Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Synthesis, structures and photophysical properties of two regioisomeric phenalenocarbazoles



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ARTICLE INFO

Article history: Received 30 June 2017 Received in revised form 15 December 2017 Accepted 3 January 2018 Available online 04 January 2018

Keywords: Pyrene Regioisomer Phenalenocarbazole Fluorescence

ABSTRACT

Two regioisomeric phenalenocarbazoles have been synthesized by direct reductive cyclization of 2'-Nitrophenylpyrene isomers respectively. Their photophysical properties and crystal structures as well as CV properties were investigated and compared with those of sulfur containing analogues. Although the fluorescence emission properties of **1N** are very similar with those of **2N**, the HOMO energy level of **1N** is 0.16 eV higher than that of **2N** indicating that **1N** has better electron donating ability.

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1. Introduction

Carbazole has been extensively studied and functionalized as a flexible synthon of biologically active natural product and pharmaceutical drug [1–3]. Due to its highly rigid structure and excellent blue-emission property, the carbazole moiety has also found wide application as a key building block of organic optoelectronic material in organic light-emitting device (OLEDs) [4,5] and polymeric light-emitting diode (PLEDs) [6]. Recently, carbazole derivatives were also adapted as electron donors in the thermally activated delayed fluorescence (TADF) materials demonstrating very high external quantum efficiency [7–9]. In addition, the carbazole embedded organic field-effect transistor (OFET) materials were also reported [10].

Generally, benzo-annelation and introducing heteroatom into a local aromatic compound are very common strategies to build or extend organic conjugate systems for organic materials. Nitrogen and sulfur are the most popular doped elements. Certainly, even changing the mode and sites of annelation between same building blocks will result in different electronic structures and properties. As analogue of angular polycyclic aromatic hydrocarbons (PAH), the annellated carbazoles, such as dibenzo[*c*,*g*]carbazole, naphtho[2,3-*b*]carbazole benzo[*a*]naphtho-[2,3-

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h]carbazole, dinaphtho[2,3-*b*:2',3'-*h*]carbazole, indolo[3,2-*b*]carbazole, have been experimentally and theoretically studied [11]. However, although pyrene seems match the basic requirement as organic semiconductor due to its remarkable intramolecular π -conjugation and intermolecular π - π interaction, the pyrene anellated carbazole derivatives were still seldom reported in literatures.

As part of our continuing work on pyrene-based PAH for optoelectronic materials applications [12–14], we have presented interesting structurally isomeric pyrene-thienoacenes (PTAs) through very different synthetic routes. To examine the role of ring cyclization mode and heteroatom for tuning their photo-physical properties, we also tried to synthesize some structurally isomeric phenalenocarbazole. Among the recently reported methods for the synthesis of carbazole derivatives [15-21], nucleophilic substitution of dibenzothiophene dioxides with anilines under transition-metal-free conditions was developed by Yorimitsu and co-workers for N-substituted carbazoles [22]. Although our PTA could be oxidized to sulfone-bridged phenyl-pyrene [13], it cannot be easily converted to a targeting N-H carbazole derivative through this route. The modified Cadogan reaction was reported by Freeman et al. to cyclize the 2-nitrobiphenyls via reductive deoxygenation of the nitro groups and directly gives the related N-H carbazoles [23]. This straightforward reaction is very convenient to execute and tolerate a broad range of functional groups, so it was adapted in our research.

We present here the synthesis, crystal structures and light emitting properties of two phenalenocarbazoles. To easily identify the structural difference, these two compounds were named as nitrogen-bridged





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phenyl-pyrene and abbreviated as **1N** and **2N** hereafter. The comparison between regioisomers and between sulfur [12] and nitrogen bridged phenyl-pyrene derivatives are especially emphasized to understand structure-property relationships.

2. Experimental

2.1. Materials and Instruments

Pyrenyl-1-boronic acid is commercial available and 2-Bpin-pyrene was prepared as previously reported by Marder et al. [24]. All the other reagents were purchased from Acros Ltd. All solvents were freshly distilled before using. ¹H and ¹³C NMR spectra were recorded with Bruker 300 or 400 spectrometers in CDCl₃ with TMS as internal references. High-Res Mass spectra were recorded using MALDI (DHB matrix) or DART modes.

UV–vis absorption spectra were recorded on a Shimadzu UV 2550 spectrometer with $C = 5.0 \times 10^{-6}$ mol·L⁻¹. Steady state fluorescence emission spectra were recorded on an Edinburgh FLS920 fluorescence spectrometer equipped with a 450 W Xe lamp. Reconvolution fits of the fluorescence decay curves were made with F900 analysis software to obtain the lifetime values. To measure the quantum yields of these compounds, pure pyrene and coumarin 307 were used as the reference.

Cyclic voltammetric measurements were carried out in a conventional three-electrode cell using a Pt wire working electrodes, a Pt wire counter electrode, and a Ag/AgCl reference electrode on AMETEK Parstat 2273 instrument. Freshly distilled DCM was used as the solvent and tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) as supporting electrolyte in 0.1 M·L⁻¹ with a scan rate of 100 mV·s⁻¹. Fc⁺/Fc was used as external reference.

2.2. Crystallography

Suitable single crystals of **1N** and **2N** were grown from their DCM solutions. The diffraction data were collected on a Bruker ApexII CCD diffractometer using a graphite mono-chromated Mo K α radiation ($\lambda = 0.71073$ Å) at 20 °C. The structures were solved by directed method using the program SHELXL and refined by full-matrix least-squares method on F^2 . The crystal structure of **1N** and **2N** were deposited at the Cambridge Crystallographic Data Centre with deposition numbers CCDC 1559505 and 1559409, respectively.

2.3. Theoretical Calculations

For all calculation, the B3LYP hybrid functional and 6-311G basis set were used, as incorporated in the Gaussian 03 package. The ground state geometries of **1N** and **2N** molecules were optimized using the initial geometry derived from their molecular structures as determined by X-ray diffraction. Based on the optimized ground state geometries, the single point excited state calculations were performed using time-dependent density functional theory (TD-DFT) with the B3LYP functional.

2.4. General Procedure for Synthesis of Phenalenocarbazoles (1N and 2N)

To a solution of Pyrenyl-1-boronic acid or 2-Bpin-pyrene (1.0 mmol) in toluene (10 mL), was added 1-iodo-2-nitro-benzene (0.25 g, 1.0 mmol), Pd(PPh₃)₄ (10 mg, 0.01 mmol) and aqueous solution Na₂CO₃ (1.0 M, 2 mL). Then the mixture was heated to 80 °C for 12 h. The organic phase was washed with water and extracted with DCM, then the solvent was removed under vacuum and the residue was purified by column chromatography using dichloromethane as eluent to afford yellow powders of products **1** (or **2**).

To a solution of 2'-nitro-phenyl-1-pyrene (**1**) or 2'-nitro-phenyl-2pyrene (**2**) (0.10 g, 0.34 mmol) in dried 1,2-dichloro-benzene (10 mL), was added tri-phenyl-phosphine (0.26 g, 1.0 mmol) and the mixture was heated to reflux for 12 h. The solvent was removed under vacuum and the residue was purified by column chromatography using dichloromethane as eluent to afford yellow crystalline products.

1: 75% yield. M.p. 168 °C. ¹H NMR (300 MHz, CDCl₃) δ 8.21 (d, 2H, *J* = 10.0 Hz), 8.14–8.06 (m, 7H), 7.98 (dd, 1H, *J* = 10.8 Hz, *J* = 1.2 Hz), 7.74–7.65 (m, 2H), 7.60–7.55 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 149.64, 136.778, 135.05, 132.90, 132.35, 131.39, 131.19, 128.32, 128.15, 127.28, 126.23, 125.39, 124.38, 124.28, 124.21, 124.15. HRMS (ESI +): m/z[M + Na]⁺ 346.0833, calcd for C₂₂H₁₃NO₂Na⁺ 346.0844.

2: 70% yield. M.p. 175 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, *J* = 8.0 Hz, 2H), 8.18–8.13 (m, 2H), 8.11 (d, *J* = 1.2Hz, 2 H), 8.02 (t, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.75 (dt, *J* = 7.8 Hz, *J* = 1.2 Hz, 1H), 7.71 (d, *J* = 9.2 Hz, 1H), 7.65 (dt, *J* = 7.8 Hz, *J* = 1.2 Hz, 1H), 7.59 (dd, *J* = 7.8 Hz, *J* = 1.2 Hz, 1H), 1³C NMR (101 MHz, CDCl₃) δ 150.04, 135.77, 133.59, 132.62, 132.55, 131.39, 131.25, 130.87, 128.71, 128.28, 127.91, 127.38, 126.35, 126.20, 125.58, 125.33, 124.74, 124.71, 124.64,



Scheme 1. Synthetic approach to isomers of phenalenocarbazoles 1N and 2N.



Fig. 1. Crystal structures of 1N (a) top view (b) side view (some of disordered atoms are not presented for clarity); and 2N (c) top view (d) side view.

124.40, 124.06. HRMS (ESI+): $m/z[M + Na]^+$ 346.0850, calcd for $C_{22}H_{13}NO_2Na^+$ 346.0844.

1N: 56% yield. M.p. 178 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.92 (s,1H, N-*H*), 8.85 (s,1H), 8.40–8.36 (m, 2H), 8.23–8.15 (m, 4H), 8.03 (m, 2H), 7.92 (m, 1H), 7.66 (m, 1H), 7.54 (m, 1H). ¹H NMR (400 MHz, DMSO) δ 12.48 (s,1H, N-*H*), 9.05 (s,1H), 8.82 (d, 1H, *J* = 8.8 Hz), 8.47 (d, 1H, *J* = 7.8 Hz), 8.33 (d, 1H, *J* = 8.8 Hz), 8.27–8.24 (m, 2H), 8.21 (d, 1H, *J* = 7.2 Hz), 8.04–7.98 (m, 2H), 7.78 (m, 1H, *J* = 8.8 Hz), 7.59 (td, 1H, *J* = 7.8 Hz, *J* = 0.8 Hz), 7.37 (td, 1H, *J* = 7.8 Hz, *J* = 0.8 Hz). ¹³C NMR (101 MHz, CDCl₃) δ 139.95, 134.66, 131.68, 131.28, 128.52, 127.25, 126.95, 126.28, 125.86, 125.62, 125.56, 124.64, 124.35, 124.23, 123.93, 121.55, 120.73, 120.23, 120.05, 117.08, 115.12, 110.97. HRMS (ESI+): *m*/*z*[M + H]⁺ 292.1128, calcd for C₂₂H₁₃N⁺ 292.1126.

2N: 60% yield. M.p. 165 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.16 (d, *J* = 9.1 Hz, 1H), 8.83 (d, *J* = 7.9 Hz, 1H), 8.59 (s, 1H, N-*H*), 8.38 (d, *J* = 9.1 Hz, 1H), 8.29 (d, *J* = 7.6 Hz, 1H), 8.21 (d, *J* = 9.7 Hz, 2H), 8.13 (d, *J* = 9.0 Hz, 1H), 8.07 (d, *J* = 9.0 Hz, 1H), 7.99 (t, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 140.24, 138.18, 130.47, 130.40, 129.91, 128.33, 127.60, 127.20, 126.77, 125.64, 125.50, 125.33, 125.13, 124.63, 123.84, 123.53, 122.81, 120.18, 120.10, 117.34, 110.76, 107.15. HRMS (ESI +): m/z[M + H]⁺ 292.1120, calcd for C₂₂H₁₃N⁺ 292.1126.

3. Results and Discussion

3.1. Synthesis and Structures

As shown in Scheme 1, all phenalenocarbazoles compounds were synthesized starting from pyrenyl-1 or -2 boronic acid(ester) through

a two-step route. The precursors, (2'-nitro-phenyl)pyrene (1 and 2) could be prepared via typical Suzuki coupling with high yield. If only count the symmetry of the precursors 1 and 2 in mind, the straightforward producing of 1N from 1 is reasonable and no doubt, considering the fact of 2'-nitro-phenyl connecting at 2-position of pyrene, and therefore no other cyclization could happen. However, the cyclization of 2 may give either 6-member ring with N atom connect to 10-position of pyrene. Actually, for the sulfur-containing analogues, we had only obtained **4-S-PTA** containing a 6-member ring with S connect to 4-position of pyrene via acid-induced cyclization of 1-(2'-methyl sulfoxide-phenyl)pyrene [12]. However, in this nitrogen-containing case, the only isolated product was exclusively determined by X-ray diffraction as **2N**, which have a 5-member ring formed with N atom connect to 1-position of pyrene.

The difference between these two kinds of cyclization reactions may be related to the nature of electronic structure of pyrene. As generally accepted mechanism, the acid-induced cyclization of aromatic methyl sulfoxides was taken place via S⁺ intermediate [25,26]. Because 2-position of pyrene normally lies in the node plane of frontier orbitals, thus the 4-position of pyrene is more electrophilic than 2-position and thus 6-member ring structure is favored. As proposed by Freeman et al. [23], the mechanism of reductive cyclization of nitro-biphenyl may have a N⁻ key intermediate being involved. In addition, Park et al. also only got a 5-member ring structure using this triphenylphosphine-mediated reductive cyclization of 4-(2'-nitro-phenyl) pyrene [27]. Thus, the formation of the 5-member ring structure should be reasonable due to the different reactive-site selectivity relying on the different mechanism.



Fig. 2. UV-vis absorption spectra of phenalenocarbazoles 1N, 2N and PTAs in hexane (C = 5.0×10^{-6} mol·L⁻¹).



Fig. 3. Normalized fluorescence emission spectra (λ_{ex} = 375 nm) of phenalenocarbazoles 1N, 2N and PTAs in hexane (C = $5.0 \times 10^{-6} \text{ mol·L}^{-1}$).



Fig. 4. Cyclic voltammogram of phenalenocarbazoles **1N** and **2N** in CH_2Cl_2 solution with 0.1 M Bu_4NPF_6 as supporting electrolyte (CV of **1-S-PTA**, **2-S-PTA** and Fc were shown for comparison).

The structures of **1N** and **2N** were confirmed by single-crystal X-ray diffraction (Fig. 1). Although the molecular structure of **1N** is asymmetric, the crystal of **1N** belongs to tetragonal $I4_1$ cd space group and the molecules are mirror disordered. The disorder precludes obtaining highly accurate parameters, but it still can be seen that the molecular keep in nearly perfect co-planar manner. **2N** crystallized in the monoclinic $P2_1/c$ space groups. The dihedral angle between the phenyl and pyrenyl is only 4.06°. The bond length of CC bond, which connect phenyl and pyrenyl in **2N** is 1.439 Å, which is obviously shorter than that of **2S**–**PTA** (1.476 Å).

3.2. Optical and Electrochemical Properties

The photophysical properties of **1N** and **2N** were examined. The absorption and emission spectra of 1N and 2N comparing with those of un-cyclized precursor (1 and 2) and Sulfur-containing analogues are shown in Fig. 2 and Fig. 3 and supplementary data (Fig. S-1 and S-2). Generally, the absorption spectra of un-cyclized precursors (1 and 2) are quite similar to those of pyrene maintaining the well-resolved vibronic structures and strong absorption band at around 334 nm which corresponds to the $S_0 \rightarrow S_2$ transition of pyrene as found in many other pyrene derivatives. The spectral shapes of isometric 1N and **2N** are quite different but cover the similar range. The typical S_0 \rightarrow S₂ transition of pyrene (280–340 nm) was degenerated for **1N** and almost disappeared for 2N. Both of 1N and 2N have weak absorption bands corresponding to the $S_0 \rightarrow S_1$ transition at 417 nm and 410 nm, respectively, which are greatly red-shifted by near 100 nm relative to those of un-cyclized precursors. However, the molar extinction coefficient of **1N** at about 415 nm is nearly 4 times of that of **2N**, indicating that the fusion mode of **1N** seems much efficient than **2N**. As shown in Fig. 2, comparing with those of PTAs, the longest absorption bands of 1N and 2N are generally red-shifted by 13 nm (404 nm to 417 nm), indicating a narrower HOMO-LUMO gap caused by linking a benzene ring to pyrene with fusion mode via N-bridge rather than S-bridge.

As shown in Fig. 3, the fluorescence emission spectra of **1N** and **2N** possess nearly the same position ($\lambda_{em} = 423$ nm) and very similar vibronic structures. **2N** has a higher quantum yields and longer fluorescence lifetime ($\Phi = 0.38$, $\tau = 8.6$ ns) than those of **1N** ($\Phi = 0.28$, $\tau = 5.7$ ns), but they are all comparable with those of **PTAs**. However, the comparison of radiative transfer rate ($K_r = \Phi/\tau$) and non-radiative transfer rates ($K_{nr} = (1-\Phi)/\tau$) for **1N** and **2N** show that the two isomeric compounds share similar K_r ($4.4 \times 10^7 \text{ s}^{-1}$ for **1N** and $4.9 \times 10^7 \text{ s}^{-1}$ for **2N**) but the K_{nr} of **2N** ($1.26 \times 10^8 \text{ s}^{-1}$) is almost double that of **1N** ($7.2 \times 10^7 \text{ s}^{-1}$).



Fig. 5. The isosurface (isovalue = 0.02 a. u.) of selected molecular orbitals of 1N and 2N, as calculated by DFT at B3LYP/6-311G(d) level.

The electrochemical properties of **1N** and **2N** were investigated by cyclic voltammetry (CV) (Fig. 4) using ferrocene/ferrocium (Fc/Fc⁺) couple [28] as external standard (the HOMO energy level was taken to be -4.80 eV) [29]. Although the reduction wave are not clearly measurable in CH₂Cl₂ under this condition, the CV of both **1N** and **2N** show reversible oxidation wave with half-wave potentials at 0.85 eV for **1N** and 1.01 eV for **2N** and that of ferrocene is 0.48 eV, respectively. Thus, the HOMO energy level could be estimated as of -[4.8 + (0.85-0.48)] = -5.17 eV for **1N** and -[4.8 + (1.01-0.48)] = -5.33 eV for **2N**. Clearly, the fusion mode of **1N** can efficiently heighten the HOMO energy level and enhance electron-donating ability.

As reported before, the isometric **1-S-PTA** and **2-S-PTA** have very similar oxidation potentials at about 0.80 eV (vs Ag/AgCl). So the direct comparison between phenalenocarbazoles and **PTAs** clearly indicated the N-bridged fusion mode can effectively extend the π -delocalization with little lower HOMO level than S-bridged fusion mode. Considering the narrower bandgap from the absorption spectroscopy (2.97 eV for **1N**, 3.02 eV for **2N**, 3.07 eV for **1-S-PTA** and **2-S-PTA**, calculated at $\lambda_{abs} = 417$ nm for **1N** and $\lambda_{abs} = 410$ nm for **2N**, $\lambda_{abs} = 404$ nm for **1-S-PTA** and **2-S-PTA**), the LUMO energy level of phenalenocarbazoles are much lower than those of **PTAs**.

3.3. Theoretical Calculations

In order to gain insight into the π -conjugation modes and understand the photophysical properties of the present molecules, we conducted some theoretical calculations of them. The pictorial drawing of frontier molecular orbitals are shown in Fig. 5. Generally, the TD-DFT calculated lowest energy transitions of phenalenocarbazoles seem able to reproduce their main absorption bands and relative energy of frontier orbitals as observed experimentally very well. Especially, the calculated energy level of HOMO of **1N** is 0.11 ev higher than that of **2N**, which is very close to the experimental CV results.

It is well known, that the nature and the site of substituent will obviously tune the photophysical properties of pyrene derivatives [30-32]. Marder et al. had reported that in the 2-substituted pyrene derivatives, the substituent only make strong influence on the $S_1 \leftarrow S_0$ excitation, which is initially a weak excitation; In contrast, the 1-substituted pyrene derivatives display a strong influence on both the $S_1 \leftarrow S_0$ and the $S_2 \leftarrow S_0$ excitations [32]. In other words, the substituents at 1 position make the main influence on the excitations between the frontier orbitals. In our cases, the conjugations of phenalenocarbazoles isomers are greatly depend on the substituent of the position 1 of pyrene: phenyl or N atom with lone pairs. As shown in Fig. 5, there are nodal planes in the HOMO and LUMO of pyrene motif passing through the 2- and 7positions, perpendicular to the molecular plane, which mean the substituent will not involve in the excitations between the frontier orbitals. For 1N, the phenyl ring is bonded with pyrene through the 2-position of pyrene, and the orbital coefficients of the frontier orbitals are relative small on the phenyl group. However, the N atom is clearly involved in the frontier orbitals since it is bonded at the 1-position of pyrene for 1N. Vice versa, in the case of 2N, phenyl is more involved in the frontier orbitals instead of N atom. Combined with the experimental data, it seems that the position of N atom play much important role than phenyl to increase the electron-donating ability in these phenalenocarbazoles cases.

4. Conclusions

Two regioisomeric phenalenocarbazoles, named as N-bridged pyrene-phenyl carbazole derivatives, have been synthesized by direct reductive cyclization of 2'-Nitrophenyl-pyrene isomers. The comparison between these N bridged phenalenocarbazoles and earlier reported S-bridged **PTA** indicate that phenalenocarbazoles will greatly extend the conjugation as presented spectral red-shifts and keep good quantum yield and electronical properties. Considering the ground potential of post-functionalizing of carbazole moiety, we believe these preliminary results will provide new insight for the further design and application of pyrene-based heteroatom-containing PAHs.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21672130), the Fundamental Research Funds of Shandong University (2017JC011), the State Key Laboratory of Crystal Materials and also open project of Key Laboratory of Synthetic and Self-Assembly Chemistry for Organic Functional Molecules (K2017-5).

Appendix A. Supplementary Data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.saa.2018.01.004.

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