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Simple electron donor molecules based on triphenylamine and carbazole derivatives

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ABSTRACT

Electron donating carbazole and triphenylamine derivatives are widely used in molecular electronic materials and in biological fluorescent or active probes. Novel easy-to access, highly substituted, electron-rich carbazole and triphenylamine compounds were designed, synthesized and characterized in photophysical and electrochemical experiments. These compounds, with an unusual D-π-D-π-D molecular design are based on carbazole and triphenylamine cores, thiophene conjugated linker and donor aromatic extremities. They showed excellent light-absorbing and emitting properties with high fluorescent quantum yield along with low oxidation potential and excellent electron donating properties. Computational calculations complete the experimental data, and enlighten about the redox and photophysical processes.

1. Introduction

Carbazole and triphenylamine units are ubiquitous in organic donor materials. Carbazole derivatives are widely used in molecular electronic materials, such as organic light-emitting diodes like blue, green, red, and white emitters or as dye sensitive solar cells [1–3]. With their rigid plane and their long conjugation length, they are excellent light-emitting materials and they can undergo reversible oxidation processes that make them suitable hole carriers [4]. The nitrogen atom in the carbazole ring bestows indeed the electron-donating capability. Their bifunctional properties of both light emission capability combined with their electron donating and hole-transporting properties make them an important class of organic compounds for applications in optoelectronic devices. Flat carbazole structure shows in addition high morphological and thermal stability. If the carbazole unit exhibits a bluish photo- or electroluminescence, properties of carbazole derivatives can be easily tuned by introduction of new groups on many positions, mostly 3,6-linked and 2,7-linked compounds [5–7]. Meanwhile, much attention has also been paid to triarylamines and particularly triphenylamines (TPA) during the recent years [8]. Triphenylamine based compounds are indeed also widely used as both molecular electronic materials and luminescent probes [9–11] due to their redox activity, fluorescence and hole-transporting properties *via* radical-cation species. Triphenylamine derivatives are considered for example among the strongest electron donors for dye-sensitive solar cells (DSSCs). Triphenylamines show an extended π-conjugation compared to their carbazole counterparts, allowing a red-shifted absorption and emission. Molecular structures such as D-(π)-A and A-(π)-D-(π)-A type, in which A refers to an electron acceptor unit and D refers to an electron donor unit, are very common in both light-emitting materials and donor materials [12]. These types of compounds are also named push-pull materials and present a strong intramolecularcharge transfer (ICT) upon excitation. By modifying the donor unit, acceptor moiety (ies) and possible π-conjugation spacer between acceptor and donor units, the structure properties can be finely and easily tuned, along with HOMO and LUMO levels of the sensitizers [13,14].

In parallel, the heterocyclic carbazole scaffold is a privileged pharmacophore found in many biologically active compounds [15–17]. Moreover, some triphenylamine and carbazole derivatives were reported as dyes or photosentitizers in biological and cellular media and in particular, specific ultrabright DNA stainers with high absorption and strong minor groove binding affinity were designed [18–20]. In our quest of strong electron-donating photoredox scaffolds for biomolecules sensitization, we investigated a new class of simple carbazole and triphenylamine based compounds. Instead of the standard D-π-A molecular design, we decided to investigate carbazole and triphenylamine

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derivatives with D-π-D-π-D structures in order to study the enhancement of the donor capability of the sensitizers. Only few examples of these structures were indeed reported and the latter have most of the time very extended structures, typically starburst compounds with carbazole and triphenylamine patterns as both core(s) and extremities. Herein, we thus present the design and the straightforward synthesis of small and simple derivatives with thiophene units as π-linker, much more suitable for biomolecule applications than extended structures. These compounds were then characterized in absorption, luminescence and voltammetry studies. Density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations support experimental data, and shed light on the redox and photophysical processes.

2. Experimental section

2.1. Synthesis of the photosensitizers

All boronic acids, 3,6-dibromo-9-phenyl-9H-carbazole and tris(4-(thiophen-2-yl)phenyl)amine and Tetrakis (triphenylphosphine)palladium (0) were purchased from TCI chemicals while *N*-bromosuccinimide was obtained from Acros. Magnesium sulfate was purchased from VWR and carbonate sodium as well as silica were from Sigma Aldrich. NMR analyses were performed using a Bruker Avance 500 Ultra-Shield with precession frequencies of 500 MHz for proton and 125 MHz for carbon. High resolution mass spectrometry analyses were carried out either on a Xevo™ G2 QTOF (Waters) for ESI-MS spectra or on a GCT Premier (Waters) when DCI-MS technic was chosen. Compounds **1**, **2**, **3**, **4**, **6** and **7** are newly synthesized molecules.

2.1.1. 9-phenyl-3,6-di(thiophen-2-yl)-9H-carbazole (*1*)

3,6-dibromo-9-phenyl-9H-carbazole (0.5 mmol, 1eq.), 2-thienylboronic acid (2.6 eq., 172 mg), $Pd(PPh_3)_4$, aqueous Na_2CO_3 (2 M, 10 mL) and THF (16 mL) were mixed in a round bottom flask. The mixture was degassed and then refluxed for 48 h under argon current. Water was added to the reaction media after cooling then the mixture was extracted with dichloromethane. The organic phase was washed with water and brine, then dried over sulfate magnesium and solvent was evaporated to dryness under reduced pressure. Purification was carried out on silica column with cyclohexane-dichloromethane (80: 20) to get the desired compound. Yield = 96.7%. m.p. 164–165 °C. ^{1}H NMR (CD_2Cl_2, 300 MHz), δ (ppm): 8.41–42 (m, 2H); 7.68–7.72 (m, 2H); 7.60–7.64 (m, 4H); 7.47–7.53 (m, 1H); 7.38–7.42 (m, 4H); 7.27–7.30 (m, 2H); 7.10–7.13 (m, 2H). ^{13}C NMR (CD_2Cl_2, 125 MHz), δ (ppm): 144.4; 140.0; 136.4; 129.2; 127.3; 126.9; 126.2; 126.1; 123.9; 123.1; 122.9; 121.5; 116.9; 109.6. ESI-MS (positive mode) *m/z*: 408.0883 $[M+H]^+$. HRMS calc. for $C_{26}H_{18}NS_2$: 408.0881, exp. 408.0883 (+0.5 ppm).

2.1.2. 3,6-bis(5-bromothiophen-2-yl)-9-phenyl-9H-carbazole (*2*)

9-phenyl-3,6-di(thiophen-2-yl)-9H-carbazole (0.42 mmol, 1eq.) was dissolved in 10 mL of chloroform and cooled down with an ice bath. A solution of *N*-bromosuccinimide (2.03 eq., 153 mg) in chloroform (5 mL) was then added slowly to the mixture, which was then let to warm up to room temperature and stirred for 24 h. The mixture was then washed with water and brine. Purification was carried out on silica column with cyclohexane to get the desired compound. Yield = 39.1%. m.p. 155–156 °C. ^{1}H NMR (CD_2Cl_2, 500 MHz), δ (ppm): 8.32 (s, 2H); 7.65–7.67 (m, 2H); 7.61 (dd, J = 8.5 Hz, J = 1.5 Hz, 2H); 7.57–7.58 (m, 2H); 7.51–7.54 (m, 1H); 7.40 (d, J = 8.5 Hz, 2H); 7.14 (m, 2H); 7.10 (m, 2H). ^{13}C NMR (CD_2Cl_2, 125 MHz), δ (ppm): 147.1; 141.4; 137.3; 131.4; 130.4; 128.2; 127.2; 126.5; 124.8; 123.9; 122.9; 117.8; 110.9; 110.4. DCI-CH_4 HRMS calc. for $C_{26}H_{15}NS_2Br_2$: 562.9013, exp. 562.9016 (+0.5 ppm).

2.1.3. Suzuki coupling protocole for *3* and *4*

In a round bottom flask, **1** (1 eq.) was incorporated with (4-methoxyphenyl)boronic acid or (4-(dimethylamino)phenyl)boronic acid (2.6 eq.), $Pd(PPh_3)_4$ (5% mol), aqueous Na_2CO_3 (2 M, 10 mL) and THF (16 mL). The mixture was degassed and then refluxed for 48 h under argon current. Water was added to the reaction media after cooling then the mixture was extracted with dichloromethane. The organic phase was washed with water and brine, then dried over sulfate magnesium and solvent was evaporated to dryness under reduced pressure. Purification was carried out on silica column with cyclohexane-dichloromethane (90: 10) to get the desired compound.

3,6-bis(5-(4-methoxyphenyl)thiophen-2-yl)-9-phenyl-9H-carbazole (**3**). Yield = 25%. m.p. 275–276 °C. ^{1}H NMR (CD_2Cl_2, 500 MHz), δ (ppm): 8.45 (s, 2H); 7.72–7.74 (m, 2H); 7.65–7.68 (m, 2H); 7.60–7.62 (m, 6H); 7.51–7.54 (m, 1H); 7.43–7.45 (m, 2H); 7.37 (d, J = 3.5 Hz, 2H); 7.25 (d, J = 4 Hz, 2H); 6.95–6.97 (m, 4H); 3.85 (s, 6H). ^{13}C NMR (CD_2Cl_2, 125 MHz), δ (ppm): 159.7; 143.9; 143.0; 141.2; 137.6; 130.4; 128.2; 127.6; 127.4; 127.3; 127.1; 124.8; 124.1; 123.6; 123.5; 117.7; 114.7; 110.8; 55.8. DCI-CH_4 HRMS calc. for $C_{40}H_{30}NO_2S_2$: 620.1718, exp. 620.1732 (+2.3 ppm).

3,6-bis(5-(4-N-dimethyl)thiophen-2-yl)-9-phenyl-9H-carbazole (**4**) Yield = 25%. m.p. 238–239 °C. ^{1}H NMR (CD_2Cl_2, 500 MHz), δ (ppm): 8.43–8.44 (m, 2H); 7.71–7.73 (dd, J = 8.5 Hz, J = 2.0 Hz, 2H), 7.61–7.68 (m, 4H); 7.54–7.56 (m, 4H); 7.50–7.54 (m, 1H); 7.41–7.44 (d, J = 8.7 Hz, 2H); 7.34–7.35 (d, J = 3.5 Hz, 2H); 7.19–7.20 (d, J = 3.5 Hz, 2H); 6.76–6.77 (d, J = 9 Hz, 4H); 3.00 (s, 12H). ^{13}C NMR (CD_2Cl_2, 125 MHz), δ (ppm): 150.5; 144.0; 142.5; 141.1; 137.7; 130.4; 128.1; 127.6; 127.3; 126.7; 124.6; 124.2; 123.5; 123.0; 122.1; 117.5; 112.9; 110.7; 40.6. DCI-CH_4 HRMS calc. for $C_{42}H_{36}N_3S_2$: 646.2351, exp. 646.2361 (+1.5 ppm).

2.1.4. Tris(4-(5-bromothiophen-2-yl)phenyl)amine (*5*):

Tris(4-(thiophen-2-yl)phenyl)amine (0.61 mmol, 1eq.) was dissolved in chloroform (20 mL) and cooled down with an ice bath. A solution of *N*-bromosuccinimide (3.05 eq., 333 mg) in chloroform (5 mL) was then added slowly to the mixture, which was then let to warm up to room temperature and stirred for 24 h. The mixture was then washed with water and brine. The organic phase was dried over anhydrous magnesium sulfate and the desired product was obtained without further purification after solvent evaporation under reduced pressure. Yield = 87.7%. ^{1}H NMR (CD_2Cl_2, 300 MHz), δ (ppm): 7.40–7.43 (m, 6H); 7.09–7.12 (m, 6H); 6.99–7.01 (m, 6H). ^{13}C NMR (CD_2Cl_2, 125 MHz), δ (ppm): 146.6; 145.4; 130.8; 128.6; 126.6; 124.4; 122.6. DCI- CH_4 HRMS calc. for $C_{30}H_{18}NS_3Br_3$: 728.81130, exp. 728.8109 (−0.55 ppm). Melting point: 192–193 °C.

2.1.5. Suzuki coupling protocol for *6* and *7*

Tris (4-(5-bromothiophen-2-yl)phenyl)amine (0.14 mmol, 1eq.), (4-methoxyphenyl)boronic acid or (4-dimethylamino)boronic acid (4 eq.), $Pd(PPh_3)_4$ (5% mol), aqueous Na_2CO_3 (2 M, 8 mL) and THF (12 mL) were mixed in a round bottom flask. The mixture was degassed and then refluxed for 48 h under argon current. Water was added to the reaction media after cooling then the mixture was extracted with dichloromethane. The organic phase was washed with water and brine, then dried over sulfate magnesium and solvent was evaporated to dryness under reduced pressure. Purification was carried out by precipitation by heptane to get the desired compound for tris(4-(5-(4-methoxyphenyl)thiophen-2-yl)phenyl)amine while 4-(5-(4-(bis(4-(5-(4-(dimethylamino)phenyl)thiophen-2-yl)phenyl)amino)phenyl)thiophen-2-yl)-*N*,*N*-dimethylaniline was obtained after silica column chromatography with dichloromethane-cyclohexane (50:50).

Tris(4-(5-(4-methoxyphenyl)thiophen-2-yl)phenyl)amine (**6**): Yield = 89.3%. m.p. 218–219 °C. ^{1}H NMR (CD_2Cl_2, 500 MHz), δ (ppm): 7.55–7.58 (m, 12H); 7.24 (m, 3H); 7.20 (m, 3H); 7.14–7.17 (m, 6H); 6.92–6.94 (m, 6H); 3.83 (s, 9H). ^{13}C NMR (CD_2Cl_2, 125 MHz), δ (ppm): 159.4; 146.4; 142.9; 142.2; 129.2; 127.0; 126.7; 126.3; 124.4; 123.4;