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Synthesis and Characterization of Six N-(long-alkyl)carbaldehyde

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Synthesis and Characterization of Six N-(long-alkyl)-carbaldehyde

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Six carbazole aldehyde compounds were synthesized and characterized by ¹H NMR, UV-Vis, and IR spectroscopy. Fluorescence spectroscopy was also discussed, and they all have strong fluorescence. The thermal properties of compounds were studied by TGA-DTA. The compounds are considered to be promising and assistant materials for organic photo-electronic functional materials.

Keywords carbazole, aldehyde carbazole, synthesis, TGA-DTA

INTRODUCTION

Carbazole and its many derivatives have been widely used as organic photo-electronic functional materials due to their \prod conjugated structure, intermolecular charge transfer, and special photo-electronic properties such as electro-photographic receptors and light-emitting diodes.^[1–5] They have been covalently incorporated into polymeric systems both in main-chain^[6,7] as building blocks and in side-chains as pendant group.^[8–11] Carbazole-containing polymers acting as hole-transporting materials and optical materials have been extensively studied.

Carbazole molecules are also quite interesting due to their own photophysical and redox properties: they exhibit relatively intense luminescence^[12] and undergo reversible oxidation processes which make them suitable as hole carriers.^[13] The properties of these carbazole systems prompted us to introduce carbazole branches in porphyrin complexes.^[14] Construction of a rigid carbazole dendron around a porphyrin core may result in interesting photochemical, electrochemical, and catalytic properties. However the synthesis of carbazole aldehyde is also considerablely important to incorporate carbazole unit to porphyrin.

Herein we report the synthesis of six long-chain N-alkyl ($-C_nH_{2n+1}$, n = 12, 14, 16) carbazole substitutes aldehyde. (Scheme 1). The characterization was confirmed by ¹H NMR, UV-Vis, IR, fluorescence spectrometry, XRD, DSC and TGA-

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EXPERIMENTAL

Reagents and Materials

Carbazole (C. P. chemica purity), N, N-dimethylformamide (A. R. analytical reagent), 1-Bromododecane (C. P.), Bromotetradecane (C. P.), Cetyl bromide (C. P.). NaH (A. R.), Perroleum ether (A. R.), Silica gel for Thin-layer Chromatography (C. P.). Phosphorus oxychloride(A. R.), Dichloromethane (A. R.)

Apparatus and Measurements

UV-Vis spectra were recorded on a Shimadzu UV-240 spectrophotometer using dichloromethane as solvents. The IR spectra were recorded on a Nicolet 5PC-FTIR spectrometer in the region 400–4000 cm⁻¹using KBr pellets.¹H NMR spectra were collected on a Varian Unity-400 (MHz) NMR spectrometer using CDCl₃ as solvent, chemical shifts were expressed with tetramethylsilane as the internal reference and reported as position ($\delta_{\rm H}$), relative integral. TGA were carried out by DTG-60 Simultaneous DTA-TGA Apparatus (Sample: 3-8 mg; heating rate: 10°C min⁻¹; atmosphere: Air; Flow rate: 20 ml min⁻¹; Range of temperature: 4°C-1000°C.). Fluorescence spectra were recorded at room temperature with a Shimadzu RF-5301PC spectrofluorometer using dichloromethane as solvent in the region of 300-600 nm and excitation wavelength is 425 nm. DSC (differential scanning calorimetry) was recorded on a NETESCH DSC 204.

Synthesis of the Compounds

Synthesis of the N-Bromododecaned Carbaldehyde (1) and N-Bromododecaned-3, 6-diformylcarbazole (2)

Phosphoryl chloride (0.097 mol, 8.81 ml) was added slowly to DMF (0.194 mol, 12.83 ml), with purging with nitrogen and cooling to 0°C. The Vilsmeier reactant was then allowed to warm to room temperature, stirred for 1 h, and then cooled to 0°C. After that, a solution of N-Bromododecaned carbazole (0.039 mol, 13 g) in 1, 2-dichloroethane (20 mL) was added, and after 1 h the system was warmed to 90°C for 8 h. Finally, the

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SCH. 1. Synthetic routes to N-(long-alkyl)-carbaldehyde (n = 12, 14, 16).

cooled solution was poured into water, extracted with CH_2Cl_2 , and dried with anhydrous magnesium sulfate. The crude product was purified by column chromatography on silica gel (CH_2Cl_2 /Perroleum ether 1.5:1, v/v), the first band gives 9.16 g (65%) of a light yellow solid (1); the second gives 5.31 (35%) of a white solid (2). [17] The other products was obtained by the procedure used for the preparation of 1, 2 and purified by column chromatography.

N-Bromododecaned Carbaldehyde (1)

Yield: 65%. UV-Vis (dichloromethane, λ max/nm, molar extinction coefficients are in parentheses, cm² mol⁻¹) 237(5.05 × 10⁴) 278(5.53 × 10⁴) 294(5.41 × 10⁴) 327 (2.30 × 10⁴); IR (KBr): ν^{\sim} = 3049, 2953, 2918, 2850, 1691, 1625, 1593, 1566, 1493, 1381, 807 cm⁻¹; a strong peak at 1691 cm⁻¹ is the ν_s of a C = O moiety. 2850 (v_s of a C-H in the CHO), 809 (C-H aromatic ring out-of-plane);¹H NMR (CDCl₃, 400 MHz): δ = 10.10 (s, 1 H, -HC=O), 7.62–8.62 (7 H, Ar–H), 4.32–4.36(t, 2 H, -NCH₂–), 1.23–1.91 (20 H, -CH₂–), 0.86–0.89 (t, 3 H, -CH₃) ppm.

N-Bromododecaned-3, 6-diformylcarbazole (2)

Yield: 35%. UV-Vis (dichloromethane, $\lambda \max/nm$, molar extinction coefficients are in parentheses, cm² mol⁻¹) 270 (4.34 × 10⁴) 343(2.64 × 10⁴); IR (KBr): ν^{\sim} = 2953, 2918, 2847, 1681, 1626, 1593, 1488, , 1383, 806 cm⁻¹; a strong peak at 1681 cm⁻¹ is the ν_s of a C = O moiety.;¹H NMR (CDCl₃,

400 MHz): $\delta = 10.104$ (s, 2 H, -HC = O), 7.26–8.68 (6 H, Ar–H), 3.77–4.41 (t, 2 H, –NCH₂–), 1.23–1.93 (20 H, –CH₂–), 0.85–0.89 (t, 3 H, –CH₃) ppm.

N-Bromotetradecaned Carbaldehyde (3)

Yield: 60%. UV-Vis (dichloromethane, $\lambda max/nm$, molar extinction coefficients are in parentheses, cm² mol⁻¹) 238(4.47 × 10⁴) 278(4.77 × 10⁴) 294(4.36 × 10⁴) 327 (2.01 × 10⁴); IR (KBr): ν^{-} =3049, 2953, 2917, 2850, 1690, 1625, 1593, 1567, 1470, 809, 1381, 807 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ = 10.10 (s, 1 H, -HC = O), 7.26–8.62 (7 H, Ar–H), 4.32–4.36(t, 2 H, -NCH₂–), 1.23–1.91 (24 H, -CH₂–), 0.86–0.89 (t, 3 H, -CH₃) ppm.

N-Bromododecaned-3, 6-diformylcarbazole (4)

Yield: 37%. UV-Vis (dichloromethane, $\lambda max / nm$, molar extinction coefficients are in parentheses, cm² mol⁻¹) 269(6.41×10⁴) 342(3.75×10⁴); IR (KBr): $\nu^{\sim} = 2954$, 2918, 2848, 1684, 1626, 1594, 1570,1488, 1383, 806 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): $\delta = 10.104$ (s, 2 H, -HC=O), 7.26–8.68 (6 H, Ar–H), 3.49–4.41(t, 2 H, -NCH₂–), 1.23–1.92 (24 H, -CH₂–), 0.86–0.94 (t, 3 H, -CH₃) ppm.

N-Cetyl Bromided Carbaldehyde (5)

Yield: 58%. UV-Vis (dichloromethane, λ max/nm, molar extinction coefficients are in parentheses, cm² mol⁻¹) 235(3.90 \times 10⁴) 276(4.20 \times 10⁴) 293(4.12 \times 10⁴) 329(1.77 \times 10⁴); IR



FIG. 1. (a) UV-Vis spectra of N-(long-alkyl)-carbaldehyde (1, 3, 5).(b) UV-Vis spectra of N-(long-alkyl)-3, 6-diformylcarbazole compounds (2, 4, 6).

TABLE 1 UV-Vis spectra of compounds

Compounds I II III IV 1 237 (5.05×10^4) 278 (5.53×10^4) 294 (5.41×10^4) 327 (2.30×10^4)	Max. absorption peaks(λ max nm); (ε max L mol ⁻¹ cm ⁻¹)					
$1 237 (5.05 \times 10^4) 278 (5.53 \times 10^4) 294 (5.41 \times 10^4) 327 (2.30 \times 10^4)$						
	(0^4)					
2 $270 (4.34 \times 10^4)$ $343 (2.64 \times 10^4)$	$0^{4})$					
3 $238 (4.47 \times 10^4)$ $278 (4.77 \times 10^4)$ $294 (4.73 \times 10^4)$ $327 (2.01 \times 10^4)$	0^{4}					
4 $269 (6.40 \times 10^4)$ $342 (3.75 \times 10^4)$	0^{4}					
5 $235 (3.89 \times 10^4)$ $276 (4.20 \times 10^4)$ $293 (4.12 \times 10^4)$ $329 (1.77 \times 10^4)$	$0^{4})$					
6	0^{4}					

FIG. 2. UV-Vis spectra of compounds 3 and 4.

(KBr): $\nu^{\sim} = 2954$, 2912, 2850, 1692, 1595, 1567, 1471, 1381, 809 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): $\delta = 10.10$ (s, 1 H, –HC=O), 7.26–8.62 (7 H, Ar–H), 4.32–4.36(t, 2 H, –NCH₂–), 1.23–1.91 (24 H, –CH₂–), 0.86–0.89 (t, 3 H, –CH₃) ppm.

N-Cetyl Bromided-3, 6-diformylcarbazole (6)

Yield: 38%. UV-Vis (dichloromethane, $\lambda max/nm$, molar extinction coefficients are in parentheses, cm² mol⁻¹) 270(5.07 × 10⁴) 342(2.99 × 10⁴); IR (KBr): $\nu^{\sim} = 2954$, 2917, 2848, 1686, 1627, 1594, 1570,1488, 1383, 807 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): $\delta = 10.14$ (s, 2 H, -HC=O), 7.26–8.68 (6 H, Ar–H), 3.77–4.41(t, 2 H, -NCH₂–), 1.23–1.93 (28 H, -CH₂–), 0.86–0.92 (t, 3 H, -CH₃) ppm.

RESULTS AND DISCUSSION

UV-Vis Spectra

UV-Vis absorption spectra of the six compounds 1-6 in dichloromethane at the room temperature are shown in Figure 1. Table 1 gives the absorption spectrum of six compounds. In



FIG. 3. (a) Fluorescence spectra of N-(long-alkyl)-carbaldehyde (1, 3, 5). (b) Fluorescence spectra of N-(long-alkyl)-3, 6-diformylcarbazole compounds (2, 4, 6).

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Compounds	Dec. temp.(1) (°C)	Dec. temp.(2) (°C)	Com.temp. (°C)	Lost weight (%)	Exothermal peaks (°C)
1	318		495		354, 548
2	351	440	553	57.87	387, 473, 580
3	323		518		358,543
4	333	431	529	65.02	373, 467, 547
5	355		528		378, 552
6	349	453	540	61.16	384, 472, 561

TABLE 2 Detailed thermal analytical data



FIG. 4. Fluorescence spectra of compounds 3 and 4.

the absorption spectrum of the N-(long-alkyl)-carbaldehyde (1, 3, 5), the absorption bands at 235–238 nm originate from intraligand $\pi - \pi^*$ transition of carbazole unit, and the absorption bands at about 276–329 nm are due to n- π^* transition in carbazole ring. However, there are no absorption bands at about 235–238 nm in three N-(long-alkyl)-3, 6-diformylcarbazole compounds (2, 4, 6). Their maximum absorption bands at about 270, 342 nm are all attributed to n- π^* transition of the carbazole ring, and maybe the absorption bands arising from n- π^* transition in the carbazole ring lay over the one arising from $\pi - \pi^*$ transition inner carbazole unit. The absorption band of the compounds 2, 4, 6 exhibits a red shift comparing to that in compounds 1, 3, 5. (see Figure 2).

Fluorescence Spectra

Luminescent properties of the six compounds were investigated in dichloromethane solution at room temperature. The fluorescence spectra of six compounds are shown in Figure 3. The fluorescent spectra of the N-(long-alkyl)-carbaldehyde (1, 3, 5) display maximum emission wavelengths (λ em, max) at 405–410 nm with excitation wavelengths at 270 nm in dichloromethane solution, and maximum emission wavelengths (λ em, max) at



FIG. 5. TGA and DTA curves of compounds 3 and 4.

367 nm with excitation wavelengths at 296 nm for the N-(longalkyl)-3, 6-diformylcarbazole compounds (**2**, **4**, **6**), respectively. Compared with the N-(long-alkyl)-carbaldehyde (**1**, **3**, **5**), the N-(long-alkyl)-3, 6-diformylcarbazole compounds (**2**, **4**, **6**) exhibit a red shift in dichloromethane solution (see Figure 4).

Thermal Analysis

Thermal gravimetric analyses of the N-(long-alkyl)carbaldehyde (1, 3, 5) and N-(long-alkyl)-3, 6-diformylcarbazole compounds (2, 4, 6) have been carried out. Table 2 gives the detailed thermal analytical data. These six compounds were seen to be thermally stable up to 300–350°C. However, the N-(long-alkyl)-3, 6-diformylcarbazole compounds (2, 4, 6) and the N-(long-alkyl)-carbaldehyde (1, 3, 5) show slightly different thermal processes. Three N-(long-alkyl)-carbaldehyde (1, 3, 5) exhibit similar TG curves with only one obvious loss weight process. They began to decompose at about 317-355°C and completed at 495-528°C, which indicated continuous exothermic processes occurred in this step. Three N-(long-alkyl)-3, 6-diformylcarbazole compounds (2, 4, 6) exhibited similar TG curves with second obvious loss weight processes. 2 is taken as an example. The first stage started at 351°C and completed at 440 °C with the loss of long-alkyl. The observed weight loss was 41.84%, in good agreement with the calculated weight loss 42.80%. The second stage attained a strong exotherm at 472.83°C while the process is complete up to 553.08°C, corresponding to the carbazole skeleton collapses. Compared with the N-(long-alkyl)-3, 6-diformylcarbazole compounds (2, 4, 6), the N-(long-alkyl)- carbaldehyde (1, 3, 5) exhibited continuous decomposed processes. Figure 5 presents the TG and DTA curves of compound 3 and 4, respectively.

REFERENCES

- Morin, J. F., Leclerc, M., Ades, D., and Siove, A. Polycarbazoles. *Macromol Rapid Commun.* 2005, 26, 761–778.
- Grigalevicius, S. 3, 6 (2, 7), 9-Substituted carbazoles as electroactive amorphous materials for optoelectronics. *Synth. Met.* 2006, 156, 1–12.

- Konig, B., Polka, M., Zieg, H., Ritter, T., Bouas-Laurent, H., Bonneau, R., and Desvergne, J.P. Photoinduced electron transfer in a phenothiazineriboflavin dyad assembled by zinc-imide coordination in water. *J. Am. Chem. Soc.* **1999**, 121(8), 1681–1687.
- Dalton, L.R., and Sapochak, L. S. Recent advances in non-linear of spectroscopy and nonlinear optical materials. J. Phys. Chem. 1993, 97(12), 2871–2883.
- Bailey, N. The future of organic light-emitting diodes. *Informatin Display* 2003, 3, 12–16.
- Sotzing, G. A., Reddinger, J.L., Katritzky, A. R., Soloducho, J., Richard, M., and John, R. R. Multiply colored electrochromic carbazole-based polymers. *Chem. Mater.* 1997, 9(7), 1578–1587.
- Zhang, Y. D., Wada, T., and Sasabe, H. J. Carbazole main-chain polymers for multifunctional materials: Synthesis and characterization. *Polym. Sci. A: Polym. Chem.* **1996**, 34 (12), 2289–2298.
- Ho, M. S., Barrett, C., Paterson, J., Esteghamatian, M., Natansohn, A., and Rochon, P. Synthesis and optical properties of poly(4-nitrophenyl)-[3-[*N*-[2-(methacryloyloxy) ethyl]-carbazolyl]] diazene. *Macromolecules*. 1997, 29(13), 4613–4618.
- Gratt, J., and Cohen, R.E. Synthesis of block copolymers containing pendant carbazole groups via living ring-opening metathesis polymerization. *Macromolecules*. 1997, 30, 3137–3140.
- Tsai, F. C., Chang, C. C., Liu, C. L., Chen, W. C., and Jenekhe, S. A. New thiophene–ILinked conjugated poly (azomethine)s. *Theoretical Electronic Structure, Synthesis, and Properties, Macromolecules* 2005, 38, 1958–1966.
- Dobarro, A., Velasco, D., Arnim, V., and Finkelmann, H. Synthesis of symmetric and asymmetric carbazolyl monomers and their siloxane polymers. Effect of the 2, 3, 6, 7, 9-substitution in the carbazole unit on its mesomorphic behaviour. *Macromol. Chem. Phys.* **1997**, 198 (8), 2563–2581.
- (a) Howell, A. G., Taylor, A. G., and Phillips, D. Chem. Phys. Lett. 1992, 188, 119–125. (b) Yu, H., Mohd Zain, S., Eigenbrot, I.V., Phillips, D. Chem. Phys. Lett. 1993, 202, 141–147.
- Kido, J., Hongawa, K., Okuyama, K., and Nagai, K. Appl. Phys. Lett. 1993, 63, 2627–2629.
- McClenaghan, N. D., Passalacqua, R., Loiseau, F., Campagna, S., Verheyde, B., Hameurlaine, A., and Dehaen, W. J. J. Am. Chem. Soc. 2003, 125, 5356– 5365.
- Yang, J.X., Tao, X.T., Yuan, C.X., Yan, Y.X., Wang, L., Liu, Z., Ren, Y., and Jiang, M.H. A facile synthesis and properties of multicarbazole molecules containing multiple vinylene bridges. *J. Am. Chem. Soc.* **2005**, 127(10), 3278–3279.
- Xu, T.H., Lu, R., Qiu, X.P., Liu, X.L., Xue, P.C. Tan, C.H., Tan, Y.B, and Zhao, Y.Y. Synthesis and characterization of carbazole based dendrimers with porphyrim cores. *Eur. J. Org. Chem.* 2006, 4014– 4020.