Persulfurated Benzene-Cored Asterisks with π-Extended ThioNaphthyl Arms: Synthesis, Structural, Photophysical and Covalent Dynamic Properties

Sapna Gahlot,[a] Alessandro Gradone,[b, e] Myriam Roy,[a, c] Michel Giorgi,[d] Simone Conti,[b] Paola Ceroni,[a, b] Marco Villa,*[a, b] and Marc Gingras*[a]

Dedicated to Professor Vincenzo Balzani for his 85th birthday.

Abstract: The synthesis of regioisomeric asterisks (**5**) and (**6**) incorporating a benzene core with six 1-naphthylthio or six 2-naphthylthio arms are reported in search for new materials with optoelectronic properties. The consequences on the extension of a π system surrounding a persulfurated benzene core provide a new avenue to study the structural, photophysical, and chemical properties of such family of all-organic phosphors. It also diverts the persulfuration mechanism after two radical cyclizations for making a [5]dithiohelicene by-product (**7**) and favors dynamic sulfur component exchange reactions surrounding the core. These exchanges convert asterisks (**5**) and (**6**), non-phosphorescent at 20 °C to the highly phosphorescent (**4**) ($\phi \sim 100\%$, solid state at 20 °C). For asterisks (**5**) and (**6**), the absence of the typical phosphorescence of the per(phenylthio)benzene core in the solid state at 20 °C and the presence of a weak naphthalene-based phosphorescence at 77 K is attributed to an energy transfer from the triplet state of the persulfurated benzene core to the outer naphthalene moieties, resulting in an antenna system.

Introduction

The enhanced emission of light in rigid, constrained or crystalline state, is commonly called: "Aggregation-Induced Emission (AIE)". It has gained a wide attention in the last years[1–4] due to the development of light-emitting molecular systems and devices, luminescent sensors and bioimaging. In most cases, the emission enhancement is triggered by crystallization or self-assemblies (aggregation), which causes restriction of intramolecular motions, rotation or vibration, thus decreasing the non-radiative deactivation and favoring radiative deactivation of the lowest excited state.[5] Some of the most emissive AIE systems are based on a family of persulfurated aromatic molecules,[6] hereafter called molecular asterisks,[7]

where a central benzene ring is bound to six phenylthio groups. The parent compounds, hexakis(phenylthio) benzene (**3**)[8] and hexakis (4-methylphenylthio)benzene (**4**),[9] are known since 1957 and 1975, respectively. In spite of their early discovery, and being reported in patents since 1963,[9] their exalted AIE properties were overlooked, and we disclosed them in 2013.[10,11] These compounds are not emissive in solution. However, when intramolecular motions are restricted in the solid state or in a rigid matrix, a bright green phosphorescence appears. A striking example of such phenomena is from (**4**), which is one of the best phosphorescent emitters known to date in the solid state, with an emission quantum yield reaching almost 100 %.[12] This phenomenon is called "rigidification-induced phosphorescence" (RIP). Several structural and photo-

[a] S. Gahlot, Prof. Dr. M. Roy, Prof. Dr. P. Ceroni, Dr. M. Villa, Prof. Dr. M. Gingras
Aix Marseille Univ, CNRS, CINaM
Marseille (France)
E-mail: marc.gingras@univ-amu.fr

[b] A. Gradone, S. Conti, Prof. Dr. P. Ceroni, Dr. M. Villa
Department of Chemistry ("Giacomo Ciamician")
University of Bologna
Via Selmi, 2, 40126 Bologna (Italy)
E-mail: marco.villa11@unibo.it

[c] Prof. Dr. M. Roy
Sorbonne Université, CNRS
Institut Parisien de Chimie Moléculaire
75005 Paris (France)

[d] Dr. M. Giorgi
Aix Marseille Univ, CNRS, Centrale Marseille, FSCM
Marseille (France)

[e] A. Gradone
Institute for Microelectronics and Microsystems
Italian National Research Council, Section of Bologna
Via Piero Gobetti 101, 40129, Bologna (Italy)

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physical studies on this family of molecules have been carried out, but most of them focused on the functionalization of the outer phenyl rings at *para* or *ortho* positions (–H, –CH₃, –OCH₃).[12–14] According to the van der Waals volume and the electronic contribution of these substituents, they could modulate the conformational dynamics, supramolecular interactions, and the opto-electronic properties of these asterisks. For instance, substituents like amide units[15,16] and chiral groups[17,18] were designed to generate RIP by some cohesive supramolecular interactions. Another example comes from the nano-organized formation of silica nanoparticles encapsulating covalently-bound phosphorescent asterisks in the search for new oxygen-sensing devices.[16] The central persulfurated benzene core was also covalently-linked to some metal-chelating moieties like terpyridine[19] or carboxylic acids[20] to "turn on" phosphorescence by a selective complexation with some metal ions like Ag(I), Mg(II), Zn(II) or Pb(II). Structural rigidification occurs by ions complexation, thus generating a self-assembly of a supramolecular polymer (nanoparticles), with simultaneous enhanced phosphorescence by RIP in a dual mode detection of metal ions (simultaneous nanoparticles formation and light emission).

Here, the purpose of this work is to report the consequences on the chemical, photophysical, and structural features of these molecular systems, after extending the peripheral π-system of a persulfurated benzene-cored asterisk (**3**). Figure 1 lists a set of two regioisomeric asterisks (**5**) and (**6**) under study, with thionaphthyl substituents, along with a comparison (or guidance) with reference naphthalene derivatives (**1**) and (**2**). In short, most investigations on hexathio benzene-cored asterisks are relevant to the functionalization of the thiophenyl arms. However, an extension of the peripheral π-system with polycyclic aromatic hydrocarbons (PAH), such as naphthalene, has only been reported once in a structural study with (**6**),[21] by overlooking at the chemical, photophysical and electronic properties. No comparison to other regioisomeric asterisks such as (**5**) was reported. Thus, an extension of the π-system surrounding a persulfurated benzene core could be interesting for new photophysical and electronic properties, due to electronic couplings with the central core. Additionally, a structural study is suited for evaluating the contribution of steric and electronic effects in search for new multi-responsive all-organic phosphors. To top it all off, we report new sulfur component exchange reactions in the frame of reversible S_NAr in Dynamic Covalent Chemistry (DCC) in a continuation of previous observations.[22]

Results and Discussion

Synthesis

Prior to some chemical, photophysical and structural studies on the π-extended thionaphthyl systems (**5**) and (**6**), the preparation of reference persulfurated benzene-cored asterisks (**3**)[8] and (**4**)[9] was achieved according to known literature methods. The reference thiomethylated naphthalene regioisomers (**1**)[23] and (**2**)[24] were also synthesized (see Supporting Information), according to common procedures for methylating aromatic thiols. Thus, 1-naphthalenethiol reacted with an excess of iodomethane (potential carcinogen!) in the presence of dry potassium carbonate in DMF as a polar aprotic solvent. After sealing the mixture under argon in a pressure tube, it was stirred for four days at 50 °C. However, the reaction was incomplete, and stirring was continued for seven days at 70 °C, and then for four days at 80 °C to ensure completion. These conditions were required because 1-naphthalenethiol is much less reactive at a peri position than for 2-naphthalenethiol. The latter reacted under milder conditions for two days and half at 40 °C for providing 98 % yield of the expected thioether (**2**).

The synthesis of the π-extended thionaphthyl systems (**5**) and (**6**) started from hexachlorobenzene (1.0 mol-eq) with a 1.5 fold excess of thiol (9.0 mol-eq) and potassium carbonate (9.0 mol-eq) in DMF. After bubbling argon for removing dioxygen and sealing the reaction tube, the mixture was vigorously stirred at 84 °C for seven days in the case of asterisk (**5**). After purification by chromatography, it afforded
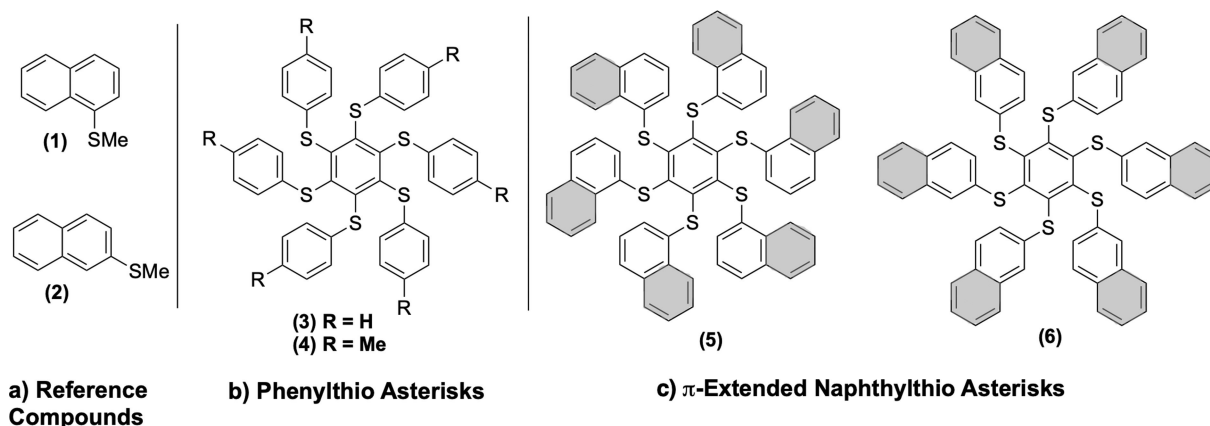

Figure 1. List of compounds under study: a) reference (methylthio)naphthalene regioisomers (**1**) and (**2**); b) reference hexakis(phenylthio) benzene (**3**) and hexakis(4-methylphenylthio)benzene (**4**); c) regioisomeric π-extended hexakis(naphthylthio) benzene asterisks (**5**) and (**6**) (gray rings indicate π extension).

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(**5**) as a yellow solid in a 95% yield. A similar synthetic procedure was followed for (**6**), while heating at 80°C for 4 days. It afforded (**6**) as a yellow solid in a 73% yield (see Supporting Information).

Mechanistic issue

When synthesizing asterisk (**5**), we isolated the side-product (**7**) and its structure was determined by sc-XRD, as shown in Figure 2 (see Supporting Information). An incomplete sulfuration of hexacholorobenzene led to a 1,2,3,4-tetrasulfurated benzene core, which underwent a double cyclization to produce dibenzothiophene units in a helical [5]dithiohelicene structure (**7**).

A tentative mechanistic rationale for both cyclizations would involve two radical cyclizations. The latter could be
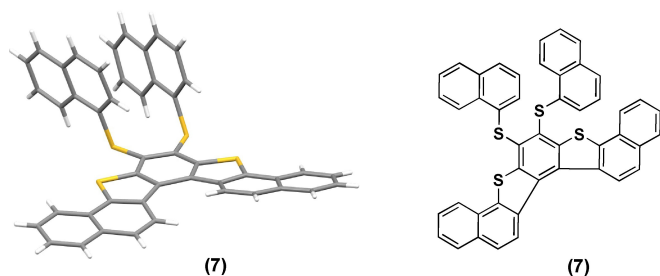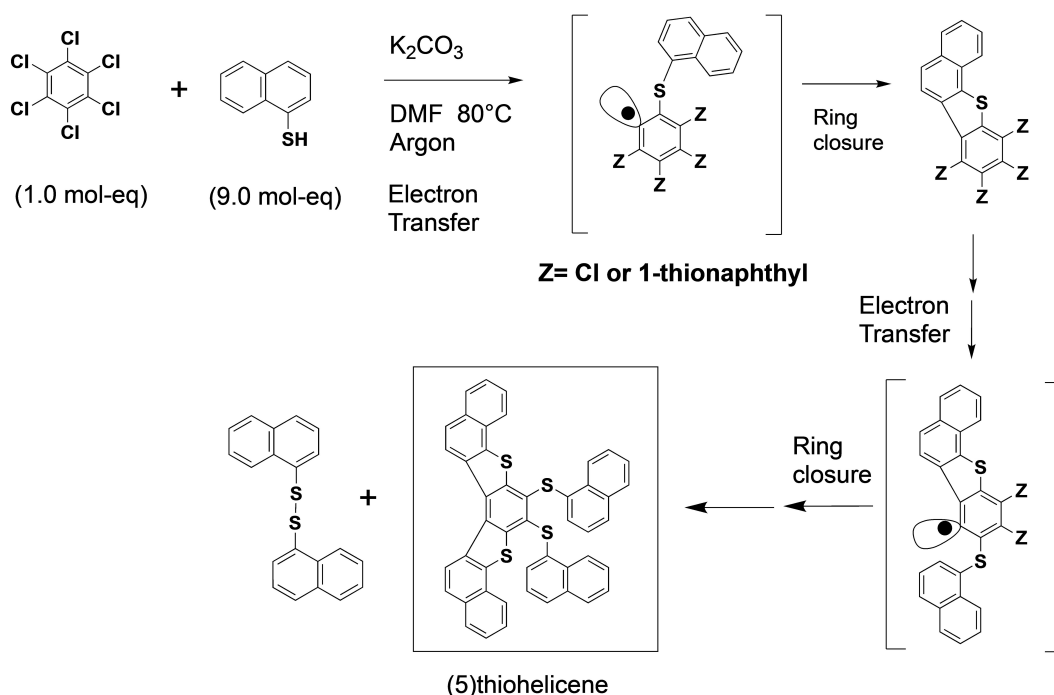
initiated either from some radical nucleophilic substitutions (S$_{RN}$1), or from some electron-transfers coming from the thionaphthyl anions, as a reducing agent. It is not known at which stage of the sulfuration these radical processes could take place Scheme 1.
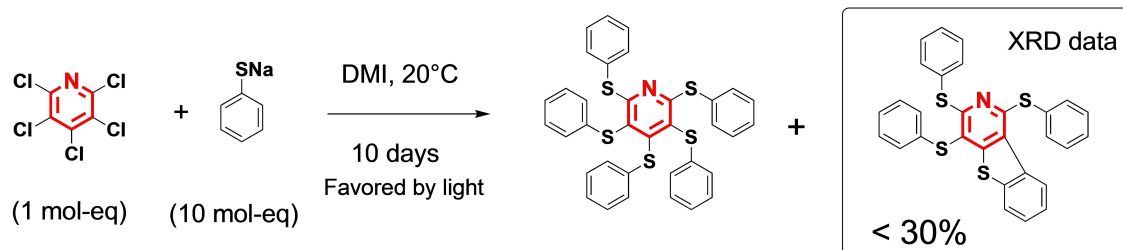
This mechanistic proposal is in agreement to a literature precedent for explaining the formation of a benzothienopyridine unit by a radical cyclization during the persulfuration of pentachloropyridine, as shown in Scheme 2.[25]

## Sulfur exchange components (the "sulfur dance")

Continuing our studies on dynamic sulfur exchange reactions by S$_N$Ar[22] of potent uses in dynamic covalent chemistry (DCC), we investigated the exchanges of thionaphthyl units by thiophenyl ones (Scheme 3). In light of leaving groups abilities, it is expected that a naphthylthio unit should be replaced with a preference to a 4-methylphenylthio one. Indeed, the naphthylthiolate anion is more stable than the 4-methylphenylthiolate anion. We thus ran experiments under conditions toward a full conversion of asterisk (**5**) or (**6**) into asterisk (**4**), by using a large excess of 4-methylbenzenethiol (12 mol-eq) in the presence of K$_2$CO$_3$ in DMF at 100°C. Analysis of both reaction mixtures indicated the presence of the corresponding naphthyl disulfides, as oxidized leaving groups, and the formation of asterisk (**4**) as a major component (>50% yield; Figure 3). It should be pointed out that poorly emissive asterisks (**5**) or (**6**) can be converted to (**4**) as one of the most phosphorescent solids known to date.[12] These results convey new information on benzene-cored asterisks with π-extended

Figure 2. Structure determination by sc-XRD of by-product (**7**) isolated from the synthesis of (**5**). It incorporates two fused dibenzothiophene units in a [5]dithiohelicene structure.

Z= Cl or 1-thionaphthyl

(5)thiohelicene

Scheme 1. A radical mechanism is tentatively proposed to explain the formation of (**7**) incorporating dibenzothiophene units, after the persulfuration of hexachlorobenzene.

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Scheme 2. Proposed radical mechanism to explain the formation of a benzothienopyridine unit during the persulfuration of pentachloropyridine.
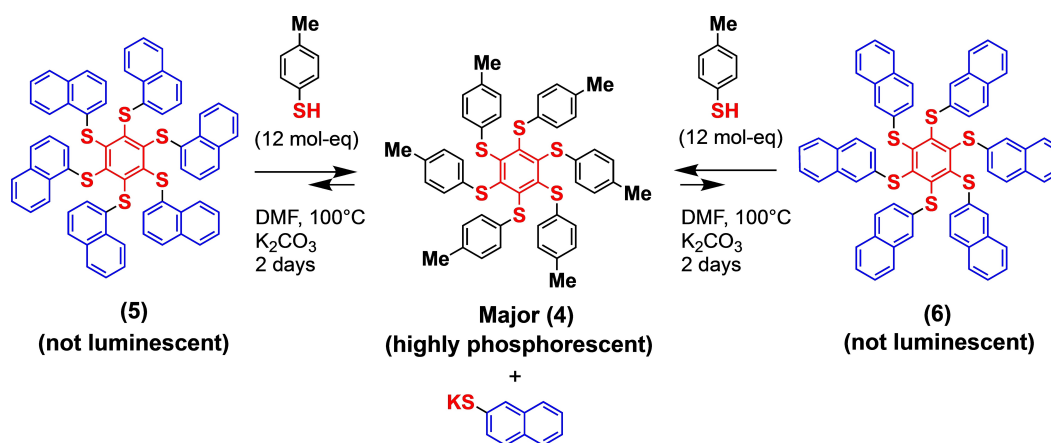
Scheme 3. Sulfur component exchange reactions. Conversion of poorly emissive π-extended 1- or 2-naphthylthio benzene-cored asterisks (**5**) or (**6**) into highly phosphorescent asterisk (**4**) (solid state) in a >50% yield.

systems, and broaden the scope of sulfur exchange reactions in the "sulfur dance" around a benzene core by dynamic S_NAr reactions.

The absorption spectra of (**5**) and (**6**) are reminiscent of the numerical sum of the spectra of their model compounds, namely (**4**) and 6 times (**1**) or (**2**) (See Figure S13 Supporting Information). The emission spectra of the asterisks and their model compounds in dichloromethane solution are reported in Figure 4, and compared to those recorded in CH_2Cl_2/MeOH (1:1 v/v) in a rigid matrix at 77 K. Asterisk (**5**) shows two emission peaks at 350 and 430 nm (solid red line in Figure 4a). The high-energy band can be attributed to the naphthalene fluorescence by comparison with the model compound (**1**) (solid orange line in Figure 4a): the corresponding fluorescence quantum yield is strongly diminished (Table 1), demonstrating an efficient quenching mechanism. The same situation is observed in the comparison between asterisk (**6**) and (**2**) emission spectra (Figure 4b). It is worth noting that the fluorescence bands of (**6**) are red-shifted compared to those of (**5**), in agreement with the red-shift observed for model compound (**2**) versus (**1**).

The fluorescence band at 430–450 nm is somewhat reminiscent of the fluorescence of naphthalene excimers,[27–29] but the very short lifetime (<0.2 ns, Table 1) rules out this assignment. It has never been observed for previously investigated hexakis(phenylthio) benzene-cored asterisks, and we tentatively attribute this emission to the fluorescence decay of the per-

(phenylthio)benzene core, suggesting a less efficient intersystem crossing to the lowest triplet state for asterisks (**5**) and (**6**) compared to (**4**). In solid state, asterisks (**5**) and (**6**) are not luminescent and the typical green phosphorescence of (**4**) (Figure 4) is not observed, confirming that the presence of the peripheral naphthalene units strongly affects the luminescence properties of the asterisks and the population of the triplet state of the persulfurated core.

The emission spectra of (**5**) and (**6**) in a CH_2Cl_2/MeOH (1:1 v/v) rigid matrix at 77 K (dashed lines in Figure 4) show a
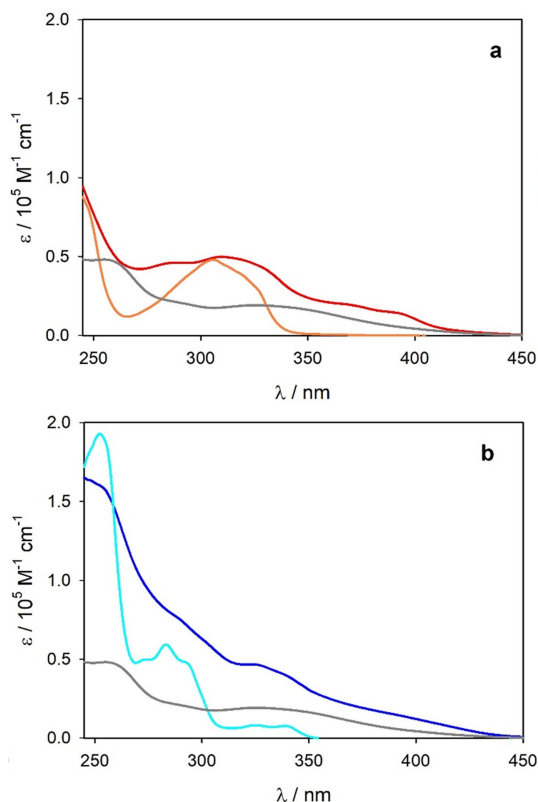
Table 1. Most relevant photophysical data of the asterisks (**5**) and (**6**) in CH_2Cl_2 at 298 K and in CH_2Cl_2/MeOH (1:1 v/v) at 77 K.

Compound	λ_{em} [nm]	298 K Φ_{em}	τ [ns]	77 K λ_{em} [nm]	τ [s]
1-Thionaphthyl Asterisk (**5**)	350	<0.01%	[a]	525	0.12
	430	0.17%	<0.2		
2-Thionaphthyl Asterisk (**6**)	365	0.2%	[a]	535	0.30
	455	2.7%	<0.2		
1-MeS-Naphthalene (**1**)	370	1.9%	0.60	510	0.20
2-MeS-Naphthalene (**2**)	375	4.3%	1.56	490	0.31
4-Me-Thiophenyl Asterisk (**4**)	[b]	[b]	[b]	505	4.0×10^{-3}

[a] The emission intensity is too weak to measure the corresponding lifetime. [b] No emission is observed in DCM solution at 298 K and a strong phosphorescence in the solid state at 513 nm with $\Phi_{em}=100\%$ and $\tau=3.0$ μs.[12]

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Figure 3. Absorption spectra in air-equilibrated CH_2Cl_2 solution : (a) Asterisk (**5**) (red line) and asterisks (**4**) (grey line) and model compound (**1**) (orange line), (b) Asterisk (**6**) (blue line) and asterisks (**4**) (grey line) and model compound (**2**) (cyan line). For the sake of comparison, the molar absorption coefficient of (**1**) and (**2**) has been multiplied by 6.

Figure 4. Normalized emission spectra in air-equilibrated CH_2Cl_2 solution at room temperature (solid lines) and in CH_2Cl_2/MeOH 1:1 rigid matrix at 77 K (dashed lines) : a) Asterisk (**5**) (red line) and asterisk (**4**) (grey line) and model compound (**1**) (orange line), b) asterisk (**6**) (blue line) and asterisks (**4**) (grey line) and model compound (**2**) (cyan line). $\lambda_{ex} = 300$ nm.

vibrationally structured band with the highest energy peak at 550 nm. The model compounds (**1**) and (**2**) show a very similar emission spectra with a small blue shift. The corresponding lifetimes are in the second range, in agreement with the phosphorescence decay of (**1**) and (**2**) and 3 orders of magnitude higher than that observed for the phosphorescence of (**4**) (Table 1).

The absence of the typical emission of a per(phenylthio)benzene core in the solid state, and the phosphorescence with long lifetime in a rigid matrix at 77 K could be explained by an energy transfer from the triplet state of the persulfurated benzene-cored asterisks to the outer naphthalene moieties, as schematically depicted in Figure 5. This result is confirmed by the fact that excitation in the range 400–450 nm, where only the persulfurated core absorbs light, results in the typical naphthalene phosphorescence.

Structural and supramolecular studies by sc-XRD

A structural study by sc-XRD (single-crystal X-ray diffraction) leading to the characteristics of both regioisomeric systems (**5**) and (**6**) is useful to better understand the systems, which itself, should be modulated b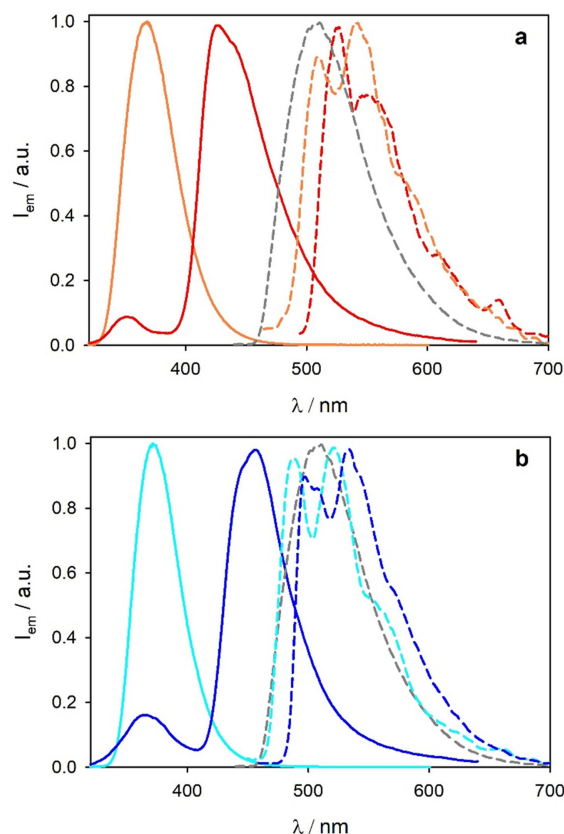y the conformational features, distortion of π-system and supramolecular interactions. Figures 6 and 7 represents the two crystalline regioisomeric asterisks (**5**) and (**6**) after sc-XRD analysis.

In compound (**5**) the center of the central π cycle (centroid of Cg1) lies on the crystallographic center of symmetry and thus the asymmetric unit is only half of the asterisk. Two opposite S-naphthyl units are almost perpendicular to that ring (dihedral equal to 88.27(8)°) and they are engaged into symmetric intramolecular CH/π interaction with it: the distance C5–Cg1 = 3.688(2) Å and the angle C5-H5–Cg1 is equal to 140°. The four remaining thionaphtyl units are parallel by adjacent pairs and have angles of 67.23(10)° and 64.06(10)° respectively with the central π cycle (Figure 6). They interact by pairs through intramolecular π-π stacking (dihedral equal to 6.32(7)°) but are also engaged into intermolecular CH/π and π-π interactions with symmetry-related molecules within the lattice (Table S1: see Supporting Information).

Shown in Figure 7, the behavior of (**6**) is different. The asymmetric unit is in general positioned within the unit cell, and the thionaphtyl substituents are not related by symmetry. They adopt an up-down-up-(down)₃ conformational sequence relative to the central π cycle. The dihedrals of the S-naphthyl group to the mean central ring have a large
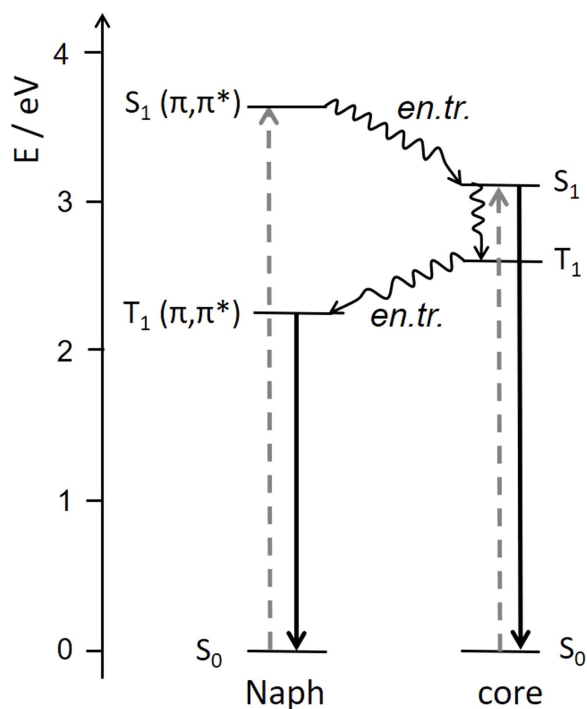
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Figure 5. Schematic energy level diagram showing the absorption (dashed grey lines), emission (solid black lines), and non-radiative processes (wavy lines) occurring in asterisks (**5**) and (**6**) at 77 K.
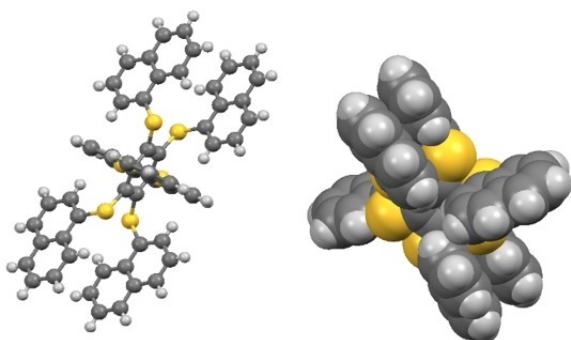

Figure 6. Structural and conformational analysis of (**5**) by sc-XRD.

diversity and range from 63.0(5)° to 117.5(5)°. Opposite to (**5**), this arrangement only favors CH/π interactions; no intra- or intermoleular π-π stacking is observed (Table S2, see Supporting Information).

These different organizations within both asterisks have a remarkable influence on the deformation of the central benzene ring. The central benzene core of (**5**) is not distorted (weighted average absolute torsion angle = 4.85°) while the puckering value Q for the ring in (**6**) is equal to 0.144(3) Å with a weighted average absolute torsion angle equal to 8.01° (Figure 8).[30,31]

In compound (**5**), the benzene core is protected from external influences by the symmetric arrangement of the substituents and the interactions they provide. On the contrary,
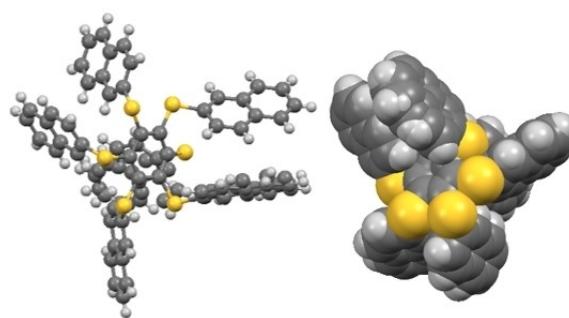

Figure 7. Structural and conformational analysis of (**6**) by sc-XRD.

Figure 8. Distorted central benzene core of (**6**).

the same ring in (**6**) is affected by the sum of the strains brought by all the asymmetric intra and intermolecular CH/π interactions. The better accessibility of the benzene core in (**6**) is also reflected by the presence of several intermolecular S–H interactions (C(H)–S distances around 3.7 Å) while the C(H)–S distances in (**5**) are all longer than 3.8 Å.

Interestingly, the distortion of the central benzene core in (**6**) is comparable to that observed in the previously published naphthalenethio benzene-cored asterisk, despite different arrangement of the naphthalene moieties.[20] In that previous report, the puckering value Q is about 0.12 Å and the weighted average absolute torsion angle is equal to 8.45°, but the substituents are in a conformational sequence up-up-down-down-up-down. Unlike (**6**), this conformation allows the formation of some intermolecular π-π interactions.

Conclusion

Two regioisomeric benzene-cored asterisks (**5**) and (**6**) were synthesized for investigating the influence of peripheral π-extended systems on their photophysical, structural and dynamic chemical properties, compared to (**3**) and (**4**). The by-product (**7**) incorporates a [5]dithiohelicene unit, which could result from two radical cyclizations via $S_{RN}1$ or other electron-transfer mechanisms. Different conformations, distortions, and supramolecular interactions of (**5**) and (**6**) in the crystalline state are found. The higher symmetry of (**5**) provides intramolecular π-π interactions with the naphthyl units, whereas a more disymmetrical order of (**6**) generates many C–H/π interactions, and a strong distortion of the benzene core to accomodate these interactions. Asterisks (**5**) and (**6**) are weakly fluorescent and exhibit weak phosphorescence only in a rigid matrix at 77 K, in contrast to (**3**) and (**4**). The lifetimes of the two phosphorescent excited states of

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(**5**) and (**6**) are in the second time scale, 3-order of magnitude larger than that of (**4**) at 77 K.[11,12] This difference is due to the nature of their electronic transitions and the corresponding rate of spin-forbidden transitions: a charge-transfer electronic transition for (**4**) and π,π^* electronic transition of a naphthalene unit for (**5**) and (**6**). The lowest triplet excited state of a thionaphthalene unit and that of persulfurated benzene asterisks (**4–6**) are very close in energy. The absence of the typical emission of a per(phenylthio)benzene core in the solid state, and the phosphorescence with long lifetime in a rigid matrix at 77 K is explained by an energy transfer from the triplet state of the persulfurated benzene core to the outer naphthalene units (Figure 5). Thus, a π-extension of the per(phenylthio) benzene unit inhibits phosphorescence in the solid state. Dynamic S_NAr converts non emissive (**5**) and (**6**) to highly emissive (**4**)[11] in the frame of DCC. Thus, π-extension results in important consequences on structural, photophysical, supramolecular and dynamic chemistry, in search for new materials.

Experimental Section

Experimental procedures, characterization of compounds, structural (sc-XRD) and photophysical data are provided in the Supporting Information.

Deposition Numbers 2128174 (for **5**); 2128175 (for **6**), 2128176 (for **7**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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