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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].

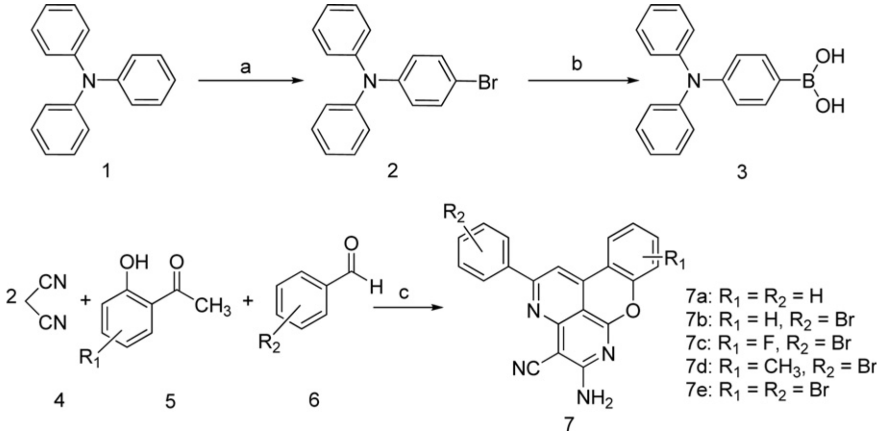


Fig. 1. Synthetic routines for compound **3** and **7a**–**e**. *Reagents and conditions*: (a) triphenylamine:NBS = 1:1, CCl_4, 80 °C; (b) n-BuLi (1.2 equiv), THF, −78 °C, $(CH_3O)_3B$ (1.5 equiv), H_2O/HCl. (c) Silica gel, water, 80 °C.

2.5.3. 5-Amino-2-(4′-(diphenylamino)biphenyl-4-yl)-9-(4-(diphenylamino)phenyl)chromeno[4,3,2-de][1,6]naphthyridine-4-carbonitrile (*8c*)

Yield (0.48 g) 82%, Yellow solid, ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.81 (s, 1H), 8.56–8.54 (m, 3H), 7.96 (s, 2H), 7.87–7.85 (d, $J = 7.6$ Hz, 2H), 7.81–7.79 (d, $J = 8.4$ Hz, 2H), 7.74–7.72 (d, $J = 8.0$ Hz, 2H), 7.58–7.56 (d, 1H, J = 8.0), 7.50 (s, 1H), 7.37–7.34 (m, 8H), 7.10–7.08 (m, 15H) ppm. HRMS [Found: m/z 592.2162 (M-H), Calcd for $C_{40}H_{27}N_5O$: M, 593.2216].

2.5.4. 5-Amino-2-(4′-(diphenylamino)biphenyl-4-yl)chromeno[4,3,2-de][1,6]naphthyridine-4-carbonitrile (*8d*)

Yield (0.67 g) 80%, Yellow solid, ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.67–8.65 (d, J = 8.0 Hz, 1H), 8.54–8.52 (m, 2H), 8.45 (s, 1H), 7.90–7.88 (d, $J = 8.4$ Hz, 2H), 7.77–7.70 (m, 3H), 7.55–7.49 (m, 4H), 7.38–7.34 (m, 4H), 7.12–7.05 (m, 8H) ppm. HRMS [Found: m/z 821.3030 (M-H), Calcd for $C_{57}H_{38}N_6O$: M, 822.3107].

2.5.5. 5-Amino-2-(biphenyl-4-yl)chromeno[4,3,2-de][1,6]naphthyridine-4-carbonitrile (*9a*)

Yield (0.35 g) 85%, Yellow solid, ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.90 (s, 1H), 8.64–8.61 (m, 3H), 8.04–8.02 (d, $J = 8.0$ Hz, 1H), 7.92 (s, 4H), 7.84–7.82 (d, $J = 8.0$ Hz, 2H), 7.65–7.55 (m, 6H), 7.46 (s, 2H) ppm. HRMS [Found: m/z 412.1323 (M^+), Calcd for $C_{27}H_{16}N_4O$: M, 412.1324].

2.5.6. 5-Amino-2-(biphenyl-4-yl)-10-phenylchromeno[4,3,2-de][1,6]naphthyridine-4-carbonitrile (*9b*)

Yield (0.41 g) 84%, Yellow solid, ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.68–8.66 (d, $J = 8.0$ Hz, 1H), 8.57–8.55 (d, $J = 8.4$ Hz, 2H), 8.47 (s, 1H), 7.94–7.92 (d, J = 8.0 Hz, 2H), 8.84–8.82 (d, J = 7.6 Hz, 2H), 7.75–7.71 (m, 2H), 7.56–7.52 (m, 5H), 7.45–7.42 (m, 1H) ppm.

HRMS [Found: m/z 487.1559 (M-H), Calcd for $C_{33}H_{20}N_4O$: M, 488.1637].

3. Results and discussion

Compounds **3**, **7a**–**e** were synthesized according to methods described in literature [24,39] (Fig. 1). For products **8a**–**d**, the triphenylamine or benzene moiety was introduced via a Pd(0) catalyzed Suzuki C–C coupling reaction [30] (Fig. 2). All of these new compounds were characterized by MS spectrometry, ^{1}H NMR spectroscopy. The detailed data are included in the Supporting Information.

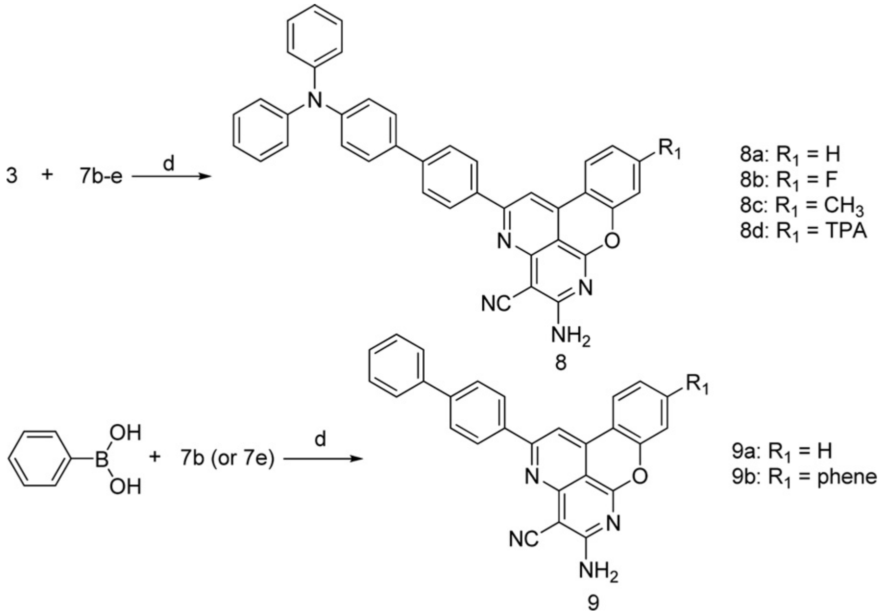


Fig. 2. Synthetic routines of **8** and **9** as a simple. *Reagents and conditions*: (d) cat. $Pd(PPh_3)_4$, 2 mol L^{-1} K_2CO_3, toluene, 90 °C.

Table 1
Optical properties of the compounds **8**, **9**.

Compound	Abs. (FWHM)	em (nm)			Φ^a
	THF (nm)	Toluene	CH_2Cl_2	THF	
8a	298 (62)	476	486	491	0.20
8b	299 (59)	477	473	484	0.28
8c	301 (59)	476	478	494	0.04
8d	302 (61)	466	553	551	0.33
9a	292 (49)	482	477	493	0.47
9b	293 (63)	473	476	493	0.44

[a] The fluorescence quantum yields (Φ) were measured in $CHCl_3$ using quinine sulfate (Φ = 0.55) as standard [23].

3.1. *Thermal properties*

Decomposition temperature (T_d) were determined with a thermal gravimetric analysis (TGA) at a heating rate of 10 °C min^{-1}. The results of these compounds are listed in Table 1. The TGA data reveal that the thermal stability of these compounds also seems to be encouraging. The thermal decomposition does not occur below 300 °C for all of these compounds. Thermal stabilities of the organic EL materials play an important role in OLEDs. The excellent thermal stability with high T_d readily leads to high-stability OLEDs, which is favorable to improve the performance and lifetime of OLEDs during operation.

3.2. *Optical properties*

The absorption spectra of these compounds were measured in THF solutions with a concentration of about 1.0×10^{-5} mol L^{-1}. The optical properties of all new compounds are summarized in Table 1. The absorption spectra of these compounds were complicated due to multiple overlapping broad bands (Fig. 3). The maximum UV–vis absorptions of the compounds **8**, **9** are located in the range of 290–302 nm, ascribed to the π–π* transition of the conjugated molecular backbone. Compound **8d** exhibits a maximum absorption peak at 302 nm indicating the formation of a more delocalized and extended π-conjugated system. With the decreasing full width at half-maximum (fwhm) values from **8a** to **8c**, a slightly red-shifted absorption of **8a**–**c** was observed. The π–π* energy gaps (E_g) of these compounds were obtained from the UV–vis absorption threshold [42]. It is obvious that the E_g's of compounds could be greatly reduced with the increasing number of triphenylamine moieties as the extension of the compound backbone (Table 1).

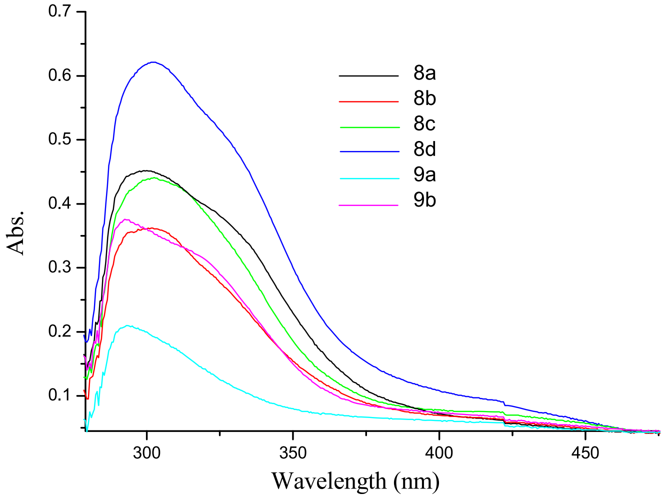


Fig. 3. The absorption spectra of compounds **8**, **9** (1×10^{-5} mol L^{-1} in THF).

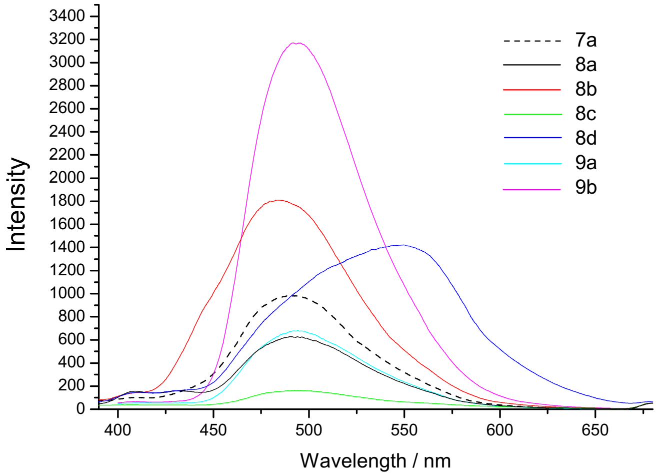


Fig. 4. The emission spectra of compounds **8**, **9** (1×10^{-6} mol L^{-1} in THF).

Fig. 4 shows the fluorescence emission spectra of compounds **8**, **9** with the excitation wave at 350 nm, exhibiting a blue to green fluorescence emission with the maximum emission peaks varying from 484 to 551 nm in THF solutions. With increasing the number of benzene or triphenylamine moieties, the fluorescence emission peaks for **8**, **9** are gradually red shifted except for **8b**. Compound **8d** exhibits strong green fluorescence emission with the maximum emission peaks at 551 nm, which may be due to **8d** possesses the maximum conjugation length caused by the introduction of two triphenylamine moieties. In the case of **8b**, the compound shows a blue fluorescence emission peaks at 484 nm as result of the F-functional group with the electron-accepting ability is introduced into molecular structure. The similar shape, position and one emission peak near 490 nm were observed in compounds **7a**, **8a**–**c** and **9a**–**b**, because these compounds possess a similar structure.

The further examination in the different emission behavior of these compounds found out that these compounds showed a red shift with increasing solvent polarity (Fig. 5) [43]. These results indicate that these compounds are more polar in the excited state than in the ground state [44] and an increase in the polarity of the solvent will lower the energy level of the excited state [45].

The fluorescence quantum yields (Φ) were measured in the THF solution using quinine sulfate (Φ = 0.55) as a standard (Table 1) [46]. The emission efficiency in dilute solution largely depends on

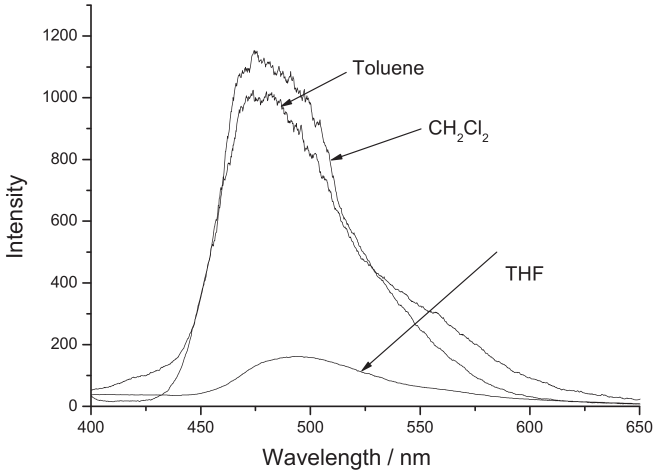


Fig. 5. The emission spectra of compound **8c** in different solvents (1×10^{-6} mol L^{-1}) as sample.

Table 2
Thermal, and electrochemical properties of the compounds **8**, **9**.

Compound	Band gap[a]	E_{HOMO}/E_{LUMO} (eV)[a]	E_g (eV)[b]	E^{ox}onset[c] (V)	E_{HOMO}/E_{LUMO}[d] (eV)	T_d[e] (°C)
8a	2.74	−4.98/−2.24	3.07	0.64	−5.04/−1.97	368
8b	2.67	−5.02/−2.35	3.06	0.96	−5.40/−2.34	348
8c	2.82	−4.95/−2.13	3.11	0.68	−5.08/−1.97	394
8d	2.79	−4.97/−2.18	2.83	1.09	−5.49/−2.66	304
9a	3.59	−5.86/−2.27	3.44	0.61	−5.01/−1.57	371
9b	3.56	−5.83/−2.27	3.15	0.74	−5.14/−1.99	380

[a] DFT/B3LYP calculated values.

[b] Optical energy gaps calculated from the edge of the electronic absorption band.

[c] Oxidation potential in CH_2Cl_2 (10^{-3} mol L^{-1}) containing 0.1 mol L^{-1} $(n\text{-}C_4H_9)_4NPF_6$ with a scan rate of 100 mV s^{-1}.

[d] E_{HOMO} was calculated by $E_{ox} + 4.4$ V, and $E_{LUMO} = E_{HOMO} - E_g$.

[e] Measured by TG-DTA analysis under N_2 at a heating rate of 10 °C min^{-1}.

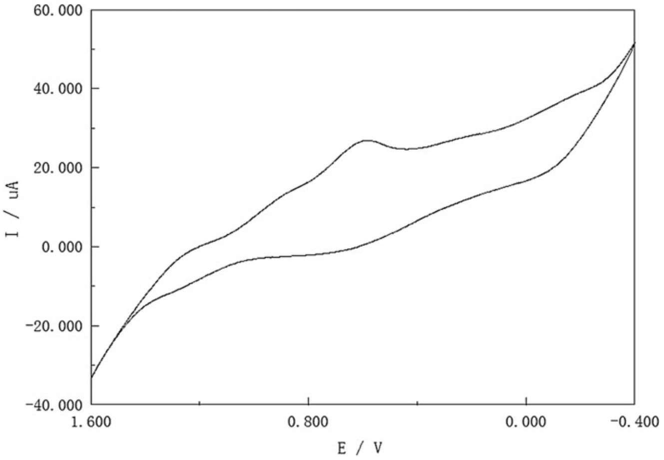


Fig. 6. Cyclic voltammogram of compound **9a** (1×10^{-3} mol L^{-1}) as sample, in 0.1 mol L^{-1} Bu_4NPF_6-$CHCl_3$, scan rate 100 mV/s.

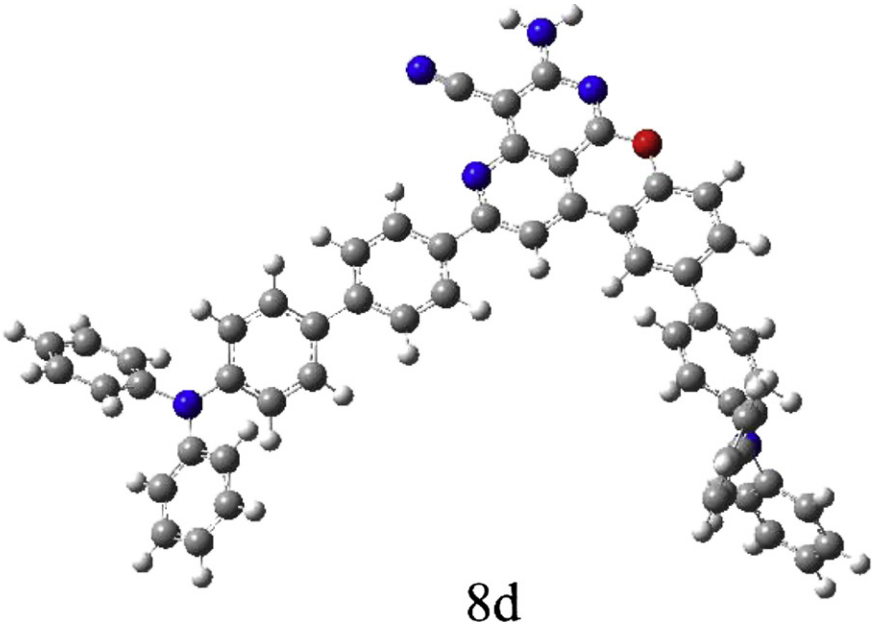
the molecular structure. The fluorescence quantum yields of the compounds are in the range of 0.04–0.47. The Φ value of 0.44 and 0.47 was observed for **9a** and **9b**, which was higher than that of compounds **8a**–**d**. This might be due to the introduction of triphenylamine moieties leading to decrease of coplanarity degree of compounds **8a**–**d**. Moreover, this difference of the quantum yields may result from the change of the molecular size [47,48].

3.3. Electrochemical properties

The electrochemical properties of compounds **8**–**9** are explored by the cyclic voltammetry in the CH_2Cl_2 solutions in the presence of tetrabutylammonium hexafluorophosphate (0.10 mol L^{-1}) as the supporting electrolyte (Table 2). All of compounds **8**–**9** have one reversible oxidation peak which is an indication of a stable cation radical (Fig. 6). According to a reference to ferrocene (4.8 eV), the HOMO energy of these materials was calculated to get a range of −5.01 to −5.49 eV [49,50]. Since the HOMO energy level is close to that of the most widely used hole-transport material 4,4′-bis(1-naphthylphenylamino)biphenyl (NBP) (−5.20 eV, −2.4 eV), it might be beneficial for the hole-transport capacity [51]. Similarly, the optical edge was utilized to deduce the band gap and the LUMO energies. As expected, these compounds are of lower LUMO (−1.57 to −2.66 eV) energies and smaller band gaps compared with the other triphenylamine derivatives [51]. Their LUMO levels represent a small barrier for the electron injection from a commonly used cathode such as barium, which has a work function of −2.2 eV [52]. Therefore, these compounds might be very useful as hole-transporting and electron-transporting materials in applications for OLEDs [52].

3.4. Theoretical calculations

The electronic configurations were further examined using the theoretical models implanted in the Gaussian 03 program [53]. The calculations based upon Density functional theory (DFT) (B3LYP; 6-31G*) were carried out to obtain information about the HOMO and LUMO distributions of the compounds **8**, **9**. Due to the presence of the electron-rich amine moieties and an increase in the conjugation lengths, all of these compounds in Table 2 possess a high HOMO energy level (−4.95 to −5.86 eV), which could lead to their better hole-transport properties (Figs. 7 and 8) [51]. The low LUMO energy of these compounds (−2.13 to −2.35 eV) is supposed to facilitate



8d

Fig. 7. Optimized ground-state geometry of compounds 8d with B3LYP/6-31G* in gas phase.

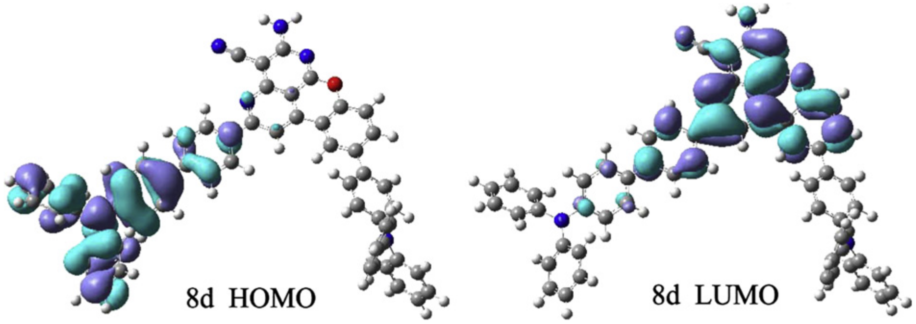


Fig. 8. Calculated spatial distributions of the HOMO, LUMO levels of compound **22** as sample.

the acceptance of electrons from the cathode. It is generally indicative of a HOMO/LUMO absorption transition to bear a significant charge-transfer character. According to the DFT calculations and the experimental data from the UV-absorption spectra, the calculated band gaps show a similar trend except for the compound **9**. The higher HOMO/LUMO energy levels than those corresponding estimations from the experimental data may be related to various effects from conformation and solvents, which have not been taken into account here. Moreover, the electrochemistry is complicated owing to the reversibility of one of the redox process and the accuracy of the E_g value is relatively limited [54].

4. Conclusions

In summary, a series of entirely new framework fluorescence dyes based on chromeno[4,3,2-de][1,6]naphthyridine derivatives have been prepared by a stepwise route involving a Pd(0) catalyzed Suzuki coupling reaction in good yields. The optical properties clearly indicate that the fluorescent emission properties of these compounds rely largely on the molecular structure. As expected, the optical band gaps decrease considerably as the number of triphenylamine moieties introduced into chromeno[4,3,2-de][1,6] naphthyridine framework increases. Moreover, compounds exhibit high fluorescence quantum yields, high thermal stability, excellent luminescence emission from blue to green. The DFT calculations establish that they all possess a high HOMO energy level (−4.95 to −5.86 eV) due to the presence of the electron-rich amine moieties and increased conjugation lengths, giving rise to more balanced charge-transport characteristics, which have promising potential for application in OLEDs as a multifunctional material.

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