of functionalized persulfurated benzene molecules were synthesized. Their photophysical properties and crystal structures were analyzed. All compounds are non-emitting in solution at room temperature, but in a sharp contrast, quantum yields can be very high (up to 100%) in the solid state at 298 K or in a rigid matrix at low temperatures. This is a consequence of a decrease of intramolecular rotations and motions, but conformational and rotamer issues along with substituent effects might also play a role. These compounds are among the rare examples of highly phosphorescent organic materials, due to a Crystallization Induced Phosphorescence or to an Aggregation Induced Phosphorescence. Compound **1** is among the most phosphorescent solid known to date. They thus represent an alternative to heavy metal ion-based triplet emitters in solid state.

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## 1. Introduction

In recent years, organic luminescent solids have become a cornerstone in materials science, while covering several fields of application, such as stimuli responsive switches [1,2], optoelectronic devices [3,4] and chemosensors [5,6]. Because of their availability and lower toxicity, they represent an important alternative to heavy metal ion-based triplet emitters in the solid state and to quantum dots incorporating toxic elements.

Luminescent organic materials and some supramolecular assemblies have been developed and those architectures can exhibit very attractive physical, photochemical and chemical properties [7,8]. However, it is well known that many organic luminophores have their emission highly or totally quenched in the condensed phase, where aromatic molecules could self-aggregate by making  $\pi$ - $\pi$  interactions, thus self-perturbing their own  $\pi$ -systems [9,10]. This phenomenon is referred to as Aggregation-Caused Quenching

(ACQ). To the contrary, Aggregation Induced Emission (AIE) results from a decrease of intramolecular rotations and motions, which engenders a luminescence enhancement [11–13]. More recently, some attention was paid to AIPE (Aggregation Induced Phosphorescence Effect), when a luminogen displays phosphorescence enhancement as a result of aggregation [14,15]. This effect is most frequently observed for metal complexes involving heavy atoms (e.g., Pt<sup>II</sup>, Ir<sup>III</sup>, Re<sup>I</sup>) whose presence can promote intersystem crossing and spin-forbidden radiative transitions. On the other hand, the AIPE effect of organic molecules has been rarely reported so far, and only scarce examples of organic phosphorescent solids displaying a high quantum yield are known [16].

Along those lines, persulfurated benzene molecules are intriguing pigments, easily obtained from cheap and commercial starting materials since their first synthesis in 1957 [17,18]. However, it is surprising that the photophysical properties of this family of compounds had remained relatively unexplored [19,20]. Only recently, hexakis(4-methyl-1-phenylthio)benzene (**1**, Fig. 1) had been shown to exhibit enhanced photophysical properties with a very intense green phosphorescence ( $\phi = 1.0$ ) when the molecule experiences a rigid environment (i.e. in a frozen solution at low temperatures or in the solid phase) [21]. It is among the most phosphorescent organic molecules known in the solid state.

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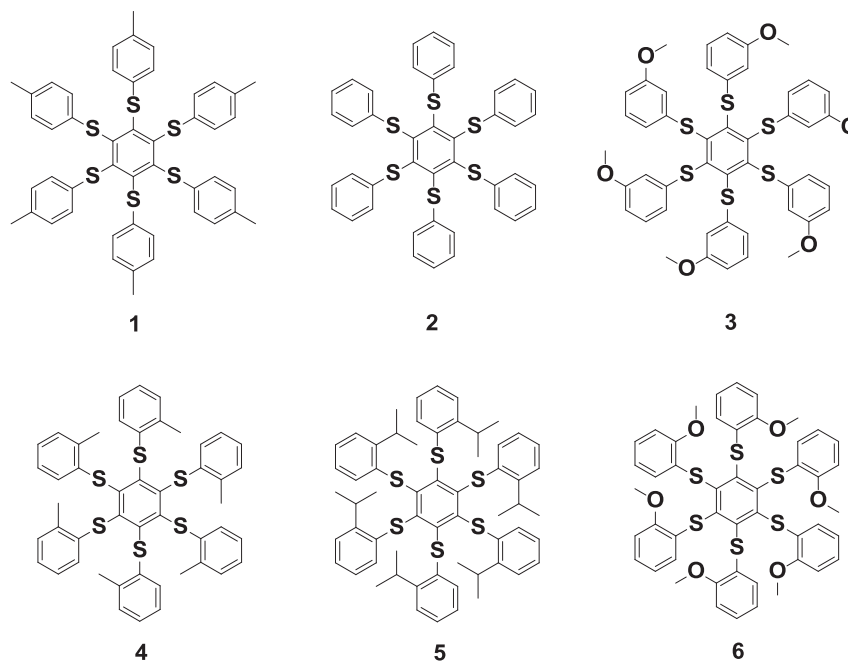


Fig. 1. Chemical structures of phosphorescent molecular asterisks under study.

Due to this exceptional feature, and in order to further study this family of compounds, five other luminogens (**2–6**, Fig. 1) were recently synthesized by varying their steric and electronic characteristics. Sterically hindered derivatives **5** and **6** are unknown in the literature, and the photophysical behaviors of **2–6** have never been reported. We wanted to screen compounds **1–6** to empirically correlate their photophysical properties to some substituent effects, in the hope for predicting and further modulating their properties. More importantly, we also devise these experiments to voluntarily modify the conformational behavior of those molecules, which has already been shown to be important in other family of luminogens involving AIE [14]. We first focused on a hexathiobenzene core connected to six phenyl arms possessing variable steric congestion at the ortho and meta positions, for modifying the molecular rotations and conformations, in the hope for other strong AIE effects. A set of three compounds (**4–6**) in an asterisk-like geometry comprises hindered groups at the ortho positions of the outer benzene rings. As a second parameter, the electronic contribution was varied by appending groups with different electron donating ability. The synthesis of all compounds is described, together with an analysis of their molecular structure and crystal lattices (as determined by X-ray diffraction), their aggregation state and properties, and their photophysical behavior as a function of temperature.

This work will thus open wider perspectives toward the uses of a new family of phosphorescent molecules, while providing further insights into their photophysical and aggregation properties, along with their interactions and conformations in the crystalline state.

## 2. Experimental section

### 2.1. Materials, general methods and analytical equipment

All reagents and compounds were bought from Sigma–Aldrich, Alfa Aesar and TCI and used without further purification, unless specifically mentioned. Solvents were purchased from Sigma–Aldrich, Acros Organics or Carlo Erba (analytical or reagent grade) with a low water content and stored over freshly activated 3 Å molecular sieves (activated for 3 h at 250 °C).  $^1\text{H}$  and  $^{13}\text{C}$  NMR were

recorded on a Bruker Avance 250 spectrometer equipped with an automatic sampler. Chemical shifts are provided in ppm relative to TMS ( $\delta = 0$  ppm) for  $^1\text{H}$  (250 MHz) and  $^{13}\text{C}$  NMR (62.90 MHz). Otherwise, some internal standards came from the solvents used:  $\text{CDCl}_3$  ( $^1\text{H}$  NMR:  $\delta = 7.26$  ppm;  $^{13}\text{C}$  NMR: 77.36 ppm) or  $\text{DMSO}-d_6$  ( $^1\text{H}$  NMR:  $\delta = 2.50$  ppm;  $^{13}\text{C}$  NMR:  $\delta = 39.5$  ppm), according to the literature data [22]. The resonance multiplicities in the  $^1\text{H}$  NMR spectra are described as “s” (singlet), “d”(doublet), “t” (triplet), “q” (quartet), sept (septuplet), “m” (multiplet) or “b” (broad). HRMS spectra using electrospray ionization (ESI) were recorded at the Spectropole of Marseille (France) in triplicate with double internal standards on a QStar Elite (Applied Biosystems SCIEX) instrument equipped with an atmospheric ionization source (API) and a TOF analyzer in a positive mode. LRMS analyses were performed on a Shimadzu GC–MS QP2010SE instrument equipped with a DI2010 direct introduction unit with an electronic impact ionization source at 70 eV. Infrared absorption spectra were recorded on solids with a Perkin–Elmer Spectrum 100 FT-IR spectrometer equipped with a universal ATR accessory (contact crystal: diamond). Thin-Layer chromatography (TLC) was performed on precoated silica gel (Alugram<sup>®</sup> SilG/UV<sub>254</sub> gel) aluminium plates from Macherey–Nagel. Flash chromatography was performed over silica gel 60, Merck type 230–400 mesh (40–63  $\mu\text{m}$ ). Melting points (uncorrected) were recorded on a IA9200 apparatus purchased from Thermo Fischer Scientific (Electrothermal) after a calibration with standards. X-ray diffraction data were recorded at 203 K on a Bruker Nonius Kappa CCD diffractometer using  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073$  Å). Data collection was performed with COLLECT (Nonius, 2001), cell refinement and data reduction with DENZO/SCALEPACK (Otwinowski & Minor, 1997). The determination of the hydrodynamic diameter distributions of the nanocrystals was carried out from DLS measurements with a Malvern Nano ZS instrument with a 633 nm laser diode.

### 2.2. Photophysical measurements

Absorption spectra in the 190–1100 nm range were recorded at room temperature in solutions contained in quartz cuvettes (optical pathlength 1 cm and 5 cm, Hellma<sup>®</sup>) by using a Perkin Elmer

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