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Blue-light-emitting carbazole derivates with high thermal stability

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ABSTRACT

A new series of fluorescent compounds containing tricarbazolyl groups have been synthesized. The compounds have very high glass transition temperatures in the range 243–266 °C, high decomposition temperatures of 506–527 °C, and exhibit strong blue fluorescence with maximum emission wavelengths at 445–457 nm. The compounds have good solubility in common solvents even though they contain rather rigid wholly aromatic structures. The thermal stability of these compounds exhibits a marked odd–even effect corresponding to the number of phenylene bridges in the compound. In the solid, the maximum photoluminescence emission wavelength with *n* odd have a slight bathochromic shift in comparison to those with *n* even.

1. Introduction

A large number of blue light-emitting materials have been investigated for possible applications as organic light-emitting diodes (OLEDs) [1–4]. However, it is not easy to produce blue light-emitting materials with the required levels of brightness and thermal stability. The undesirable properties include: (1) a wide band gap; (2) a low glass transition temperature (T_g); and (3) aggregation quenching [5–7]. Recently, the synthesis and application of carbazole derivatives with well-known charge-transporting and high thermal properties [8–12], as well as blue luminescent properties has been of great interest for chemists and materials scientists alike [13,14]. In this study, we investigated the possibility of developing a new class of tricarbazole-derived blue light-emitting materials with high levels of both fluorescence efficiency and thermal stability.

2. Experimental

2.1. Materials and methods

All reagents and chemicals purchased from Alfa–Aesar were used as received. ^{1}H NMR was measured with a Mercury-Plus 300 spectrometer with chemical shifts reported as ppm (in $CDCl_3$, with tetramethylsilane (TMS) as the internal standard). Mass spectra (MS) were measured with Thermo spectrometers (MAT95XP-HRMS). Elemental analysis (EA) was done with an Elementar Vario EL Elemental Analyzer. Fluorescence spectra were determined with a Shimadzu RF-5301PC spectrometer. The fluorescence quantum yields (Φ_{FL}) were measured by the standard optically diluted method [15] in degassed CH_2Cl_2 solutions (ca. 10^{-5} M) using 9,10-diphenylanthracene ($\Phi_{FL} = 0.90$, in CH_2Cl_2) as a reference standard [16,17]. Differential scanning calorimetry (DSC) curves were obtained with a TA thermal analyzer (Q10) at a heating rate of 10 °C/min under a N_2 atmosphere. Thermogravimetric analysis (TGA) was done with a TA thermal analyzer (A50) under a N_2 atmosphere at a heating rate of 20 °C/min. The thermal decomposition temperatures reported correspond to a 5% weight loss.

2.2. General procedure for Wittig–Horner reaction

A solution of compound **3** (11 mmol) and corresponding diphosphonate ylide reagent (5 mmol) in anhydrous tetrahydrofuran (50 mL) was stirred under a N_2 atmosphere at 0 °C. Potassium tert-butoxide (15 mmol) was added quickly and the mixture was stirred continuously for 5 h at room temperature, and then precipitated into ethanol. The crude product was collected, and washed three times with ethanol. The crude product was recrystallized

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from dichloromethane/*n*-hexane (1:5, v/v) to obtain the pure compounds **CCPVP$_1$**, **CCPVP$_2$**, **CCPVP$_3$**, and **CCPVP$_4$.**

2.2.1. *CCPVP1*

Yellow powder; yield 86.5%;^{1}H NMR (300 MHz, CDCl$_3$) 7.28–7.32 (12H, m), 7.37–7.43 (16H, m), 7.60–7.79 (16H, m), 7.85–7.91 (4H, d), 8.13–8.19 (8H, m), 8.29 (4H, d); IR 3044, 1597, 1492, 1460, 1336, 1270, 1226, 1151, 810, 749 cm^{-1}; FAB-MS (*m*/*z*) 1273 [M$^+$]; Anal. calcd for $C_{94}H_{60}N_6$ (1273.52): C 88.65, H 4.75, N 6.60; found: C 88.78, H 4.69, N 6.48.

2.2.2. *CCPVP2*

Yellow powder; yield 83.9%;^{1}H NMR (300 MHz, CDCl$_3$) 7.29–7.35 (12H, m), 7.37–7.43 (16H, m), 7.62–7.79 (20H, m), 7.84–7.91 (4H, d), 8.13–8.19 (8H, m), 8.29 (4H, d); IR 3039, 1597, 1492, 1462, 1326, 1276, 1226, 1156, 817, 749 cm^{-1}; FAB-MS (*m*/*z*) 1349 [M$^+$]; Anal. calcd for $C_{100}H_{64}N_6$ (1349.62): C 88.99, H 4.78, N, 6.23; found: C 89.08, H 4.85, N 6.15.

2.2.3. *CCPVP$_3$*

Yellow powder; yield 90.9%;^{1}H NMR (300 MHz, CDCl$_3$) 7.27–7.35 (12H, m), 7.37–7.45 (16H, m), 7.60–7.66 (4H, d), 7.68–7.80 (20H, m), 7.85–7.92 (4H, d), 8.13–8.20(8H, m), 8.29 (4H, d); IR 3029, 1597, 1487, 1467, 1326, 1276, 1226, 1156, 820, 749 cm^{-1};FAB-MS (*m*/*z*) 1426 [M$^+$]; Anal. calcd for $C_{106}H_{68}N_6$ (1425.71): C 89.30, H 4.81, N 5.89; found: C 89.27, H 4.77, N, 5.81.

2.2.4. *CCPVP$_4$*

Yellow powder; yield 74.3%;^{1}H NMR (300 MHz, CDCl$_3$) 7.27–7.35 (12H, m), 7.36–7.44 (16H, m), 7.61–7.66 (4H, d), 7.66–7.81 (24H, m), 7.85–7.92 (4H, d), 8.13–8.20 (8H, m), 8.29 (4H, d); IR 3029, 1592, 1477, 1381, 1321, 1276, 1226, 1151, 810, 745 cm^{-1}; FAB-MS (*m*/*z*) 1502 [M$^+$]; Anal. calcd for $C_{112}H_{72}N_6$ (1501.81): C 89.57, H 4.83, N 5.60; found: C 89.51, H 4.79, N 5.56.

3. Results and discussion

3.1. Synthesis

Our strategy for the synthesis of the new class of tricarbazole derivatives is outlined in Fig. 1. The intermediate compounds 4-(9H-carbazol-9-yl)benzaldehyde (**1**) [18], 4-(3,6-diiodo-9H-carbazol-9-yl) benzaldehyde (**2**) [19], 4-(6-(9H-carbazol-9-yl)-3,9′-bi(9H-carbazol)-9-yl)benzaldehyde (**3**) [20], and the terphenyl and quaterphenyl diphosphonate ylide reagents [21,22] were synthesized by modification of methods in the literature. The other reagents and chemicals were purchased from commercial sources as analytical grade reagents and used without further purification. The Wittig–Horner reaction of the corresponding diphosphonate ylide reagents with a slight excess of **3** in the presence of potassium t-butoxide gave four target compounds (named **CCPVP$_1$**, **CCPVP$_2$**, **CCPVP$_3$**, and **CCPVP$_4$** according to the number (*n*) of phenylene bridges) in yields of >74% after purifi-

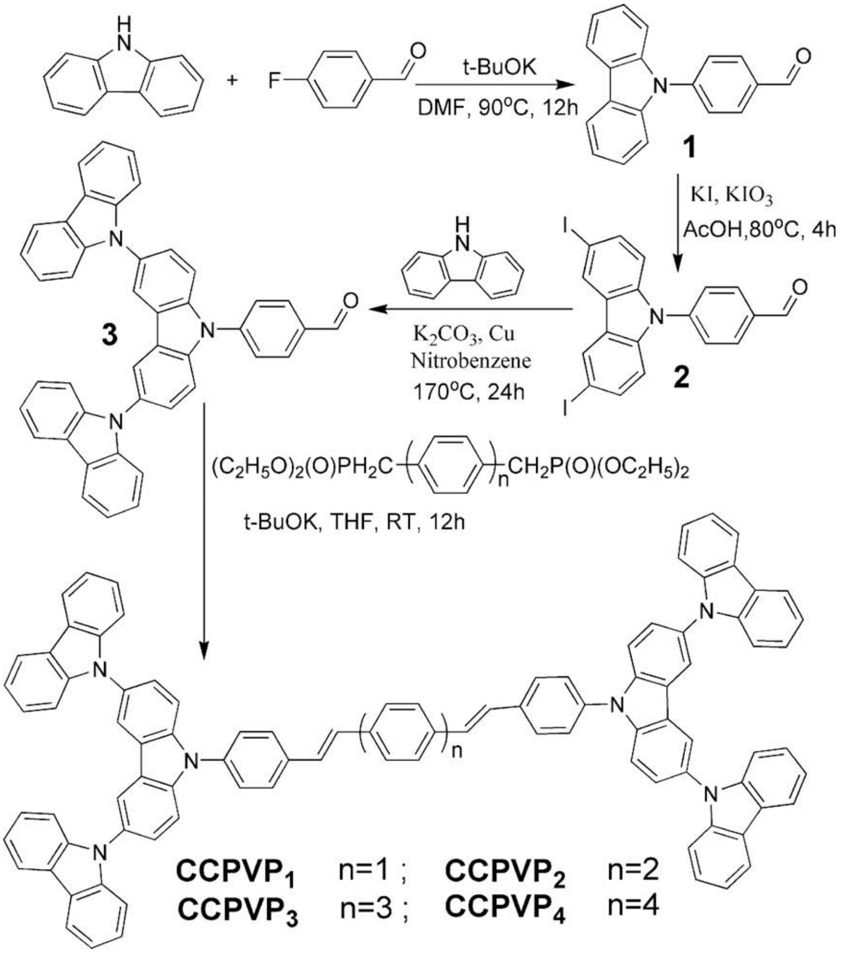

Fig. 1. Synthetic routes to the derivatives.