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Triphenylamine/oxadiazole hybrids differing by the substitution pattern: Influence on the electroluminescence properties of yellow and green emitting diodes

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ABSTRACT

In this study, three donor-acceptor-donor triphenylamine/oxadiazole hybrids differing by the substitution pattern were synthesized and characterized by means of experimental and density functional theory (DFT) methods. The new compounds were used as hosts for the design of yellow- and green organic light emitting diodes (OLEDs), exhibiting very different EL characteristics. The position of the triphenylamine substituents relative to the central phenyl-oxadiazole-phenyl core was found to greatly influence the EL performances. The results indicate that the increased internal torsion and the disrupture of the interring π-conjugation of the hosts impacts importantly the triplet energies andthe EL performance of OLEDs. OLEDs fabricated with the best host afforded an external quantum efficiency (EQE) of 17.1%, a current and power efficiency of 59.3 cd/A and 29.5 lm/W while doping the emissive layer at 10 wt% with the triplet emitter $Ir(ppy)_3$.

1. Introduction

During the past decade, Organic Light Emitting Diodes (OLEDs) have focused a great deal of interest due to their potential applications in solid-state lighting and flat panel displays. Clearly, these devices are in the midst of revolutionizing the lighting industry [1–3]. To reach high efficiency, choice of the light-emitting material is of crucial importance and selection of triplet emitters to produce light ensures for devices an internal quantum efficiency (IQE) of 100% as a result of the phosphorescent nature of the emission [4–6]. Indeed, due to the strong spin-orbit coupling existing in transition metal complexes and the efficient intersystem crossing close to unity, 100% of the excitons can be harvested for light emission in contrary to fluorescence-based devices where the IQE is capped to 25% [7,8]. Among triplet emitters, iridium complexes are candidates of choice by exhibiting a bright emission at room temperature, a facile tunability of the emission over the visible spectrum and their relative short excited state lifetimes that limit the undesirable triplet-triplet annihilation [9]. Apart from the emitters, a careful selection of the host is another key element to fabricate OLEDs exhibiting a high energy-to-photon conversion. To reach this goal, the energy level of the host should be selected so that the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the host align well with those of the triplet emitters [10,11]. As a result of this favorable alignment, an efficient energy transfer from the host to the guest can occur. Over the years, organic and organometallic materials have been examined as potential hosts for OLEDs [12,13]. To achieve efficient and stable devices, ambipolar charge transportation is required, what can be obtained by combining within a single molecule an electron and a hole-transport material. In this field, the combination of the electron-transport oxadiazole with the hole-transport triphenylamine units is really popular [14]. While focusing on the direct linkage of one oxadiazole unit with two triphenylamine units, this association is less common, as evidenced by the number of publications [15–18]. Besides, a common characteristic of all these triphenylamine/oxadiazole derivatives is the symmetric substitution of the triphenylamine relative to the central oxadiazole core. In this work, we examined only unsymmetrically substituted triphenylamine/oxadiazole derivatives as hosts for Ir(bzq)(acac) and $Ir(ppy)_s$ as the dopants. As expected, the TPA-core linking topology impacted the EL characteristics of the corresponding OLEDs. Parallel to this, the three

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hosts were also examined regarding their thermal, photophysical and electrochemical properties.

2. Experimental details

2.1. General information

^{1}H and ^{13}C NMR spectra were determined at room temperature in 5 mm o.d. tubes on a Bruker Avance 250 spectrometer equipped with a QNP probe head: ^{1}H (250 MHz) and ^{13}C (63 MHz). The ^{1}H chemical shifts were referenced to the solvent peak: $CDCl_3$ (7.26 ppm), DMSO-d_6 (2.49 ppm), and the ^{13}C chemical shifts were referenced to the solvent peak: $CDCl_3$ (77.0 ppm) DMSO-d_6 (39.5 ppm). All starting materials and solvents were purchased from Aldrich or Lumtec and used as received commercially. $Ir(bzq)_2(acac)$ [19], 4-bromobenzohydrazide **1** [20], 3-bromobenzohydrazide **8** [21] and 4-(diphenylamino)phenyl-boronic acid **11** were synthesized as previously reported in the literature, without modifications and in similar yields. Absorption and emission spectra were recorded with a UV MC2 spectrophotometer from the SAFAS Monaco Society and a Photon Technology International spectrofluorimeter. Absolute fluorescence quantum yields in solution and in the solid state were measured by a Hamamatsu Photonics Quantaurus QY at room temperature. Cyclic voltammetry (CV) was performed on a potentiostat/galvanostat (VMP, Biologic-SA). A single cell three-electrode configuration was used at a scan rate of 100 mV/s, at room temperature in CH_2Cl_2 solution (10^{-3} M), with tetrabutylammonium hexafluorophosphate at 0.1 M concentration as the supporting electrolyte. The working and the counter electrodes were platinum discs, whereas Ag wire was used as a pseudo-reference electrode. Ferrocene was used as the internal standard material.

2.2. Synthetic procedures

2.2.1. General procedure for the synthesis of bromo-N'-(bromobenzoyl) benzohydrazide 3, 6 and 9

To a solution of the appropriate bromobenzohydrazide (10.7 g, 49.75 mmol) in dry THF (120 mL) was slowly added the appropriate bromobenzoyl chloride (10.9 g, 49.75 mmol, 1 eq.) in dry THF (20 mL) at room temperature under nitrogen. During the addition, a white solid formed. The reaction mixture was stirred for 24 h. Then, pyridine (10 mL) was added to the mixture and the stirring was maintained for an additional 30 min. The reaction mixture was poured into water (250 mL). The white solid was collected by filtration and dried under high vacuum.

3-Bromo-*N'*-(4-bromobenzoyl)benzohydrazide **3** (16.2 g, 82% yield). ^{1}H NMR (DMSO-d_6) δ 7.50 (t, 1H, J = 7.9 Hz), 7.72–7.93 (m, 6H), 8.08 (d, 1H, J = 1.6 Hz), 10.63 (brs, 2H, NH); ^{13}C NMR (DMSO-d_6) δ 122.3, 126.3, 127.0, 130.0, 130.6, 131.3, 131.9, 132.1, 135.0, 164.8, 165.4; HRMS (ESI MS) *m/z*: theor: 395.9109 found: 395.9111 ($[M]^{+\cdot}$ detected).

2-Bromo-*N'*-(4-bromobenzoyl)benzohydrazide **6** (14.4 g, 76% yield). ^{1}H NMR (DMSO-d_6) δ 7.38–7.56 (m, 3H), 7.68 (d, 1H, J = 0.9 Hz), 7.73 (d, 2H, J = 8.6 Hz), 7.88 (d, 2H, J = 8.6 Hz), 10.40, (s, 1H, NH), 10.7 (s, 1H, NH); ^{13}C NMR (DMSO-d_6) δ 119.8, 126.2, 128.1, 129.9, 130.1, 131.9, 132.0, 132.1, 133.5, 137.1, 165.1, 167.0; HRMS (ESI MS) *m/z*: theor: 395.9109 found: 395.9108 ($[M]^{+\cdot}$ detected).

2-Bromo-*N'*-(3-bromobenzoyl)benzohydrazide **9** (17.4 g, 88% yield). ^{1}H NMR (DMSO-d_6) δ 7.36–7.52 (m, 4H), 7.70 (d, 1H, J = 8.3 Hz), 7.80 (d, 1H, J = 8.1 Hz), 7.94 (d, 1H, J = 8.6 Hz), 8.11 (s, 1H), 10.80 (brs, 2H, NH); ^{13}C NMR (DMSO-d_6) δ 119.8, 122.2, 127.1, 128.1, 129.9, 130.7, 131.3, 134.9, 135.1, 137.1, 164.5, 166.9; HRMS (ESI MS) *m/z*: theor: 395.9109 found: 395.9107 ($[M]^{+\cdot}$ detected).

2.2.2. General procedure for the synthesis of 2,5-bis(bromophenyl)-1,3,4-oxadiazole 4, 7 and 10

The appropriate bromo-*N'*-(bromobenzoyl)benzohydrazide 3, 6 or 9 (10 g, 25.12 mmol) was suspended in $POCl_3$ (100 mL) and the reaction mixture was heated at 85 °C for 4 hours. During that time, the initial precipitate dissolved and a clear solution formed. The reaction mixture was carefully poured onto ice. The aqueous phase was extracted with CH_2Cl_2 several times, the organic phases were combined, dried over magnesium sulfate and the solvent removed under reduced pressure. It was used without any further purification.

2-(3-Bromophenyl)-5-(4-bromophenyl)-1,3,4-oxadiazole **4** (7.1 g, 74% yield). ^{1}H NMR (DMSO-d_6) δ 7.55 (t, 1H, J = 8.1 Hz), 7.81–7.87 (m, 3H), 8.07-8.15 (m, 3H), 8.28-8.29 (t, 1H, J = 8.1 Hz); ^{13}C NMR (DMSO-d_6) δ 122.8, 122.9, 125.8, 126.2, 126.3, 129.2, 129.6, 132.1, 132.9, 135.3, 163.4, 164.2; HRMS (ESI MS) *m/z*: theor: 377.9003 found: 377.9001 ($[M]^{+\cdot}$ detected).

2-(2-Bromophenyl)-5-(4-bromophenyl)-1,3,4-oxadiazole **7** (6.4 g, 67% yield). ^{1}H NMR (DMSO-d_6) δ 7.52–7.65 (m, 2H), 7.83 (d, 2H, J = 8.3 Hz), 7.89 (dd, 1H, J = 8.2 Hz, J = 1.4 Hz), 8.02 (d, 2H, J = 8.3 Hz), 8.06 (dd, 1H, J = 8.2 Hz, J = 1.4 Hz); ^{13}C NMR (DMSO-d_6) δ 121.3, 122.8, 124.9, 126.4, 128.8, 129.1, 132.3, 133.1, 133.9, 134.9, 163.4, 164.2; HRMS (ESI MS) *m/z*: theor: 377.9003 found: 377.9004 ($[M]^{+\cdot}$ detected).

2-(2-Bromophenyl)-5-(3-bromophenyl)-1,3,4-oxadiazole **10** (8.1 g, 85% yield). ^{1}H NMR (DMSO-d_6) δ 7.51–7.62 (m, 3H), 7.79-7.87 (m, 2H), 8.03-8.08 (m, 2H), 8.25 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 121.3, 122.9, 124.7, 125.6, 126.2, 128.7, 129.4, 132.1, 132.3, 133.8, 134.9, 135.4, 163.4, 163.5; HRMS (ESI MS) *m/z*: theor: 377.9003 found: 377.9002 ($[M]^{+\cdot}$ detected).

2.2.3. General procedure for the synthesis of m-TPA-p-OXD, o-TPA-p-OXD and o-TPA-m-OXD

To a solution of 2,5-di(bromophenyl)-1,3,4-oxadiazole **4, 7** or **10** (0.61 g, 1.61 mmol) and 4-(diphenylamino)phenylboronic acid **11** (1.20 g, 4.15 mmol, 2.6 eq.) in dry THF (40 mL), was added $Pd(PPh_3)_4$ (120 mg) and aqueous KOH solution (10 mL, 2 M). The mixture was refluxed for 72 hours under nitrogen. Then the mixture was poured into NH_4Cl solution. The aqueous layer was extracted with $CHCl_3$. The combined organic phase was washed with brine and dried ($MgSO_4$). The residue was purified by column chromatography (SiO_2) using CH_2Cl_2:acetone 5:1 as the eluent. For a higher purity, the product was dissolved in a minimum of CH_2Cl_2 and addition of precipitated a light yellow solid.

2'-(5-(4′-(diphenylamino)-[1,1′-biphenyl]-4-yl)-1,3,4-oxadiazol-2-yl)-*N,N*-diphenyl-[1,1′-biphenyl]-4-amine ***o*-TPA-*p*-OXD** (1.0 g, 88% yield). ^{1}H NMR ($CDCl_3$) δ 6.98 (td, 2H, J = 7.3 Hz, J = 1.3 Hz), 7.03–7.12 (m, 9H), 7.12-7.23 (m, 13H), 7.32 (d, 2H, J = 7.7 Hz), 7.46-7.56 (m, 4H), 7.60 (dd, 1H, J = 7.6 Hz, J = 2.4 Hz), 7.69 (d, 2H, J = 9.5 Hz), 7.85 (d, 2H, J = 7.7 Hz), 8.14 (d, 1H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ122.0, 122.9, 123.0, 123.2, 123.3, 123.4, 124.4, 124.8, 127.0, 127;2, 127.5, 127.7, 129.3, 129.4, 129.6, 130.4, 130.9, 131.4, 133.1, 134.4, 141.7, 143.8, 147.4, 147.5, 148.1, 164.6, 165.3 HRMS (ESI MS) *m/z*: theor: 710.3046 found: 710.3044 ($[M]^{+\cdot}$ detected).

3'-(5-(4′-(Cyclohexa-2,4-dien-1-yl(phenyl)amino)-[1,1′-biphenyl]-4-yl)-1,3,4-oxadiazol-2-yl)-*N,N*-diphenyl-[1,1′-biphenyl]-4-amine ***m*-TPA-*p*-OXD** (1.0 g, 91% yield). ^{1}H NMR ($CDCl_3$) δ 7.04 (td, 4H, J = 7.1 Hz, J = 1.2 Hz), 7.15–7.21 (m, 12H), 7.27-7.34 (m, 8H), 7.47-7.59 (m, 5H), 7.73-7.78 (m, 3H), 8.09 (d, 1H, J = 7.7 Hz), 8.21 (d, 2H, J = 8.3 Hz), 8.36 (s, 1H); ^{13}C NMR ($CDCl_3$) δ122.0, 123.2, 123.3, 123.4, 123.6, 124.4, 124.6, 124.8, 125.0, 125.2, 127.0, 127.4, 127.8, 127.9, 129.3, 126.4, 129.5, 129.9, 133.1, 133.5, 141.7, 143.9, 147.4, 147.5, 147.9, 148.1, 164.6, 164.7; HRMS (ESI MS) *m/z*: theor: 710.3046 found: 710.3044 ($[M]^{+\cdot}$ detected).

2'-(5-(4′-(diphenylamino)-[1,1′-biphenyl]-3-yl)-1,3,4-oxadiazol-2-yl)-*N,N*-diphenyl-[1,1′-biphenyl]-4-amine ***o*-TPA-*m*-OXD** (1.1 g, 94% yield). ^{1}H NMR ($CDCl_3$) δ 6.95–7.22 (m, 23H), 7.28-7.34 (m, 3H), 7.48-