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Emission properties of Si-based styryl-carbazole derivatives: Role of *meta*- and *para*-vinyl substituents and silicon atom

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ABSTRACT

A series of styryl-carbazole derivatives (with and without a silicon atom) were investigated in *n*-hexane and in acetonitrile in terms of their spectroscopic and photophysical properties. The major question addressed in this work is how the presence of a trimethylsilyl group modifies the absorption and emission properties of styryl-carbazoles depending whether vinyl groups are in a *meta*- or *para*- position. It was observed that only *para*-styryl-carbazole containing silicon undergoes a solvent-induced inversion of its lowest singlet excited states whereas *meta*-styryl-carbazole containing silicon retains the properties of the *meta*-styryl-carbazole itself. The different character of the emissive state was deduced from its 7-fold larger radiative rate constant in acetonitrile compared to results in *n*-hexane. DFT calculations revealed on the molecular level why inversion of the excited states occurs only for this silicon-based styryl-carbazole whose vinyl group is in the *para*- and not in the *meta*- position.

1. Introduction

Silicon-based carbazole derivatives constitute a class of compounds having a potential for serving as light emitting materials [1,2]. As such, their emission properties and the possible modifications of these properties are of interest [3–6]. In our previous work [6] we showed how the introduction of silicon can modify the emission properties of selected silicon-based styryl carbazole derivatives. We proved that inversion of the excited states and subsequent change in the character of the emissive state occurs in trimethylsilylstyryl-*N*-isopropylcarbazole but not in its carbon analogue. The role of a silicon atom in the reordering of these excited states was due to its lowering the energy of the LUMO.

In the current work we will show that the presence of silicon, although necessary for the excited states to flip, is not the only condition. We show why *para*-phenylene vinylene type isomers have an advantage over *meta*-isomers as materials with tunable emission properties.

Para-phenylene-silylene-vinylene type compounds are the subject of numerous papers [7–11] because they constitute modifications of the poly(*para*-phenylene vinylene) polymer (*para*-PPV), the first polymer employed in light-emitting diodes [12–14]. *Meta*-PPV chromophores received notably less attention, and they are usually incorporated into polymeric chain as spacers to reduce π-conjugation and thus shift the color of emission toward shorter wavelengths [15,16]. Likewise, *para*-phenylene-silylene-vinylene compounds are of more interest than their *meta*-analogues. An interesting example showing that *meta*- and *para*-phenylene-silylene-vinylene compounds display different emission properties can be found in the paper of Yamashita et al. [17] The authors of this paper reported that a polymer built from *para*-divinylbenzene (*para*-DVB) fragments shows longer-wavelength emission that originates from DVB-DVB intrachain interactions whereas *meta*-DVB polymer emits mainly at 350 nm which is typical emission from the local excited state of the divinylbenzene chromophore. Similar systems were investigated by Luh and Cheng et al. [18,19]. In their summary of recent advances on the chemistry and photophysics of silylene-spaced divinylarene copolymers [20] they presented results for three types of polymers, i.e. one containing the *para*-divinylbenzene chromophore, one containing the *meta*-divinylbenzene chromophore and one with an alternating arrangement of *para*- and *meta*-DVB moieties. In their review they reported the emission properties of these polymers as a function of the polymer length. This experiment allowed them to conclude that the longer-wavelength emission must be due to intrachain interactions whose strength increases with the polymer length because the longer polymer is more prone to form coiled structures. These through-space interactions were the most significant for the all-*para*-DVB polymer, weaker for the *para*-*meta*-DVB polymer and the weakest for the all-*meta*-DVB-polymer, showing that the position of the vinyl group significantly affects the emission properties. Among examples of *meta*-phenylene-silylene-vinylene compounds one can find examples of those containing carbazole [21]. Yamashita et al. presented

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emission spectra for polymers having *meta*- or *para*-DVB chromophores linked by silylene bridges in the main chain and *N*-vinyl carbazole as pendants. These authors showed that the polymer with *meta*-DVB gives a typical carbazole emission (fluorescence maxima at 349 nm, 366 nm in THF) due to chain-to-pendant energy transfer, but the polymer with *para*-DVB fluoresces in the visible range (fl. max. at 432 nm in THF) [21].

In the current paper we will present another example in which the *meta*- and *para*- positions of the vinyl group govern the emission properties of the phenylene-silylene-vinylene type compound containing carbazole, and their different behaviour in emission will be discussed on the molecular level based on DFT calculations.

2. Experimental section

2.1. Materials and methods

The solvents used for photophysical measurements were acetonitrile and *n*-hexane (gradient grade for liquid chromatography, Merck).

The chemicals used for synthesis were obtained from the following sources: toluene, petroleum ether, dichloromethane (DCM), chloroform ($CHCl_3$), pentane, *n*-hexane, acetone and dimethylformamide (DMF) were purchased from Chempur Gli, magnesium sulfate ($MgSO_4$) and $RuCl_3 \times 3H_2O$ from P.O.Ch. Gliwice, carbazole (95%) from Alfa Aesar, $CDCl_3$, tetrabutylammonium fluoride (TBAF), 2-bromopropane, *N*-bromosuccinimide (NBS), potassium carbonate (K_2CO_3), 4-vinylphenylboronic acid (97%), phenylboronic acid (95%) ethanol, THF, Celite®545, 1,5-cyclooctadiene (COD), carbazole (95%), tris(*o*-tolyl) phosphine, bis(dibenzyli-deneacetone) palladium(0) - [Pd(dba)$_2$], from Sigma-Aldrich, silica gel − 60 from Fluka, tri(cyclohexyl)phosphine, trimethylvinylsilane from ABCR. Toluene, hexane and THF were purified by a mBraun MB SPS 800 purification system. Then toluene, hexane and ethanol were stored over molecular sieves type 4 Å. The ethanol was distilled from calcium hydride under argon. All liquid substrates were distilled and degassed by the ‘bulb-to-bulb’ Schlenk's system. The palladium complex [Pd(η^2-dba)(P(*o*-tol$_3$)$_2$] (**[Pd]**) [22] and the ruthenium species [Ru(CO)H(Cl)(PCy$_3$)$_2$] (**[RuH]**) [23] were prepared according to literature synthetic procedures. The carbazole derivatives as starting materials: *N*-isopropyl-9H-carbazole and 3-bromo-*N*-isopropyl-9H-carbazole were synthesized according to the procedure described in the Ref. [6]. All of the syntheses were carried out under an inert argon or air atmosphere.

2.2. Instruments and measurements

2.2.1. Nuclear magnetic resonance (NMR) spectroscopy

^{1}H NMR (300, 500 MHz), ^{13}C NMR (75, 125 MHz) and ^{29}Si NMR (99 MHz) spectra were recorded on a Varian XL 300 MHz spectrometer, Varian VNMR-S 400 MHz spectrometer and Varian 500 MHz spectrometer in $CDCl_3$ solutions. Chemical shifts are reported in δ (ppm) with reference to the residue solvents (^{1}H δ_H = 7.26 ppm, ^{13}C δ_C = 77.36 ppm for $CDCl_3$) peak for ^{1}H, ^{13}C and to TMS (^{29}Si δ_H = 0.00 ppm). Analytical gas chromatographic (GC) analyses were performed on a Varian Star 3400CX with a DB-5 fused silica capillary column (30 m × 0.15 mm) and TCD. Mass spectra of the substrates and products were obtained by GCMS analysis (Varian Saturn 2100 T, equipped with a CP-SLI 6CB capillary column (30 m × 0.25 mm) and an ion trap detector.

High-resolution mass spectroscopic (HRMS) analyses were performed on an AMD-402 mass spectrometer. An elemental analysis was performed on a Vario EL Elementar (Germany) three times.

Melting points (mp) of organic and organosilicon carbazole derivatives were determined on a MPA120 EZ-Melt Automated Melting Point Apparatus from Stanford Research Systems (temperature resolution 0.1 °C; temperature sensor Pt RTD).

Thin-layer chromatography (TLC) was made on plates pre-coated with plastic sheets with 250 μm thick silica gel (Polygram SilG/UV254, ROTH), and column chromatography was conducted with silica gel 60 (70–230 mesh, Fluka).

2.3. Photophysical measurements

The absorption spectra were recorded at room temperature on spectrophotometers: Cary 100 and Cary 5000. Fluorescence spectra of argon-saturated samples were measured at room temperature using a Perkin Elmer LS 50B spectrofluorometer (scan speed 240 nm/min, excitation and emission slits 5 nm). All samples were purified prior to the fluorescence measurements by HPLC: Waters 600E Multisolvents Delivery System pump with a Waters 2996 photodiode array UV–vis detector. A Waters XTerra RP18 column was used, and the flow rate of acetonitrile, as a mobile phase, was set to 0.4 mL/min. Quinine sulfate in 1 N H_2SO_4 (Φ_f = 0.546) [24] was used as a reference compound to determine the fluorescence quantum yields of the investigated compounds. The fluorescence lifetimes were measured on a Fluorescence Lifetime Spectrometer (FluoTime 300 from PicoQuant) with a time-correlated single-photon counting detection system (TCSPC). The emission decay lifetimes were measured for oxygen-free samples under the excitation of a 300 nm photodiode.

2.4. Synthetic procedures

Initially, we synthesized a *N*-isopropyl-9H-carbazole as the starting material for the synthesis of new compounds. We used the fully controlled and selective N-alkylation reaction which was carried out using a carbazole (after washing by hexane twice), strong base KOH, acetone as a solvent, isopropyl bromide and tetra-*n*-butylammonium fluoride $(C_4H_9)_4NF$ (TBAF) as a phase-transfer catalyst. After that, the selective bromination process using *N*-bromosuccinimide (NBS) was applied. In accordance with the following Scheme 1, 3-brominated carbazole was quite easily produced in high yield using one equivalent of NBS (dissolved in DMF) in CH_2Cl_2 at 10–25 °C (mild conditions). The topic of the catalytic research was to develop an effective method for the synthesis of the new compounds containing a π-conjugated carbazole fragment. In order to achieve this, two fully controlled reactions were used. It allowed us to get new stereoselective organic- and organosilicon carbazole derivatives. Phenyl- (**1**) and styryl-olefin (***meta*-1b**) were prepared in a very efficient Suzuki coupling reaction catalysed by a well-defined palladium complex according to Scheme 1.

Suitable reaction conditions are essential. The molar ratio between substrates should be 1:1 or 1:1.02. We discovered that the coupling reaction of 3-bromo-*N*-isopropylcarbazole (1 equivalent (eq.)) with 4-vinylphenyl-boronic acid (1 eq.) or phenylboronic acid in the presence of (**Pd**) **-** [Pd(dba)(P(*o*-tol)$_3$)$_2$] (0.04 mol% per Br-derivative) in an open system conducted in a mixture of solvents toluene/ethanol/2 M base solution at 85 °C gave exclusively 3-styryl- or 3-phenyl-*N*-isopropylcarbazoles (***meta*-1b** or **1**) after 2–2.5 h with very good yields respectively: for ***meta*-1b** 94% and for **1** 98%. Then, we used 3-styryl-N-isoprophyl-carbazole (meta-1b) for the synthesis of *E*-silyl-carbazoles via the silylative coupling (SC) reaction catalysed by the very active and stereo-selective ruthenium (II) species - [Ru(CO)H(Cl)(PCy$_3$)$_2$] (**RuH**). This stereo-controlled catalytic process of olefin with trimethylvinylsilane was conducted following the original procedure. The SC reaction of ***meta*-1b** with trimethylvinylsilane (3 eq.) was accomplished following the well-defined route: **RuH** (0.5 mol% per olefin molecule), toluene (0.75 M solution), 90 °C for 10 h (up to 100% conversion of vinylarylene derivative), under argon atmosphere, see above Scheme 1. The ‘Schlenk’ technique closed system was used to give selectively only one isomer of new 3-(3-*((E)*-2-(trimethylsilyl)vinyl)phenyl)-*N*-isopropyl-*9H*-carbazole (***meta*-1a**). We achieved very good selectivity over 99% and a final yield of 96% as well. The progress of all of the processes was controlled by TLC and GCMS analysis. The details regarding preparation of compounds **1**, ***meta*-1a** and ***meta*-1b** together with their