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# Synthesis and characteristics of novel fluorescence dyes based on chromeno[4,3,2-*de*][1,6]naphthyridine framework

# Haiying Wang, Jingjing Shi, Chao Wang, Xiaoxiao Zhang, Lingling Zhao, Yu Wan, Hui Wu\*

School of Chemistry and Chemical Engineering, Jiangsu Normal University, Jiangsu Key Laboratory of Green Synthetic for Functional Materials, Xuzhou 221116, China

## HIGHLIGHTS

- Entirely new framework fluorescence dyes based on naphthyridine were synthesized.
- Compounds exhibited efficient green emission with high quantum yields.
- ► HOMO energy level were improved by the introduction of the carbazole units.
- Compounds might application in OLEDs as hole-transporting materials.

# A R T I C L E I N F O

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# $\mathsf{G} \hspace{0.1in} \mathsf{R} \hspace{0.1in} \mathsf{A} \hspace{0.1in} \mathsf{P} \hspace{0.1in} \mathsf{H} \hspace{0.1in} \mathsf{I} \hspace{0.1in} \mathsf{C} \hspace{0.1in} \mathsf{A} \hspace{0.1in} \mathsf{L} \hspace{0.1in} \mathsf{A} \hspace{0.1in} \mathsf{B} \hspace{0.1in} \mathsf{S} \hspace{0.1in} \mathsf{T} \hspace{0.1in} \mathsf{R} \hspace{0.1in} \mathsf{A} \hspace{0.1in} \mathsf{C} \hspace{0.1in} \mathsf{T}$

Entirely new framework chromeno[4,3,2-*de*][1,6]naphthyridine derivatives containing carbazole groups were synthesized and the optical, electrochemical properties were also investigated. Quantum chemical calculations were used to obtain optimized ground-state geometry, spatial distributions of the HOMO, LUMO levels of the compounds.



# ABSTRACT

A series of entirely new framework chromeno[4,3,2-*de*][1,6]naphthyridine derivatives containing carbazole groups have been carefully designed and prepared. The relationship of photoluminescence property and structure of these compounds was systematically investigated via 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 carbazole could be an efficient means to enhance hole-transporting ability and fluorescent quantum yield.

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SPECTROCHIMICA ACTA

# Introduction

In the last decade, efforts have been devoted to the development of novel organic fluorescent compounds useful for the

\* Corresponding author. Tel./fax: +86 516 83403163. *E-mail address:* wuhui72@yahoo.com.cn (H. Wu). fabrication of the biological labels, photovoltaic cells, light emitting diodes (LEDs), and optical sensors [1–4]. The nature of fluorescence depends largely on molecular structure and molecular assembly. Therefore, it is important to clarify the structure–property relationship of fluorescence because such a relationship would allow us to design more useful fluorescent reagents and probes which might be applied in the fields of analytical, biological chemistry and OLEDs in the future.

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Carbazole and its derivatives have been widely used as a functional building block in the fabrication of the organic photoconductors, nonlinear optical materials, and photorefractive materials [5–8] due to their specific optical and electrochemical properties. In the field of OLED technology, carbazole derivatives are usually used as promising blue light-emitting materials [9–14]. Meanwhile, a great many of carbazole homopolymers or oligomers as well as carbazole-containing polymers or small molecules, such as widely used PVK (polyvinylcarbazole) and CBP (N,N'-dicarbazolyl-4,4'-biphenyl), are of excellent hole-transport ability, due to the electron-donating capabilities [15–19].

Naphthyridine derivatives possesses a satisfactorily planarity framework. Since planarity is commonly regarded as a positive structural factor in enhancing the molecular fluorescent properties, these compounds were used not only as luminescence materials in molecular recognition [20–22], but also as new drug leaders and anticancer active screening agents in new drug discovery [23,24].

Therefore, our continuing interests in suitable fluorescent materials [25-27] for analytical and biological chemistry lead to an introduction of the carbazole units to chromeno[4,3,2de][1,6]naphthyridine framework in order to improve the holetransporting ability and fluorescent quantum yield. Although the introduction of the carbazole units reduce the planarity of the chromeno[4,3,2-de][1,6]naphthyridine framework to a certain extent, it indeed enhance the hole-transporting ability and the emission color of these compounds can be easily tuned from blue to green by changing the number of carbazole moieties as expected. Particularly, these compounds exhibit high fluorescence quantum yields and high HOMO energy level (-5.25 to -5.49 eV) due to the presence of the electron-rich amine moieties and increased conjugation lengths, giving rise to more balanced charge-transport characteristics, all of which lead to promising applications in OLEDs.

#### Experimental

#### Chemicals and instruments

All solvents were carefully dried and freshly distilled according to common laboratory techniques. All reactants were commercially available and used without further purification. Melting points were recorded on Electrothermal digital melting point apparatus and were uncorrected. Nuclear Magnetic Resonance (NMR) 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. Cyclic voltammetry was carried on a LK 1200A 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<sub>2</sub>Cl<sub>2</sub> solution in the presence of TBAHFP (tetrabutylammonium hexafluorophosphate)  $(0.10 \text{ mol } \text{L}^{-1})$  as supporting electrolyte.

#### General procedure for the synthesis of compounds 4

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, 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.

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

Yield (0.63 g) 76%, Yellow crysta, Melting points (m.p.) >300 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  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 C<sub>21</sub>H<sub>11</sub>N<sub>4</sub>BrO, M, 414.0116; found, 415.0105 (M + H)<sup>+</sup>.

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

Yield 71%, Yellow solid, m.p. >300 °C. <sup>1</sup>H NMR (400 MHz, DMSOd<sub>6</sub>):  $\delta$  8.61–8.59 (d, 2H, *J* = 8.0), 8.40–8.36 (m, 2H), 7.83–7.81 (d, 2H, *J* = 8.0), 7.79–7.75 (m, 1H), 7.62–7.57 (m, 4H) ppm. HRMS: *m/z* calcd. for C<sub>21</sub>H<sub>11</sub>N<sub>4</sub>BrO, M, 414.0116; found: 415.0115 (M + H)<sup>+</sup>.

5-Amino-2-(4-bromophenyl)-10-bromochromeno[4,3,2-

*de*][1,6]naphthyridine-4-carbonitrile (**4c**).

Yield (0.59 g) 60%, Yellow solid, m.p. >300 °C. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  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 m/z calcd. for  $C_{21}H_{10}N_4Br_2O$ : M, 493.9201; found: 493.9203 (M<sup>+</sup>).

#### 3-Bromo-9-butylcarbazole (6)

In a flask, covered with aluminum foil, a stirred solution of 9butylcarbazole **5** (4.46 g, 20.0 mmol) in CHCl<sub>3</sub> (100 mL) was cooled to 0 °C. N-bromosuccinimide (NBS) (3.56 g, 20.0 mmol) was added in small portions. The mixture was allowed to warm to room temperature overnight. CHCl<sub>3</sub> was evaporated and the crude product was purified by extraction with diethylether and water. After same work up as above, final product was obtained as colorless oil (4.23 g, 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.19 (s, 1H), 8.02 (d, J = 7.2 Hz, 1H), 7.36–7.53 (m, 3H), 7.23–7.26 (m, 2H), 4.23 (t, J = 6.8 Hz, 2H), 1.77–1.87 (m, 2H), 1.28–1.39 (m, 2H), 0.86 (t, J = 7.2 Hz, 3H) ppm.

# 9-Butylcarbazol-3-ylboronic acid (7)

A solution of 6 (3.3 g, 10.0 mmol) in anhydrous THF (50 mL) was cooled to -78 °C. n-BuLi (2.5 mol L<sup>-1</sup> 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<sub>2</sub>Cl<sub>2</sub>  $(3 \times 20 \text{ mL})$ , The organic layer was washed with brine, dried over MgSO<sub>4</sub>, concentrated. Further purification by silica gel column chromatography (petroleum ether/dichloromethane, 2/1, v/v) afforded **7** as a white solid (1.44 g, 54%). m.p. 148–150 °C, <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  8.59 (s, 1H), 8.11 (d, J = 7.5 Hz, 1H), 7.93 (s, 2H), 7.89 (s, 1H), 7.52–7.59 (m, 2H), 7.43 (t, J = 7.5 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 4.38 (t, J = 6.6 Hz, 2H), 1.71–1.76 (m, 2H), 1.25–1.32 (m, 2H), 0.87 (t, *J* = 7.5 Hz, 3H) ppm.

#### *General procedure for the synthesis of compounds* (**8**)

Under a nitrogen atmosphere, a mixture of compounds (**4a–c**) (1.0 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> catalyst (0.04 mmol) and the corresponding carbazole boronic acid was stirred in dry toluene (15 mL). Then, 2 mol L<sup>-1</sup> K<sub>2</sub>CO<sub>3</sub> (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<sub>4</sub>, filtered, concentrated and further purified by column chromatography (silica gel, hexane/dichloromethane, 10/1, v/v). The pure compounds **8a–c** were obtained.

5-Amino-2-(4-(9-butyl-9H-carbazol-3-yl)phenyl)chromeno [4,3,2-*de*][1,6]naphthyridine-4-carbonitrile **(8a).** 

Yield 85%, yellow solid, <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.87– 8.65 (m, 2H), 8.56 (d, 2H, *J* = 8.0 Hz), 8.45 (s, 1H), 8.40–8.38 (m, 1H), 8.30 (d, 2H, *J* = 8.0 Hz), 8.04 (d, 2H, *J* = 8.0 Hz), 7.94–7.91 (m, 1H), 7.83–7.81 (m, 1H), 7.74–7.72 (m, 2H), 7.55–7.49 (m, 5H), 7.27–7.23 (m, 1H), 4.48 (t, 2H, *J* = 6.6 Hz), 1.80–1.85 (m, 2H), 1.34–1.32 (m, 2H), 0.90 (t, 3H, *J* = 7.6 Hz) ppm. IR (cm<sup>-1</sup>): 3448, 3301, 2214, 1630, 1619, 1598, 1560, 1265, 1073, 1007, 825.

HRMS *m/z* calcd. for  $C_{37}H_{27}N_5O$ : M, 557.2216, Found: 556.2224 (M–H)<sup>+</sup>.

5-Amino-10-(9-butyl-9H-carbazol-3-yl)-2-phenylchromeno [4,3,2-*de*][1,6]naphthyridine-4-carbonitrile (**8b**).

Yield 84%, yellow solid, <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  8.94 (s, 1H), 8.67 (s, 1H), 8.60 (s, 1H), 8.51 (m, 2H), 8.30 (d, 1H, *J* = 8.0 Hz), 8.12 (d, 1H, *J* = 8.0 Hz), 8.00–7.95 (m, 1H), 7.75 (d, 1H, *J* = 8.0 Hz), 7.62–7.60 (m, 5H), 7.53–7.49 (m, 2H), 7.25 (m, 1H), 4.47 (t, 2H, 1H), 7.55 (m, 1H), 7.55 (m, 2H), 7.55

*J* = 6.6 Hz), 1.80–1.85 (m, 2H), 1.34–1.32 (m, 2H), 0.9 (t, 3H, *J* = 7.6 Hz) ppm. IR (cm<sup>-1</sup>): 3449, 3312, 2241, 1616, 1594, 1559, 1508, 1474, 1411, 1355, 1262, 775, 669.

HRMS m/z calcd. for  $C_{37}H_{27}N_5O$ : M, 557.2216, Found: 556.2245  $(M-H)^+$ .

5-Amino-10-(9-butyl-9H-carbazol-3-yl)-2-(4-(9-butyl-9H-carbazol-3-yl)phenyl)chromeno[4,3,2-*de*][1,6]naphthyridine-4-carbonitrile **(8c).** 

Yield 81%, yellow solid, <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  8.99 (s, 1H), 8.72 (s, 1H), 8.68–8.64 (m, 3H), 8.33 (m, 2H), 8.14 (d, 1H, J = 8.8 Hz), 8.06 (d, 2H, J = 7.6 Hz), 8.02–8.00 (m, 1H), 7.95 (m, 4H), 7.78–7.73 (m, 2H), 7.65 (d, 3H, J = 8.0 Hz), 7.54–7.50 (m, 3H), 7.28–7.23 (m, 1H), 4.48 (t, 4H, J = 6.6 Hz), 1.80–1.85 (m, 4H), 1.36–1.30 (m, 4H), 0.9–0.89 (t, 6H, J = 7.6 Hz) ppm. IR (cm<sup>-1</sup>): 3447, 3307, 2212, 1594, 1565, 1474, 1416, 1355, 1262, 799, 747.

HRMS *m/z* calcd. for  $C_{53}H_{42}N_6O$ : M, 778.3420, Found: 777.3370  $(M-H)^+$ .



Fig. 1. Synthetic routines for compound 4a-c and 7. Reagents and conditions: (a) silica gel, water, 80 °C; (b) carbazole:NBS = 1:1, CCl<sub>4</sub>, 80 °C; (c) *n*-BuLi (1.2 equiv), THF, -78 °C, (CH<sub>3</sub>O)<sub>3</sub>B (1.5 equiv), H<sub>2</sub>O/HCl.



Fig. 2. Synthetic routines of 8. Reagents and conditions: (d) cat. Pd(PPh<sub>3</sub>)<sub>4</sub>, 2 mol L<sup>-1</sup> K<sub>2</sub>CO<sub>3</sub>, toluene, 90 °C.

Table 1			
Optical properties and	electrochemical	properties	of compounds 8.

Compound	Abs. (nm)	$E_m$ (nm)	$arPhi^{a}$	Band gap <sup>b</sup>	HOMO/LUMO <sup>b</sup> (eV)	$E_g^{c}(eV)$	$E_{\mathrm{ox}}^{\mathbf{d}}(V)$	$E_{\rm HOMO}/E_{\rm LUMO}^{\rm e}~({\rm eV})$
8a	422	502	0.29	3.11	-5.30/-2.19	2.77	0.86	-5.26/-2.49
8b	422	503	0.20	3.33	-5.49/-2.16	2.77	0.89	-5.29/-2.52
8c	417	526	0.22	3.15	-5.25/-2.10	2.75	0.52	-4.92/-2.15

The fluorescence quantum yields ( $\phi$ ) were measured in THF using quinine sulfate ( $\phi$  = 0.55) as standard [17].

<sup>b</sup> DFT/B3LYP calculated values.

Optical energy gaps calculated from the edge of the electronic absorption band. Oxidation potential in  $CH_2Cl_2$  ( $10^{-3}$  mol  $L^{-1}$ ) containing 0.1 mol  $L^{-1}$  ( $n-C_4H_9$ )<sub>4</sub>NPF<sub>6</sub> with a scan rate of 100 mV s<sup>-1</sup>.

<sup>e</sup>  $E_{HOMO}$  was calculated by  $E_{ox}$  + 4.4 V (vs NHE), and  $E_{LUMO} = E_{HOMO} - E_g$ .

#### **Results and discussion**

Compounds 4a-c, 7 were synthesized according to methods described in literature [25,28] (Fig. 1). For products 8a-c, the carbazole moiety was introduced via a Pd(0) catalyzed Suzuki C-C coupling reaction [29] (Fig. 2). All of these new compounds were characterized by MS spectrometry, <sup>1</sup>H NMR spectroscopy.

## Absorption and fluorescence spectra

The absorption spectra of these compounds were measured in CH<sub>2</sub>Cl<sub>2</sub> solutions with a concentration of about  $1.0 \times 10^{-5}$  mol L<sup>-1</sup>. 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 are located in the range of 417–422 nm, which is supposed to be ascribed to the  $\pi$ –  $\pi^*$  transition of the conjugated molecular backbone. The  $\pi$ - $\pi^*$  energy gaps  $(E_g)$  of these compounds were calculated from the UVvis absorption threshold (Table 1) [30-32].

Fig. 4 shows the fluorescence emission spectra of compounds 8 in the excitation of 350 nm. Compounds 8a, 8b and 8c present a green fluorescence emission with the maximum emission peaks at 502 nm, 503 nm and 526 nm, respectively. 8a-c have similar fluorescence spectra because these compounds possess a similar structure in CH<sub>2</sub>Cl<sub>2</sub> solutions. The position of the maximum emission peaks was red-shifted at 526 nm. This is due to 8c possess maxima conjugation length by introduced two carbazole moieties.

The fluorescence quantum yields ( $\phi$ ) were measured in the THF solution using quinine sulfate ( $\phi = 0.55$ ) as a standard (Table 1) [33]. The fluorescence quantum yields of the compounds are in the range of 0.20-0.29. The emission efficiency in dilute solution largely depends on the molecular structure. Moreover, this difference of the quantum yields may appear during the change of the molecular size [34,35].

#### Electrochemical properties

The electrochemical properties of compounds 8 are explored by the cyclic voltammetry in the CH<sub>2</sub>Cl<sub>2</sub> solutions in the presence of tetrabutylammonium hexafluorophosphate  $(0.10 \text{ mol } L^{-1})$  as the supporting electrolyte (Table 1). All of compounds 8 have one irreversible oxidation peak which is an indication of a stable cation radical (Fig. 5). The HOMO energy of these materials was calculated to get a range of -4.92 to -5.26 eV [36,37], which 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) by the introduction of the carbazole moieties, it might be beneficial for the holetransport capacity [38]. Similarly, the optical edge was utilized to deduce the band gap and the LUMO energies. As expected, these compounds are of lower LUMO (-2.15 to -2.52 eV) energies, which represent a small barrier for the electron injection from a commonly used cathode such as barium, which has a work func-



**Fig. 3.** The absorption spectra of compounds **8** ( $1 \times 10^{-5}$  mol L<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>).



**Fig. 4.** The emission spectra of compounds **8**  $(1 \times 10^{-6} \text{ mol } L^{-1} \text{ in CH}_2 \text{Cl}_2)$ .

tion of -2.2 eV [39]. Therefore, these compounds might be very useful as hole-transporting and electron-transporting materials in applications for OLEDs [39].

#### Theoretical calculations

The electronic configurations were further examined using the theoretical models implanted in the Gaussian 03 program [40]. 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 (Table 1).



Fig. 5. Cyclic voltammogram of compound  $8a~(1\times 10^{-3}~mol~L^{-1})$  as sample, in  $CH_2Cl_2$  containing 0.1 mol  $L^{-1}$  (n-C\_4H\_9)\_4NPF\_6, scan rate 100 mV/s.



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



Fig. 7. Calculated spatial distributions of the HOMO, LUMO levels of compound 8c as sample.

Due to an increase in the conjugation lengths, all of these compounds possess a high HOMO energy level (-5.25 to -5.49 eV), which could lead to their better hole-transport properties (Figs. 6 and 7) [38]. The low LUMO energy of these compounds (-2.10 to -2.19 eV) is supposed to facilitate the acceptance of electrons from the cathode. According to the DFT calculations and the experimental data from the UV-absorption spectra, the calculated band gaps show a similar trend. The difference of HOMO/LUMO energy level from calculation data and 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 [41].

# 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 carbazole moieties introduced into chromeno[4,3,2-*de*][1,6]naphthyridine framework increases. Moreover, compounds exhibited high fluorescence quantum yields and excellent green luminescence emission. These compounds possess a high HOMO energy le-

vel (-4.92 to -5.29 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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#### References

- [1] C.W. Tang, S.A. Van Slyke, Appl. Phys. Lett. 51 (1987) 913-915.
- [2] J. Shi, C.W. Tang, Appl. Phys. Lett. 70 (1997) 1665–1667.
- [3] A.P. Kulkami, C.J. Tonzola, A. Bable, S.A. Jenekhe, Chem. Mater. 16 (2004) 4556– 4573.
- [4] L. Pu, Chem. Rev. 98 (1998) 2405-2494.
- [5] K.R.J. Thomas, J.T. Lin, Y.T. Tao, C.K. Ko, J. Am. Chem. Soc. 123 (2001) 9404– 9411.
- [6] K. Brunner, A.V. Dijken, H. Börner, J.J.A.M. Bastiaansen, N.M.M. Kiggen, B.M.W. Langeveld, J. Am. Chem. Soc. 126 (2004) 6035–6042.
- [7] Y. Zhang, T. Wada, L. Wang, H. Sasabe, Chem. Mater. 9 (1997) 2798-2804.
- [8] Q. Zhang, J. Chen, L. Wang, J. Mater. Chem. 14 (2004) 895–900.

- [9] R.M. Adhikari, R. Mondal, B.K. Shah, D.C. Neckers, J. Org. Chem. 72 (2007) 4727-4732
- [10] Z. Zhao, P. Zhang, F. Wang, Z. Wang, P. Lu, W. Tian, Chem. Phys. Lett. 423 (2006) 293-296.
- [11] Y. Xing, X. Xu, P. Zhang, W. Tian, G. Yu, P. Lu, Y. Liu, D. Dao, Chem. Phys. Lett. 408 (2005) 169-173.
- [12] S.W. Cha, J.I. Jin, J. Mater. Chem. 13 (2003) 479-484.
- [13] S.J.Y. Shen, X.L. Yang, T.H. Huang, J.T. Lin, T.H. Ke, L.Y. Chen, C.C. Wu, M.C.P. Yeh, Adv. Funct. Mater. 17 (2007) 983-985.
- [14] K.R. Justin Thomas, M. Velusamy, J.T. Lin, Y.T. Tao, C.H. Chuen, Adv. Funct. Mater. 13 (2004) 387-392.
- [15] B. Liu, W. Yu, Y. Lai, W. Huang, Chem. Mater. 13 (2001) 1984-1991.
- [16] C. Xia, R.C. Advincula, Macromolecules 34 (2001) 5854-5859.
- [17] O. Stephan, J.C. Vial, Synth. Met. 106 (1999) 115-119.
- [18] V. Promarak, M. Ichikawa, T. Sudyoadsuk, S. Saengsuwan, S. Jungsuttiwong, T. Keawin, Synth. Met. 157 (2007) 17-22.
- [19] J. Li, C. Ma, J. Tang, C.S. Lee, S.T. Lee, Chem. Mater. 17 (2005) 615-619.
- [20] T. Peng, T. Murase, Y. Goto, A. Kobori, K. Nakatani, Bioorg. Med. Chem. Lett. 15 (2005) 259-262.
- W. Lu, L. Zhang, X. Ye, J. Su, Z. Yu, Tetrahedron 62 (2006) 1806-1816.
- [22] T.M.D. Joost, H. Astrid, C.B. Annemarie, L. Johan, C. Jan, J. Org. Chem. 61 (1996) 1136-1139.
- [23] L. Chan, H. Jin, T. Stefanac, J.F. Lavallee, G. Falardeau, W. Wang, J. Bedard, S. May, L. Yuen, J. Med. Chem. 42 (1999) 3023-3025.
- [24] A.L. Ruchelamn, S.K. Singh, A. Ray, X.H. Wu, J.M. Yang, A. Liu, L.F. Liu, E.J. Lavoie, Bioorg. Med. Chem. Lett. 11 (9) (2003) 2061-2065.
- [25] H. Wang, J. Shi, C. Wang, X. Zhang, Y. Wan, H. Wu, Dyes Pigments 95 (2012) 268-274.

- [26] H.Y. Wang, J.J. Shi, G. Chen, X.P. Xu, S.J. Ji, Synth. Met. 162 (2012) 241-246.
- [27] H.Y. Wang, G. Chen, X.P. Xu, H. Chen, S.J. Ji, Dyes Pigments 88 (2011) 358-365. [28] A. Bhaskar, G. Ramakrishna, Z. Lu, R. Twieg, J.M. Hales, D.J. Hagan, E. Van
- Stryland, T. Goodson III, J. Am. Chem. Soc. 128 (2006) (1849) 11840-11849. [29] G.K. Paul, J. Mwaura, A.A. Argun, P. Taranekar, J.R. Reynolds, Macromolecules
- 39 (2006) 7789-7792. [30] H. Tian, Chem. Commun. (2009) 5483-5495.
- [31] Z.J. Ning, Q. Zhang, W. Wu, H. Pei, B. Liu, H. Tian, J. Org. Chem. 73 (2008) 3791-3797
- [32] N.X. Hu, S. Xie, Z.D. Popovic, B.A. Wong, M. Hor, Synth. Met. 111 (2000) 421-424.
- [33] P. Wei, X. Bi, Z. Wu, Z. Xu, Org. Lett. 7 (2005) 3199-3202.
- [34] Y. Li, J. Ding, M. Day, Y. Tao, J. Lu, M. Diorio, Chem. Mater. 16 (2004) 2165-2173
- [35] Z. Zhao, X. Xu, Z. Jiang, P. Lu, G. Yu, Y. Liu, J. Org. Chem. 72 (2007) 8345-8353. [36] S. Janietz, D.D.C. Bradley, M. Grell, C. Giebeler, M. Inbaselatan, E.P. Woo, Appl.
- Phys. Lett. 73 (1998) 2453-2455.
- [37] J. Pommerehne, H. Vestweber, W. Guss, R.F. Mahrt, H. Bässler, M. Porsch, J. Daub, Adv. Mater. 7 (1995) 551-554.
- [38] G. Yu, S. Yin, Y. Liu, Z. Shuai, D. Zhu, J. Am. Chem. Soc. 125 (2003) 14816-14824.
- [39] M. Thelakkat, H.W. Schmidt, Adv. Mater. 10 (1998) 219-223.
- [40] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, Gaussian 03, Revision C. 01, Gaussian, Inc.,, Pittsburgh (PA), 2004.
- [41] K.T. Kamtekar, C. Wang, S. Bettington, A.S. Batsanov, I.F. Perepichka, M.R. Bryce, J.H. Ahn, M. Rabinal, M.C. Petty, J. Mater. Chem. 16 (2006) 3823-3835.