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Novel fluorescence dyes based on entirely new chromeno[4,3,2-de][1,6]naphthyridine framework

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ABSTRACT

A series of entirely new framework chromeno[4,3,2-de][1,6]naphthyridine derivatives containing triphenylamine groups have been carefully designed and prepared in good yields using the Pd(0) catalyzed Suzuki couplings reactions. The relationship of photoluminescence property and structure of these compounds was systematically investigated via thermogravimetric analyzer, UV–vis, fluorescence and electrochemical analyzer. The HOMO and LUMO distributions of these compounds were calculated by density functional theory (DFT) (B3LYP; 6-31G*) method. These compounds exhibited high fluorescence quantum yields, desirable HOMO levels and high thermal stability, indicating that the combination of chromeno[4,3,2-de][1,6]naphthyridine and triphenylamine could be an efficient means to enhance hole-transporting ability and fluorescent quantum yield.

1. Introduction

Organic fluorescent compounds have been extensively investigated for a myriad of potential applications in the biological labels, photovoltaic cells, light emitting diodes (LEDs), and optical sensors etc [1–12]. Naphthyridine derivatives were used not only as luminescence materials in molecular recognition because of their rigid planar structure [13–15], but also as new drug leaders and anticancer active screening agents in new drug discovery [16,17].

Arylamine-based derivatives are well-known electron-rich compounds which are widely employed in hole transporting materials, and light emitters in the field of optoelectronics such as organic light emitting diodes (OLEDs) [18], organic field-effect transistors [19,20], non-linear materials [21,22], and xerography [23,24]. In recent years, it has been found out that the excellent solubility, good stability, high photoluminescence of triarylamines is favorable for organic sensitizers, and a large number of triarylamine-based dyes as electron donor are developed for OFETs or organic solar cells [25–38].

In our previous work, a series of chromeno[4,3,2-de][1,6]naphthyridine compounds have been synthesized by simple silica gel catalyzes in water, in which the framework possesses a satisfactorily planarity. Since planarity is commonly regarded as a positive structural factor in enhancing the molecular fluorescent properties, these compounds exhibit high fluorescence quantum yields which may have a good application as fluorescent material in the future [39].

Therefore, our continuing interests in suitable fluorescent materials [40,41] for analytical and biological chemistry lead to an introduction of the triphenylamine units to chromeno[4,3,2-de][1,6]naphthyridine framework in order to improve the hole-transporting ability and fluorescent quantum yield. Although the introduction of the triphenylamine units reduce the planarity of the chromeno[4,3,2-de][1,6]naphthyridine framework to a certain extent, it indeed enhances the hole-transporting ability and the emission color of these compounds can be easily tuned from blue to green by changing the number of triphenylamine moieties as expected. Particularly, we found that their HOMO energy levels (−5.01 to −5.49 eV) could be readily fine-tuned by changing the substituents on the phenyl groups. These compounds exhibit high fluorescence quantum yields and high thermal properties, all of which lead to promising applications in OLEDs.

2. Experimental

2.1. Chemicals and instruments

All solvents were carefully dried and freshly distilled according to common laboratory techniques. All reactants were commercially

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available and used without further purification. Melting points were recorded on electrothermal digital melting point apparatus and were uncorrected. ^{1}H and spectra were recorded at 295 K on a Bruker Advance DPX-400 MHz spectrometer using DMSO-d_6 as solvent and TMS as internal standard. UV–vis spectra were recorded on a Shimadzu UV-2501PC spectrometer. Fluorescence spectra were obtained on a Hitachi FL-4500 spectrofluorometer. High resolution mass spectroscopy (HRMS) data were measured using microTOF-Q(ESI) instrument. Thermal properties was performed under nitrogen on a SDT 2960 (heating rate of 10 °C min^{-1}). Cyclic voltammetry was carried on a Chi 1200 A electrochemical analyzer with three-electrode cell (Platinum was used as working electrode and as counter electrode, and SCE (saturated calomel electrode) as reference electrode) in CH_2Cl_2 solution in the presence of TBAHFP (tetrabutylammonium hexafluorophosphate) (0.10 mol L^{-1}) as supporting electrolyte.

2.2. N,N-diphenyl-4-bromoaniline (**2**)

Compound **1** (27.1 g, 120 mmol) and *N*-Bromosuccinimide (NBS; 21.4 g, 120 mmol) were dissolved in 500 mL of CCl_4. The solution was refluxed for 4 h. The precipitated succinimide was filtered, and the solvent was evaporated from the solution. The remaining gray oil was recrystallized from ethanol. The obtained white crystalline powder was dried in a vacuum (34.3 g 94%). White, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.20 (m, 6H), 7.11–6.99 (m, 6H), 6.97–6.90 (m, 2H).

2.3. 4-(Diphenylamino)phenylboronic acid (**3**)

A solution of **2** (3.3 g, 10.0 mmol) in anhydrous THF (50 mL) was cooled to −78 °C. n-BuLi (2.5 mol L^{-1} in hexane, 4.8 mL, 12.0 mmol) was slowly added dropwise. After complete addition, the reaction mixture was stirred for another 1 h. Then, triisopropyl borate (3.5 mL, 15.0 mmol) was added at once. The mixture was allowed to warm to room temperature for 15 h. The reaction was finally quenched with HCl (2.0 mol L^{-1}, 40 mL) and the mixture was poured into a large amount of water. After extraction with CH_2Cl_2 (3 × 20 mL), The organic layer was washed with brine, dried over $MgSO_4$, concentrated. Further purification by silica gel column chromatography (petroleum ether/dichloromethane, 2/1, v/v) afforded **3** as a white solid (1.61 g, 54%). White, ^{1}H NMR (300 MHz, d_6-DMSO): δ 7.84 (s, 2H), 7.65–7.68 (d, J = 8.4 Hz, 2H), 7.31 (t, J = 7.8 Hz, 4H), 7.00-7.08 (m, 6H), 6.87-6.89 (d, J = 8.1 Hz, 2H).

2.4. General procedure for the synthesis of compounds **7**

Compounds **7a**–**e** were synthesized according to methods described in literature [39]. A mixture of substitution-2-hydroxyacetophenone (2.0 mmol), aromatic aldehyde (2.0 mmol), malononitrile (4.0 mmol) and 0.03 g of silica gel was stirred in water (2 mL) at 80 °C. After 2 h reaction, the mixture was filtered and then concentrated. The precipitate was collected and purified by 95% EtOH-DMF (10:1). The analytical data for represent compounds are shown below.

2.4.1. 5-Amino-2-phenyl-chromeno[4,3,2-de][1,6]naphthyridine-4-carbonitrile (**7a**)

Yield (0.46 g) 69%, Yellow crystal, Melting point (M.p.) > 300 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.63–8.61 (dd, $J1$ = 1.2 Hz, $J2$ = 8.0 Hz, 1H), 8.45–8.44 (d, J = 2.0 Hz, 1H), 8.43–8.42 (d, J = 1.6 Hz, 1H), 8.39 (s, 1H), 7.74–7.70 (t, 1H), 7.63–7.60 (m, 3H), 7.60–7.47 (m 4H).

HRMS (ESI): m/z calcd. for $C_{21}H_{12}N_4O$, 337.1084; found, 337.1010.

2.4.2. 5-Amino-2-(4-bromophenyl)-chromeno[4,3,2-de][1,6]naphthyridine-4-carbonitrile (**7b**)

Yield (0.63 g) 76%, Yellow crysta, M.p. > 300 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.59 (d, J = 7.2 Hz, 1H), 8.46 (d, J = 8.8 Hz, 1H), 8.37 (s, 1H), 7.82 (d, J = 12.0 Hz, 1H), 7.73–7.66 (m, 3H), 7.53–7.47 (q, 4H).

HRMS (ESI): m/z calcd. for C21H11N4BrO, 415.0189; found, 413.2552.

2.4.3. 5-Amino-9-fluoro-2-(4-bromophenyl)-chromeno[4,3,2-de][1,6]naphthyridine-4-carbonitrile (**7c**)

Yield (0.52 g) 60%, Yellow solid, M.p. > 300 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.71–8.68 (m, 1H), 8.40 (s, 3H), 7.83–7.81 (d, J = 8.4, 2H), 7.57–7.52 (m, 3H), 7.44–7.39 (m, 1H) ppm.

HRMS [Found: m/z 423.0020 (M$^+$), Calcd for C21H10N4BrFO: M, 432.0022].

2.4.4. 5-Amino-9-methyl-2-(4-bromophenyl)-chromeno[4,3,2-de][1,6]naphthyridine-4-carbonitrile (**7d**)

Yield (0.47 g) 55%, Yellow solid, M.p. > 300 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.42–8.35 (m, 4H), 7.83–7.81 (m, 2H), 7.53–7.51 (m, 2H), 7.43–7.40 (m, 1H), 2.47 (s, 3H) ppm.

HRMS [Found: m/z 428.0270 (M$^+$), Calcd for C22H13N4BrO: M, 428.0273].

2.4.5. 5-Amino-2-(4-bromophenyl)-10-bromochromeno[4,3,2-de][1,6]naphthyridine-4-carbonitrile (**7e**)

Yield (0.59 g) 60%, Yellow solid, M.p. > 300 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.64 (d, J = 8.0 Hz, 1H), 8.40–8.371 (m, 3H), 7.82–7.80 (m, 2H), 7.71 (s, 1H), 7.58–7.51 (m, 3H).

HRMS [Found: m/z 493.9203 (M$^+$), Calcd for $C_{21}H_{10}N_4Br_2O$: M, 493.9201].

2.5. General procedure for the synthesis of compounds (**8** and **9**)

Under a nitrogen atmosphere, a mixture of compounds (**7**) (1.0 mmol), Pd(PPh$_3$)$_4$ catalyst (0.04 mmol) and the corresponding triphenylamine (or benzene) boronic acid was stirred in dry toluene (15 mL). Then, 2 mol L^{-1} K_2CO_3 (aq) solution (2 mL) was added via syringe. The reaction mixture was heated to reflux for 72 h. After cooling, the product was extracted with DCM, washed with water, dried over $MgSO_4$, filtered, concentrated and further purified by column chromatography (silica gel, hexane/dichloromethane, 10/1, v/v). The pure compounds **8** (or **9**) were obtained.

2.5.1. 5-Amino-2-(4′-(diphenylamino)biphenyl-4-yl)-9-fluorochromeno[4,3,2-de][1,6]naphthyridine-4-carbonitrile (**8a**)

Yield (0.48 g) 84%, Yellow solid, ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.75–8.68 (m, 2H), 8.52–8.50 (d, J = 8.0, 1H), 8.42–8.38 (m, 3H), 7.89–7.87 (d, J = 8.0 Hz, 1H), 7.83–7.81 (d, J = 8.0 Hz, 2H), 7.77–7.75 (d, J = 8.4 Hz, 1H), 7.60–7.52 (m, 5H), 7.44–7.34 (m, 4H), 7.12–7.05 (m, 5H) ppm.

HRMS [Found: m/z 578.2127 (M$^+$), Calcd for $C_{39}H_{25}N_5O$: M, 579.2059].

2.5.2. 5-Amino-2-(4′-(diphenylamino)biphenyl-4-yl)-9-methylchromeno[4,3,2-de][1,6]naphthyridine-4-carbonitrile (**8b**)

Yield (0.49 g) 82%, Yellow solid, ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.52–8.50 (d, J = 8.0 Hz, 2H), 8.46 (s, 1H), 8.43–8.38 (d, J = 8.4 Hz, 2H), 7.88–7.86 (m, 2H), 7.83–7.81 (d, J = 8.0 Hz, 1H), 7.76–7.74 (d, J = 8.4 Hz, 2H), 7.53–7.51 (m, 3H), 7.42–7.40 (m, 1H), 7.38–7.34 (t, J = 8.0 Hz, 4H), 7.14–7.08 (m, 7H), 2.47 (s, 3H) ppm. HRMS [Found: m/z 596.1890 (M-H), Calcd for $C_{39}H_{24}N_5FO$: M, 597.1965].