



# Novel chiral binaphthalene-linked pyrenes. Synthesis, structure, and spectroscopy



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## ABSTRACT

Novel chiral pyrene-binaphthalene compounds, (*R*)-/(*S*)-(13*Z*,21*bZ*)-dinaphtho[2,1-*e*:1',2'-*g*]pyreno[4,5-*b*][1,4]diazocine (**1**) and (*R*)-/(*S*)-(3*bZ*,5*Z*,7*Z*,9*Z*,12*bZ*,14*Z*,16*Z*,18*Z*)-bis(dinaphtho[2,1-*e*:1',2'-*g*]pyreno[4,5-*b*:9,10-*b'*]bis([1,4]diazocine) (**2**), were synthesized and characterized by a series of spectroscopic methods including MALDI-TOF mass, NMR, and electronic absorption methods. Their binaphthalene-linked pyrene nature has been unambiguously revealed on the basis of single crystal X-ray diffraction analysis of both (*R*)- and (*S*)-**1**. In addition, their electronic structure was also investigated on the basis of DFT calculations.

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## 1. Introduction

Chirality is one of the most fascinating and vital features extensively found in nature [1], which is manifested by natural products including proteins, nucleic acids, sugars, amino acids, hormones, and antibiotics as well as synthetic chemicals. Due to their specific chirality-related activity and functionality [2], immense research interest has been paid to the synthesis, separation, and detection of various kinds of chiral substances [3]. Optically active polycyclic aromatic hydrocarbons (PAHs), consisting of three or more fused benzene rings in linear, angular, and cluster arrangements, have also attracted increasing attention because of their extensive biological relevance [4]. However, reports over the chiral derivatives of one typical representative PAHs, pyrene, still remain relatively rare despite the great potential application of this species in organic synthesis, fluorescent probe, nano molecular sensors and photoelectric material. As early as in 1985, chiral cyclodextrin group was covalently introduced onto the pyrene periphery for the first time, resulting in the pyrene derivative with induced chirality [5]. This was followed by a successful fabrication

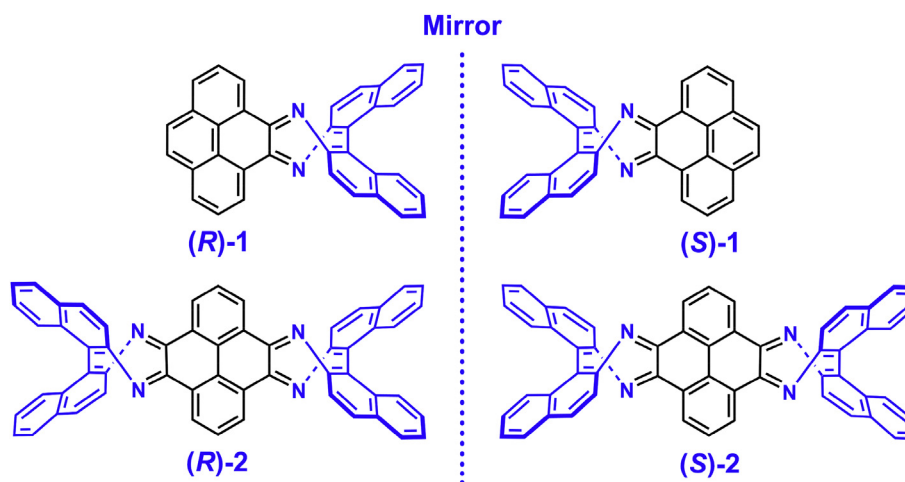
of a series of chiral pyrene compounds using the same methodology [6]. In addition, with the help of peripherally incorporated substituents like naphthalene and adamantane groups, chiral arrangement of the achiral benzene segments in the pyrene chromophore was achieved, endowing the whole molecule with the inherent chirality. [1,7] However, connection of chiral groups directly with the pyrene chromophore seems to still remain unreported, to the best of our knowledge.

Inspired by our recent synthesis of novel chiral subphthalocyanine derivatives with enhanced optical activity [8], in the present paper novel chiral pyrene-binaphthalene compounds, namely (*R*)-/(*S*)-(13*Z*,21*bZ*)-dinaphtho[2,1-*e*:1',2'-*g*]pyreno [4,5-*b*][1,4]diazocine (**1**) and (*R*)-/(*S*)-(3*bZ*,5*Z*,7*Z*,9*Z*,12*bZ*,14*Z*,16*Z*,18*Z*)-bis(dinaphtho[2,1-*e*:1',2'-*g*]pyreno[4,5-*b*:9,10-*b'*]bis([1,4]diazocine) (**2**), Scheme 1, were synthesized and characterized by a series of spectroscopic methods including MALDI-TOF mass, NMR, and electronic absorption methods for the first time. Their binaphthalene-linked pyrene nature has been unambiguously revealed on the basis of single crystal X-ray diffraction analysis of both (*R*)- and (*S*)-**1**. In addition, their electronic structure was also investigated based on DFT calculations.

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**Scheme 1.** Schematic molecular structures of the (R)-/(S)-1 and (R)-/(S)-2.

## 2. Results and discussion

### 2.1. Synthesis and spectroscopic characterization

Condensation of pyrene-4,5-dione and (*R*)- and (*S*)-(+/-)-2,2'-diamino-1,1'-binaphthalene, respectively, in dried toluene in the presence of  $\text{CF}_3\text{COOH}$  at  $60^\circ\text{C}$  under nitrogen for 3 h led to the isolation of chiral pyrene-binaphthalene compounds (*R*)-1 and (*S*)-1 in the yield of 35.4%. By employing the above-mentioned procedure with pyrene-4,5,9,10-tetraone instead of pyrene-4,5-dione, (*R*)-2 and (*S*)-2 were also obtained in the yield of 17.3%. These newly prepared compounds **1** and **2** gave satisfactory elemental analysis data, Table S1 (Supporting Information). Their MALDI-TOF mass spectra clearly show intense signals for the corresponding molecular ion  $[M]^+$ . The isotopic patterns closely resemble the simulated ones, Fig. S1 (Supporting Information). To further clarify the corresponding molecular structures and optical properties, compounds **1** and **2** were characterized with a series of spectroscopic techniques including NMR, electronic absorption, and circular dichroism (CD).

The  $^1\text{H}$  NMR spectra of **1** and **2** were recorded in  $[\text{D}_6](\text{CD}_3)_2\text{SO}$ , Figs. S2 and S3 (Supporting Information). With the help of a  $^1\text{H}$ - $^1\text{H}$  COSY analysis, Figs. S4 and S5 (Supporting Information), all the signals can be unambiguously assigned and the data are summarized in Table S2 (Supporting Information). As can be seen, the  $^1\text{H}$  NMR spectrum of **1** exhibits two doublets at  $\delta$  8.19 (2H) and 7.88 (2H) ppm, one triplet at  $\delta$  7.67 (2H) ppm, and one singlet at  $\delta$  8.00 (2H) ppm and they are attributed to the four kinds of protons of pyrene moiety. The signals observed at  $\delta$  8.06–8.02 (4H), 7.51 (2H), 7.37–7.32 (4H) and 7.01 (2H) ppm are attributed to the protons of binaphthyl moiety. In the  $^1\text{H}$  NMR spectrum of **2**, the signals due to the pyrene protons can be unambiguously identified to the doublet at  $\delta$  7.73 (4H) ppm and the overlapped multiplet at 7.39–7.32 (10H) ppm. The three doublets at  $\delta$  8.09 (4H), 8.04 (4H), and 6.95 (4H) ppm, one triplet singlets at  $\delta$  7.51 (4H) ppm and one overlapped multiplet at 7.39–7.32 (10H) ppm are attributed to the protons of binaphthyl moiety.

### 2.2. Structural studies

Single crystals of (*R*)-1 and (*S*)-1 suitable for X-ray diffraction analysis were obtained by slow diffusion of methanol and *n*-hexane, respectively, into the solution of respective species in  $\text{CHCl}_3$ .

Interestingly, despite being crystallized in different solvent systems, both (*R*)-1 and (*S*)-1 still crystallize in the same orthorhombic system with a  $P2_12_12_1$  chiral space group containing four binaphthalene-linked pyrene molecules per unit cell. Detailed crystal and structural data are listed in Table S3 (Supporting Information). Fig. 1 shows the molecular structures of (*R*)-1 and (*S*)-1. As can be seen, the molecular structures of (*R*)- and (*S*)-1 are perfect mirror symmetry. In (*R*)-1, one pyrene moiety and two naphthalene moieties are linked to a diazocine ring. The bond lengths of the C–C and C–N in the diazocine ring are in the range of 1.28–1.50 Å, indicating the significantly electronic interaction between the pyrene moiety and two naphthalene moieties. This is surely responsible for the observation of the CD signals in the electronic absorption range of the pyrene moiety. However, the benzene moiety near the diazocine ring in the pyrene moiety is obviously distorted, with an average deviation for each atom from the mean plane of the six carbon atoms amounting to 0.127 Å. This is also true for (*S*)-1.

### 2.3. Optical properties

The optical properties of **1** and **2** in chloroform are investigated via electronic absorption and CD spectroscopies. As can be seen in Figs. 2 and 3, both **1** and **2** exhibit intense absorption in the range of 250–275 nm and several medium intense absorption bands in the range of 275–425 nm. A very weak absorption in the range of 425–500 nm was also observed, which is mainly due to the electron transition from binaphthalene moiety to pyrene moiety according to the theoretical calculation as detailed below.

The CD spectra of the chiral compounds **1** and **2** are also displayed in Figs. 2 and 3. As can be clearly seen, perfect mirror image CD spectra are observed in the entire absorption region for both **1** and **2**, indicating the effective chiral information transfer from the peripheral chiral binaphthyl units to the pyrene moiety. The CD intensity for both **1** and **2** reaches up to  $10^{-2}$  deg  $\text{M}^{-1}$   $\text{cm}^{-1}$ , in line with that for optical active phthalocyanine [9], subphthalocyanine [10], and Aza-BODIPY [11] also carrying binaphthyl substituent(s). In detail, (*R*)-1 exhibits one discernible positive signal at 323 nm and three negative signals at 288, 363, and 446 nm, respectively. As for (*R*)-2, the negative significant CD signals are observed at 287, 311, 375, and 447 nm while the positive ones are present at 268 and 337 nm. Similar to the reported binaphthyl-linked phthalocyanines, subphthalocyanines, and Aza-BODIPY, these intense CD signals of

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