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Synthesis and optical properties of the isomeric pyrimidine and carbazole derivatives: Effects of polar substituents and linking topology

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ABSTRACT

A series of nonlinear oligoarylenes with a pyrimidine unit as central core and carbazole containing aryl branches in positions 2, 4 and 4, 6 of the pyrimidine ring were successfully synthesized by sequential Suzuki coupling of the corresponding 2,4- or 4,6-dichloropyrimidines. Optical properties of the compounds were thoroughly investigated in the media of different polarity. Owing to pronounced electron-accepting properties of pyrimidine core, the compounds with donating carbazole groups showed expressed intramolecular charge transfer (ICT) character of the excited states, which was proved by solvatochromic dynamics and supported by DFT calculations. ICT resulted in the dramatic enhancement of excited state lifetime (up to 5 times) with increased solvent polarity. The competition of constantly decreasing radiative and nonradiative relaxation rates resulted in non-monotonous variation of fluorescence quantum yield from 24% to 74%. The tailoring of fluorescence quantum yield of the pyrimidine derivatives via altering linking topology and polarity of the substituents is discussed.

1. Introduction

Over recent years, organic molecules with a π-conjugated backbone have received much attention in both academic and industry due to their applications in a wide range of electronic and optoelectronic devices [1]. Introduction of heteroaryl moieties into the backbone of π-extended systems considerably influence molecular orbitals, stereochemical structure and linking topology of the substituents. In particular, azaheterocyclic compounds are widely used in organic electronic devices, such as organic light emitting devices (OLEDs), solar cells, sensors [2] etc. Owing to strong aromaticity, significant π-deficiency, presence of n-π electronic states, pH sensitivity, and ability of its nitrogen atoms to take part in the chelation processes, pyrimidine, among other azaheterocycles is a desired functional moiety to be incorporated in more complex organic structures targeted for numerous applications [3]. π-Conjugated pyrimidine derivatives have been recently utilized in the fabrication of OLEDs [4], sensors [5], supramolecular assemblies [6], liquid crystals [7], and dyes for solar cells [8]. Pyrimidine ring is frequently used in push–pull structures as strong electron-withdrawing unit and together with electron-donating moieties results in intramolecular charge transfer character, which plays a key role in most of the important applications.

On the other hand, carbazole is a well-known donor featuring good hole transporting properties [9], intense blue luminescence and electroluminescence [10], rigid structure and enhanced thermal stability [11]. Thus, it has been widely used as functional building block in the fabrication of various optoelectronic devices [12]. Recently, carbazole derivatives [13]a,b and bipolar 1,3,4-oxadiazole and pyrimidine derivatives bearing carbazole based arms have been found to be useful as host materials for phosphorescent OLEDs [1g,13c–f].

Herein we report on the synthesis and photophysical properties of novel donor-acceptor-type chromophores based on a pyrimidine core and carbazolylphenyl branches at the periphery. Multifragment pyrimidine systems were analysed with an emphasis on

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emission properties induced by the polarity and linking topology of various aryl substituents.

2. Experimental section

2.1. General information

All reagents and solvents were purchased from commercial sources and dried by using standard procedures before use. Melting points were determined in open capillaries with a digital melting point IA9100 series apparatus (ThermoFischer Scientific). ^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA spectrometer (300 MHz and 75 MHz respectively) using residual solvent peaks as an internal standard.

Elemental analysis was performed with a ThermoFischer Scientific Flash 2000 elemental analyzer.

High Resolution Mass Spectrometry (HRMS) analyses were carried out on a quadrupole, time-of-flight mass spectrometer (microTOF-Q II, Bruker Daltonik GmbH, Bremen, Germany).

Column chromatography was performed using Silica gel 60 (0.040–0.063 mm) (Merck). All reactions and purity of the synthesized compounds were monitored by TLC using Silica gel 60 F_{254} aluminium plates (Merck). Visualization was accomplished by UV light.

The absorption spectra were recorded on a Perkin–Elmer UV-vis-NIR spectrophotometer Lambda 950. Fluorescence of the sample solutions was excited by 320 nm wavelength light-emitting diode and measured using back-thinned CCD spectrometer (Hamamatsu PMA-11). The fluorescence quantum yield (Φ_F) of the solutions was estimated by comparing wavelength-integrated fluorescence intensity of the solution with that of the reference. Quinine sulfate in 0.1 M H_2SO_4 was used as a reference. Optical densities of the reference and the sample solutions were ensured to be below 0.05 to avoid reabsorption effects. Estimated quantum yield was verified by using an alternative method of an integrating sphere (Sphere Optics), which was coupled to the CCD spectrometer by an optical fiber. Fluorescence transients of the sample solutions were measured using time-correlated single photon counting system (PicoQuant PicoHarp 300).

Cyclic voltammetry experiments were performed on the Edaq ER466 Integrated Potentiostat System. Pt/Ti wire, glassy carbon disk [Ø 3.0 mm] and Ag/AgCl were used as counter, working, and reference electrodes, respectively. In all cases, CV experiments were performed in DMF (*N*,*N* − dimethylformamide) with tetrabutylammonium perchlorate - as supporting electrolyte (0.1 M) under Ar flow; concentrations of compounds were 0.002 M. The scan rate was 50 mV s^{-1}.

2.2. General procedure for the synthesis of 4-aryl-2-chloro-6-methylpyrimidines (**2a–c**)

To a solution of 2,4-dichloro-6-methylpyrimidine (**1**) (0.3 g, 1.84 mmol) in dioxane (10 mL) $Pd(OAc)_2$ (20.6 mg, 0.092 mmol, 5 mol%) and PPh_3 (48.3 mg, 0.184 mmol, 10 mol%) were added and the reaction mixture was stirred for 15 min. Then the corresponding arylboronic acid (2.2 mmol) and saturated solution of sodium carbonate (1.33 ml) were added and the reaction mixture was refluxed for 6–10 h under argon atmosphere. The solvents were evaporated under reduced pressure to dryness, the residue was dissolved in water and the solution was extracted with CH_2Cl_2. The organic layer was dried with Na_2SO_4, filtered and evaporated to dryness. The obtained solid was purified by column chromatography using chloroform as an eluent.

2.2.1. 2-Chloro-4-(4-methoxyphenyl)-6-methylpyrimidine (**2a**)

The general procedure was followed using 4-methoxyphenylboronic acid (0.33 g, 2.2 mmol). Reaction time 6.5 h. Yield 0.173 g (40%), mp 66–67 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 2.59 (s, 3H, CH_3), 3.91 (s, 3H, CH_3), 7.02 (d, $J = 8.7$ Hz, 2H, CH), 7.45 (s, 1H, CH), 8.08 (d, $J = 8.7$ Hz, 2H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 24.4, 55.7, 113.9, 114.6, 127.9, 129.3, 161.5, 162.8, 166.5, 170.6. Anal. Calcd. for $C_{12}H_{11}N_2ClO$: C, 61.41; H, 4.72%; found: C, 61.49; H, 4.77%. HRMS-ESI: *m*/*z* calcd. for MH^+ ($C_{12}H_{12}N_2ClO$): 257.0452, found: 257.0457.

2.2.2. 4-(1,1′-Biphenyl-4-yl)-2-chloro-6-methylpyrimidine (**2b**)

The general procedure was followed using 4-biphenylboronic acid (0.44 g, 2.2 mmol). Reaction time 10 h. Yield 0.171 g (33%), mp 121–122 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 2.64 (s, 3H, CH_3), 7.58–7.44 (m, 4H, CH), 7.67–7.71 (m, 2H, CH), 7.77 (d, $J = 8.7$ Hz, 2H, CH), 8.19 (d, $J = 8.7$ Hz, 2H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 24.5, 114.8, 127.4, 127.9, 128.1, 128.4, 129.2, 134.3, 140.2, 144.7, 161.7, 166.6, 171.1. Anal. Calcd. for $C_{17}H_{13}N_2Cl$: C, 72.73; H, 4.67%; found: C, 72.89; H, 4.88%. HRMS-ESI: *m*/*z* calcd. for MH^+ ($C_{17}H_{14}N_2Cl$): 303.0659, found: 303.0662.

2.2.3. 2-Chloro-4-[4-(9H-carbazol-9-yl)phenyl]-6-methylpyrimidine (**2c**)

The general procedure was followed using 4-(9-carbazolyl) phenylboronic acid (0.63 g, 2.2 mmol). Reaction time 6 h. Yield 0.40 g (59%), mp 159–161 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 2.68 (s, 3H, CH_3), 7.30–7.39 (m, 2H, CH), 7.47–7.52 (m, 4H, CH), 7.63 (s, 1H, CH), 7.78 (d, $J = 8.7$ Hz, 2H, CH), 8.19 (d, $J = 9$ Hz, 2H, CH), 8.36 (d, $J = 9$ Hz, 2H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 24.6, 110.0, 114.9, 120.7, 120.8, 124.0, 126.4, 127.4, 129.3, 134.2, 140.6, 141.2, 161.8, 166.1, 171.4. Anal. Calcd. for $C_{23}H_{16}N_3Cl$: C, 74.69; H, 4.36%; found: C, 74.83; H, 4.59%. HRMS-ESI: *m*/*z* calcd. for MH^+ ($C_{23}H_{17}N_3Cl$): 392.0925, found: 392.0924.

2.3. General procedure for the synthesis of 2,4-diaryl-6-methylpyrimidines (**3a–d**)

To a solution of 4-aryl-2-chloro-6-methylpyrimidine (**2a–c**) (0.36 mmol) in anhydrous dioxane (10 ml) $Pd(OAc)_2$ (1.6 mg, 0.0072 mmol, 2 mol%) and 2-biphenyldicyclohexylphosphine (5.05 mg, 0.014 mmol, 4 mol%) were added and the reaction mixture was stirred for 15 min. Then the corresponding arylboronic acid (0.43 mmol) and K_3PO_4 (0.18 g, 0.85 mmol) were added and the reaction mixture was refluxed for 5.5–18 h under argon atmosphere. The solvent was evaporated under reduced pressure to dryness, the residue was dissolved in water and the solution was extracted with CH_2Cl_2. The organic layer was dried with Na_2SO_4, filtered and evaporated to dryness. The obtained solid was purified by column chromatography using chloroform as an eluent.

2.3.1. 2-[4-(9H-Carbazol-9-yl)phenyl]-6-methyl-4-(4-methoxyphenyl)pyrimidine (**3a**)

The general procedure was followed using 4-(9-carbazolyl) phenylboronic acid (0.12 g, 0.43 mmol). Reaction time 5.5 h. Yield 0.11 g (68%), mp 163–164 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 2.71 (s, 3H, CH_3), 3.95 (s, 3H, OCH_3), 7.1 (d, $J = 8.4$ Hz, 2H, CH), 7.35–7.57 (m, 7H, CH), 7.76 (d, $J = 9$ Hz, 2H, *CH*), 8.21 (d, $J = 7.5$ Hz, 2H, CH), 8.28 (d, $J = 9$ Hz, 2H, CH), 8.84 (d, $J = 9$ Hz, 2H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 24.9, 55.7, 110.2, 113.5, 114.5, 120.3, 120.6, 123.8, 126.3, 127.5, 129.0, 130.2, 131.2, 137.5, 139.8, 140.9, 162.2, 163.6, 163.8, 167.9. Anal. Calcd. for $C_{30}H_{23}N_3O$: C, 81.61; H, 5.25%; found: C, 81.79; H, 5.42%. HRMS-ESI: *m*/*z* calcd. for MH^+ ($C_{30}H_{24}N_3O$): 442.1914, found: 442.1922.