Article

Synthesis, Photophysical and Electrochemical Properties of Novel D-π-D and D-π-A Triphenylamino-Chalcones and β-Arylchalcones

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A series of triphenylamino (TPA)-chalcones and triphenylamino-β-arylchalcones, displaying either D-π-D or D-π-A architecture, were synthesized through aldol condensations and Heck reactions. The chalcone derivatives display intense absorption bands ranging from 389 to 432 nm and molar extinction coefficients of ca. 10^5 L mol^{-1} cm^{-1} corresponding to π-π* electronic transitions. The photoluminescence emissions are peaked between 470 and 563 nm with large Stokes shifts (80-131 nm), attributed to charge transfer in the excited state. The dyes present low fluorescence quantum yields, which is attributed to radiationless excited state deactivation related to aryl rings rotation. Spectroscopic and electrochemical methods were used to determine the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels. Both optical and electrochemical properties of the TPA-chalcone derivatives are considerably affected by the substitution pattern of the chalcones aryl rings and also by the β-arylation of the olefin moiety.

Keywords: fluorescence, chalcone, β-arylchalcone, Heck reaction, triphenylamine

Introduction

The chalcone backbone can be considered a privileged template for the synthesis of highly conjugated compounds. The careful choice of groups attached to both aryl rings allow the modulation of chalcones properties, providing derivatives with a wide range of applications, for instance, in medicinal chemistry,[1-4] analytical chemistry[5] and light technology.[6,7] Concerning photochemical applications, two architectures have been used in the design of conjugated chalcone-based dyes: D-π-D compounds, with both aryl rings possessing electron-donating groups, and D-π-A derivatives, which have one electron-rich and one electron-poor aryl ring. Chalcone derivatives with such structural features generally display intramolecular charge transfer (ICT) in the excited state and are highly emissive compounds. Chalcone-based compounds with these properties have been applied as fluorescent probes for detection of anions[5] and enzymatic acivities,[8] as water content sensor,[9] as electrochromic materials,[10] as non-linear optical materials,[11] among other applications.

Triphenylamine (TPA) is one of the most applied donor group in the design of organic dipolar chromophores. Moreover, TPA derivatives have been extensively applied as photovoltaic and hole-transporting materials.[12,13] The incorporation of the TPA group on chalcone structure has been performed and the photophysical and electrochemical properties of TPA-chalcone derivatives have been studied.[7,14] These chromophores display interesting features and depending on the structure, can be applied, for instance, as fluorescent sensor for picric acid,[15] as additive in dye sensitized solar cell,[6] as color conversion materials for white light-emitting diodes (LEDs),[16] as photosensitizer for production of singlet oxygen, among others. In this context, for the development of novel useful chromophores, the synthesis and photophysical/electrochemical characterization of novel TPA-chalcones derivatives is important.

In this paper, a series of novel D-π-D and D-π-A chalcones and β-arylchalcones substituted with TPA moiety have been synthesized and characterized. Optical, electrochemical and theoretical properties of these compounds were studied. In addition, the influence of chalcone substitution pattern on the electronic properties was evaluated and compared to the theoretical results calculated using density functional theory (DFT).

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Results and Discussion

For the synthesis of the TPA-chalcone dyes, initially, 4-aminoacetophenone (**1**) was reacted with 4-iodoanisole (**2**) in an Ullmann protocol (Scheme 1). A system composed of CuI, phenanthroline and K_2CO_3 was applied and provided the TPA-acetophenone **3** in 75% yield. Next, **3** was reacted with various arylaldehydes in the presence of KOH in order to afford the aldol products. By using ethanol as solvent, chalcone formation was not observed after 4 h at room temperature. This result was attributed to the low solubility of **3** in the alcoholic solvent. Therefore, a mixture of tetrahydrofuran (THF) and EtOH (1:1) was used as reaction media, affording the desired TPA-chalcone dyes **4a-d** in 38-78% yields. It is worth mentioning that aldehydes substituted with either electron-donating or electron-withdrawing groups were employed in these reactions, in order to obtain compounds with D-π-D or D-π-A architecture. Recently, we reported a useful methodology to arylate α- and β-positions of chalcones via Heck or Suzuki couplings.[17] In order to obtain β-aryl-TPA-chalcones, the Heck protocol (Pd(OAc)$_2$, P(*o*-Tol)$_3$, K_2CO_3, dimethylformamide (DMF)) was applied to the compounds **4b** and **4c**, with iodobenzene or iodoanisole as coupling partner. In these conditions, the desired β-arylated dyes **5a** and **5b** were obtained in 48 and 77% yields, respectively.

Taking into consideration the widespread application of carbazole core in the structure of luminescent compounds, we also designed a TPA-chalcone with architecture D-π-D, possessing the triarylamino and carbazole as donating groups. For the synthesis of this dye, in the first step, an Ullmann coupling between carbazole (**6**) and 4-bromo-benzaldehyde (**7**) was performed with a system based on CuI, 18-crown-6, K_2CO_3 and *o*-dichlorobenzene. Under these conditions, the intermediate **8** was isolated in 69% yield. Next, **8** was reacted with **4** in optimized condensation conditions, affording the target dye **9** in 44% yield.

Photophysical properties of **4a-d**, **5a-b** and **9** were studied by means of absorption and emission spectra. Initially, in order to evaluate both the solvatochromic effect and the influence of TPA-chalcones substitution pattern on UV-Vis absorption profiles, spectra were recorded in isopropanol, acetonitrile, dichloromethane, toluene and cyclohexane (Figure 1). The relevant UV-Vis data as well as the calculated oscillator strength (f_e) and radiative rate constants (k_e^0)[18] are depicted in Table 1. For all derivatives, intense absorption bands (ε ca. 10^5 L mol^{-1} cm^{-1}) peaked between 381 and 435 nm were observed. These ε values in conjunction with the calculated radiative rate constant (k_e^0) indicate spin and symmetry allowed ^{1}π-π* transitions. The optical band-gaps were calculated from the absorption spectra and values
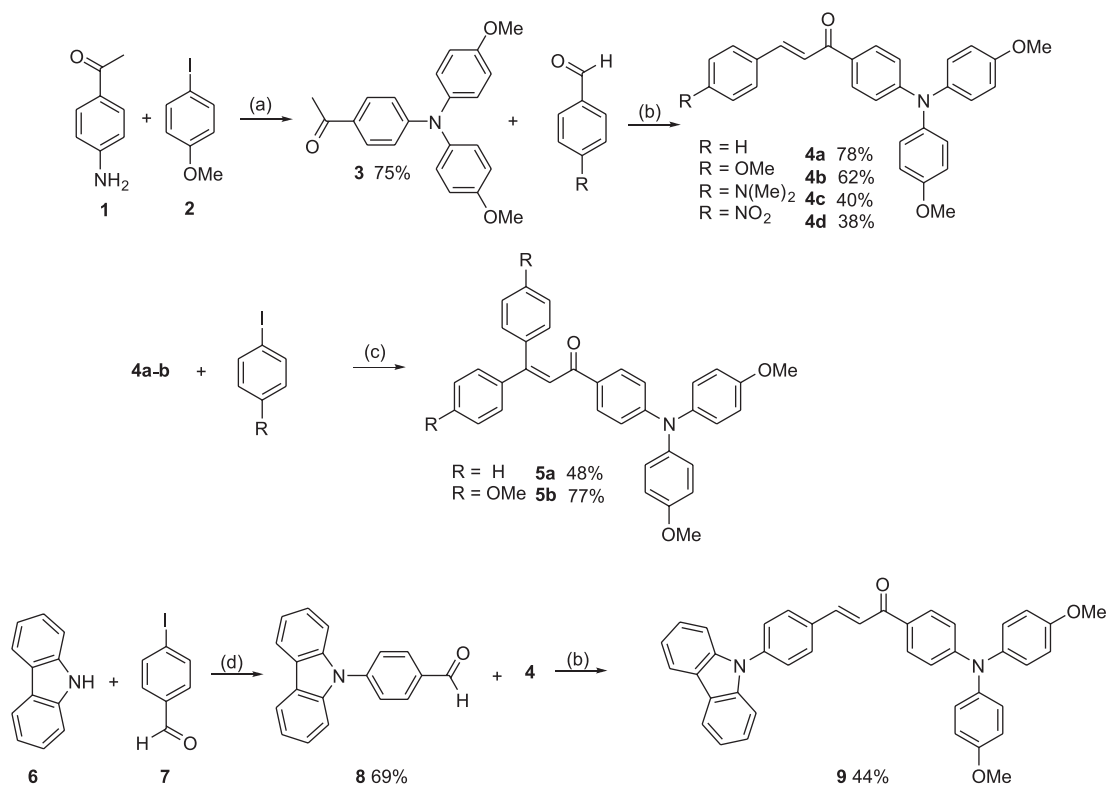
Scheme 1. Synthesis of the TPA-chalcone and β-arylchalcone derivatives. Reaction conditions: (a) CuI, phenanthroline, K_2CO_3, 120 °C, 20 h; (b) EtOH/THF (1:1), KOH, r.t., 6 h; (c) Pd(OAc)$_2$, P(*o*-Tol)$_3$, K_2CO_3, 120 °C, 24 h; and (d) CuI, 18-crown-6, K_2CO_3, *o*-dichlorobenzene, 180 °C, 48 h.

varied from 2.25 to 2.76 eV. A considerable solvatochromic effect was observed in the ground state ($\Delta\lambda_{abs}$ from 8 to 17 nm) for all TPA-chalcone derivatives. This effect was attributed to the electron delocalization between the TPA moiety and the α,β-unsaturated carbonyl system.

As expected, the insertion of both auxochrome group NMe$_2$ (**4c**) and chromophore group NO$_2$ (**4d**) to the

TPA-chalcone structure caused bathochromic shifts in comparison with the non-substituted derivative **4a**. In opposition, the insertion of additional aryl groups on olefin β-position (**5a** and **5b**) produced a small hypsochromic effect. These blue shifts can be attributed to the non-planarity of β-arylated chalcones derivatives, since a considerable torsion angle between the β-aryl groups and
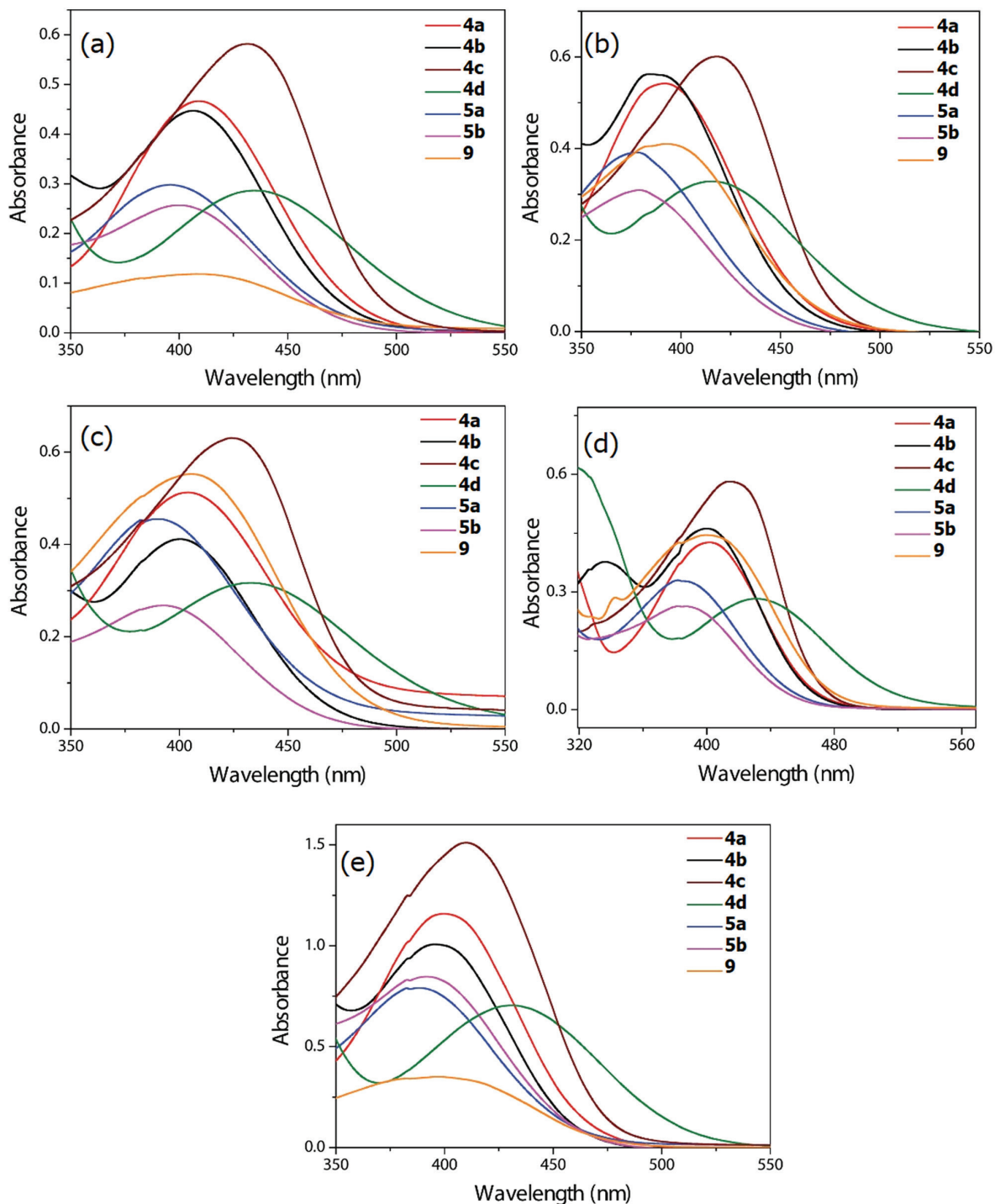

Figure 1. UV-Vis spectra of the TPA-chalcone derivatives in (a) isopropanol, (b) acetonitrile, (c) dichloromethane, (d) toluene and (e) cyclohexane. Concentration of 50 µmol L^{-1}.

Table 1. Relevant absorption data of compounds **4a-d**, **5a-b** and **9**

Dye	Solvent	λ_{abs} / nm	ε / (10^4 L mol^{-1} cm^{-1})	ΔE_{opt} / eV	f_e	k_e^0 / (10^8 s^{-1})
	i-PrOH	410	2.46	2.53	0.55	2.19
	MeCN	392	2.71	2.68	0.17	0.75
4a	CH$_2$Cl$_2$	404	2.56	2.54	0.58	2.39
	PhMe	402	2.13	2.67	0.11	0.46
	cyclohexane	402	2.31	2.67	0.51	2.96
	i-PrOH	407	2.45	2.59	0.53	2.16
	MeCN	390	2.80	2.72	0.29	1.26
4b	CH$_2$Cl$_2$	400	2.06	2.66	0.50	2.09
	PhMe	400	2.31	2.68	0.22	0.93
	cyclohexane	396	2.01	2.70	0.40	1.69
	i-PrOH	431	3.02	2.52	0.84	3.02
	MeCN	418	3.01	2.62	0.14	0.54
4c	CH$_2$Cl$_2$	424	3.15	2.54	0.93	3.47
	PhMe	415	2.91	2.65	0.12	0.46
	cyclohexane	410	3.02	2.62	0.83	3.29
	i-PrOH	435	1.56	2.34	0.33	1.17
	MeCN	416	1.64	2.47	0.16	0.73
4d	CH$_2$Cl$_2$	433	1.58	2.25	0.39	1.38
	PhMe	431	1.41	2.38	0.13	0.59
	cyclohexane	432	1.41	2.41	0.31	1.12
	i-PrOH	396	1.70	2.57	0.48	2.06
	MeCN	382	1.65	2.75	0.12	0.45
5a	CH$_2$Cl$_2$	390	2.28	2.56	0.75	3.31
	PhMe	382	1.65	2.74	0.08	0.30
	cyclohexane	389	1.58	2.70	0.38	1.68
	i-PrOH	400	1.48	2.63	0.39	1.62
	MeCN	382	1.54	2.76	0.10	0.42
5b	CH$_2$Cl$_2$	392	1.34	2.67	0.28	1.21
	PhMe	381	1.32	2.74	0.07	0.30
	cyclohexane	392	1.69	2.70	0.46	2.01
	i-PrOH	408	2.29	2.51	0.19	0.74
	MeCN	394	2.05	2.66	0.15	0.67
9	CH$_2$Cl$_2$	407	2.76	2.49	0.95	3.83
	PhMe	400	2.23	2.61	0.12	0.53
	cyclohexane	397	0.70	2.61	0.20	0.87

λ_{abs}: absorption maximum; ε: molar absorptivity; ΔE_{opt}: optical band-gap; f_e: calculated oscillator strength; k_e^0: calculated radioactive rate constant.

the enone conjugated system was observed on previously described β-arylated chalcones.[17] The substitution pattern also affected the extinction coefficient, since hypochromic effects were observed with the D-π-A compound **4d** and with the β-aryl derivatives **5a** and **5b**.

The fluorescence spectra of the dyes were recorded in cyclohexane (5 μmol L^{-1}) and the emission data are shown in Figure 2 and in Table 2. The TPA-chalcone derivatives displayed emission maxima between 470 and 563 nm. When dissolved in more polar solvents, significant decrease in the fluorescence intensities along with a considerable red shift were observed (Figure S1, Supplementary Information (SI) section). These results suggest that these molecules present high dipolar moments becoming well solvated in

the excited (S1) state. The high polar S1 state in conjunction with high Stokes shifts (80 to 131 nm in cyclohexane) suggest a charge transfer character in excited state.
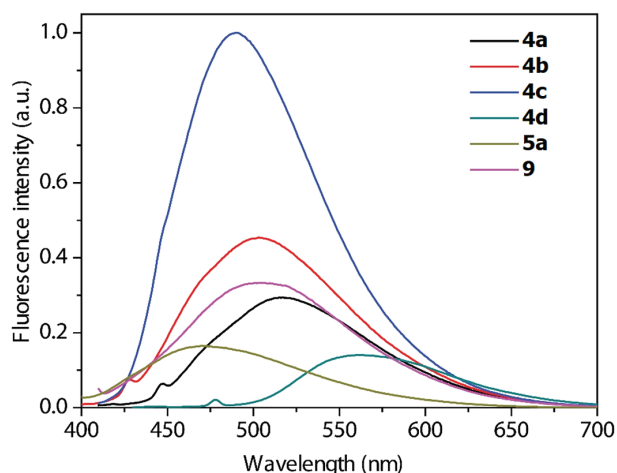

Figure 2. Fluorescence emission spectra of the TPA-chalcone derivatives in cyclohexane (concentration of 5 μmol L⁻¹).

Table 2. Relevant data of steady-state fluorescence of compounds **4a-d**, **5a-b** and **9**

Compound	λ_{emis}^{a} / nm	Stokes shift / nm	Φ_f^{b} / %
4a	517	118	1
4b	503	108	1
4c	490	80	2
4d	563	131	–
5a	470	81	–
5b	–	–	–
9	504	107	2

ᵃDetermined in cyclohexane solutions (concentration of 5 μmol L⁻¹); ᵇdetermined in cyclohexane solutions, using the comparative method[19] and fluorescein sodium salt in 0.1 mol L⁻¹ NaOH (Φ_f = 93%)[20] as standard. λ_{emis}: emission maximum; Φ_f: fluorescence quantum yield.

The influence of substituents on the emission properties of the TPA-chalcones could be evaluated through the relative fluorescence intensities (Figure 2). The most emissive compound was **4c**, possessing two strong donating amino groups. By comparing **4b**, **4c** and **9** with **4d**, it can be seen that the architecture D-π-D led to compounds with higher fluorescence than the compound with a D-π-A design. Another interesting finding was the decrease in the fluorescence intensity observed when an additional aryl group was added to the olefin β-position (**4a** and **4b** *vs.* **5a** and **5b**). This result can also be attributed to the diminished conjugation caused by the lack of planarity observed in β-arylchalcones.[17] The fluorescence quantum yields of the compounds **4a-c** and **9** were determined in cyclohexane using fluorescein, in alkaline aqueous media

(Φ_f = 0.93), as a comparison standard. Low Φ_f values were observed (1-2%), indicating predominant participation of radiationless relaxation for these dyes. The low Φ_f observed for some chalcone derivatives has been attributed to the lack of rigidity of their structure, with the dissipation of electronic energy proceeding through rotation of the aryl rings.[7,21]

In order to study the electrochemical behavior of the compounds, cyclic voltammograms from TPA-chalcones **4a-d** and β-arylchalcone **5a** were obtained in dichloromethane using tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte (Figure 3). A glassy carbon electrode (electroactive area of about 0.019 cm²) was used as the working electrode. An Ag/AgCl(KCl$_{sat}$) electrode was used as the reference and a platinum wire was used as auxiliary electrode. For **4a**, **4b**, **4d** and **5a** two oxidation peaks were observed in the positive potential range. An apparently reversible redox pair can be observed for all of the compounds with a further oxidation (not reversible) event at higher potentials. The reversible peak can be attributed to reversible oxidation of the TPA moiety, also detected in previously described TPA-chalcones.[10] For the compound **4c** only one non-reversible oxidation peak was detected, which can be related to simultaneous oxidation of both amino groups.
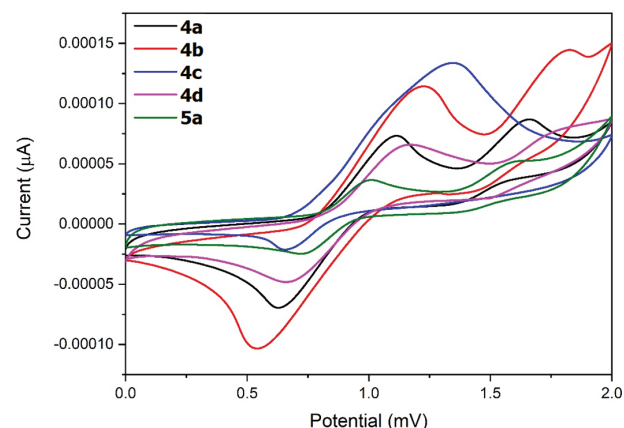

Figure 3. Cyclic voltammetry of **4a-d** and **5a** dissolved in CH₂Cl₂.

The highest occupied molecular orbital (HOMO) level of the TPA-chalcones were calculated from the onset potential using the relation $E_{HOMO} = -\left(E_{onset} - E_{\frac{FC}{FC^+}} + 4.8 \right) eV$, where $E_{\frac{FC}{FC^+}}$ is the ferrocene/ferrocenium redox couple potential. Values ranging from –5.17 to –5.04 eV were observed and the compound with smaller ionization potential was **4c**. By combining the HOMO values with

the optical band-gaps, the lowest unoccupied molecular orbital (LUMO) level was also estimated (Table 3). Values from –2.92 to –2.48 eV were observed and the D-π-A chalcone **4d** displayed the lower energy level, indicating the high electron affinity of this compound.

Table 3. HOMO, E_{gap} and LUMO obtained by cyclic voltammetry

Compound	E_{onset} / V	E_{HOMO}[a] / eV	E_{gap}[b] / eV	E_{LUMO}[c] / eV
4a	0.79	–5.15	2.54	–2.61
4b	0.78	–5.14	2.66	–2.48
4c	0.68	–5.04	2.54	–2.50
4d	0.81	–5.17	2.25	–2.92
5a	0.77	–5.13	2.56	–2.57

[a]$E_{HOMO} = -\left(E_{onset} - E_{\frac{FC}{FC^+}} + 4.8\right)$ eV. The oxidation potential of Fc/Fc⁺ against Ag/AgCl was recorded in CH_2Cl_2-Bu_4NPF_6 (5×10^{-2} M) solution as 0.49 V; [b]optical band-gap obtained from absorption spectra in dichloromethane; [c]E_{LUMO} (eV) = $E_{HOMO} + E_{gap}$. E_{onset}: onset potential.

Computational calculations using DFT method were performed in order to rationalize the experimental properties of the TPA-chalcone dyes. Becke, three-parameter, Lee-Yang-Parr (B3LYP) exchange correlation functional with 6-31G** basis set was used for the structure optimization.[22] Theoretical studies have been performed using ORCA 3.0.3 program package.[23] The obtained LUMO and HOMO energy levels, as well as the orbital distribution, are depicted in Figure 4. For all compounds, the HOMO is located mainly over the TPA moiety. For **4c** a slight HOMO orbital density can also be observed over the diarylamino unit. This finding can be related to the charge transfer feature observed for this compound in the ground state and also to the higher fluorescence of this compound in comparison with other synthesized TPA-chalcones. Concerning the LUMO coefficient, for all compounds, the orbital is concentrated over the enone and vinyl-substituted
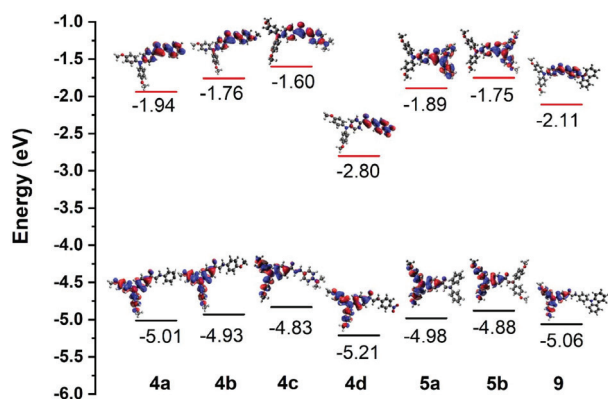

Figure 4. Energy levels and orbital distribution for HOMO and LUMO obtained from DFT calculations at the B3LYP/6-31G** level.

aryl groups. For the D-π-A dye **4d** the orbital is extended over the nitro group.

Conclusions

In summary, seven novel TPA-chalcone derivatives were synthesized and characterized. The compounds display intense absorption bands, moderate fluorescence intensity and band-gaps in appropriate range for application in electroluminescent devices. The chalcone substitution pattern plays a crucial role in the properties of the dyes. Among the compounds, **4a** presented featured properties, including higher extinction coefficient, higher fluorescence quantum yield and lower ionization potential. These features were attributed to the presence of a more electron-donating aryl group (4-dimethylaminophenyl) bonded to the acceptor α,β-conjugated carbonyl system.

Experimental

Materials and instruments

All solvents used (isopropanol, dichloromethane, cyclohexane, toluene, dichlorobenzene and DMF) were of analytical grade and purchased from Merck. Fluorescein sodium salt was from Fluka, and NaOH was from Merck. When used in Ullmann and Heck reactions, toluene, DMF and dichlorobenzene were deaerated with N_2 before the reactions.

UV-Vis absorption spectra were acquired on a PerkinElmer Lambda 35 spectrophotometer using scan velocity of 1200 nm min⁻¹, spectral bandpass of 10 nm and 1 cm path length quartz cuvettes. Photoluminescence spectra and steady state photoluminescence measurements were performed on a Horiba model FluoroMax 4 spectrophotometer. Scanning was made at 1500 nm min⁻¹ with solutions placed in 1 cm optical path length quartz cuvettes (four optically clear faces). Nuclear resonance magnetic (NMR) spectra were recorded in a Bruker model Advance III HD 400 MHz spectrometer. Electron spray ionization high-resolution mass spectrometric (ESI(+)-HRMS) analyses were performed on a Micromass Q-ToF mass spectrometer (Waters). The infrared spectra were recorded with a PerkinElmer Spectrum 2 spectrometer in the range 3500-500 cm⁻¹.

Synthesis and characterization

Synthesis of 1-(4-(bis(4-methoxyphenyl)amino)phenyl)ethanone (**3**)

An oven-dried resealable Schlenk flask was filled with 4-aminoacetophenone (270 mg, 2.0 mmol), CuI (76 mg,

0.4 mmol) and phenanthroline (83 mg, 0.5 mmol), evacuated and back-filled with nitrogen. Then, 4-iodoanisole (1.2 g, 5.0 mmol), KOH (840 mg, 15 mmol) and toluene (8 mL) were added and the reaction was stirred at 100 ºC for 12 h. After, the mixture was allowed to attain room temperature, filtered and concentrated in rotatory evaporator. The crude product was purified through column chromatography in silica gel (hexane/ethyl acetate) providing the compound **3** in 75% yield as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, *J* 9.0 Hz, 2H), 7.11 (d, *J* 9.0 Hz, 4H), 6.88 (d, *J* 9.0 Hz, 4H), 6.81 (d, *J* 9.0 Hz, 2H), 3.81 (s, 6H), 2.50 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 196.4, 157.0, 152.9, 139.2, 130.0, 128.2, 127.9, 116.8, 115.0, 55.5, 26.2.

Synthesis of 4-(9*H*-carbazol-9-yl)benzaldehyde (**8**)

The compound **8** was synthesized as described in literature.[24] In a typical reaction, 249.4 mg (1.5 mmol) of 9*H*-carbazole, 283.2 mg (1.5 mmol) of 4-bromobenzaldehyde, 58.0 mg (0.22 mmol) of 18-crown-6, 303.9 mg (2.2 mmol) of K₂CO₃, 42.3 mg (15 mmol%) CuI and 1.5 mL of *o*-dichlorobenzene were added to a 10 mL Schlenk tube. The mixture was refluxed under nitrogen atmosphere at 180 ºC for 48 h. After, the reaction was quenched with aqueous 20% HCl and extracted with chloroform. The organic phase was dried with anhydrous Na₂SO₄ and concentrated under vacuum. The product was purified by silica flash column chromatography (mobile phase: ethyl acetate/hexane 5%). The compound **8** was obtained as a white solid in 69% yield. ¹H NMR (400 MHz, DMSO-*d₆*) δ 10.14 (s, 1H), 8.28 (d, *J* 7.67 Hz, 2H), 8.21 (d, *J* 8.35 Hz, 2H), 7.92 (d, *J* 8.32 Hz, 2H), 7.53 (d, *J* 8.32 Hz, 2H), 7.47 (t, *J* 7.63 Hz, 2H), 7.34 (t, *J* 7.38 Hz, 2H); ¹³C NMR (100 MHz, DMSO-*d₆*) δ 193.1, 143.1, 140.4, 135.5, 132.3, 127.6, 127.4, 124.2, 121.7, 121.6, 110.8; infrared (IR) (attenuated total reflectance, ATR) ν / cm⁻¹ 3050, 2824, 2743, 1702, 1595, 1510, 1479, 1450, 1361, 1336, 1198, 1161, 1123, 1103, 916, 830, 749, 720, 633, 620, 567, 529, 502.

Typical procedure for synthesis of the TPA-chalcones

A mixture of **3** (347 mg, 1.0 mmol), the respective arylaldehyde (1.6 mmol), NaOH (48 mg, 1.2 mmol), ethanol (4 mL) and THF (4 mL) was stirred at room temperature for 18 h. Then, the solvent was evaporated in rotatory evaporator, the crude product was dissolved in 30 mL of dichloromethane and washed with water (3 × 10 mL). The organic solution was dried over sodium sulfate, filtered and concentrated in rotatory evaporator. The crude product was purified through column chromatography in silica gel (hexane/ethyl acetate).

(*E*)-1-(4-(bis(4-Methoxyphenyl)amino)phenyl)-3-phenylprop-2-en-1-one (**4a**)

Yellow solid; 78% yield; mp 115-117 ºC; IR (ATR)

ν / cm⁻¹ 2930, 2834, 1653, 1588, 1504, 1421, 1290, 1240, 1223; ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* 8.8 Hz, 2H), 7.78 (d, *J* 15.6 Hz, 1H), 7.65-7.60 (m, 2H), 7.53 (d, *J* 15.6 Hz, 1H), 7.40 (d, *J* 7.1 Hz, 3H), 7.13 (d, *J* 8.8 Hz, 4H), 6.88 (t, *J* 8.3 Hz, 6H), 3.82 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 188.0, 157.1, 152.9, 143.2, 139.3, 135.4, 130.3, 130.1, 129.0, 128.9, 128.3, 127.9, 122.1, 117.1, 115.0, 55.6; HRMS (ESI) *m/z* calcd. for C₂₉H₂₆NO₃ [M + H]⁺: 436.1916; found: 436.1896.

(*E*)-1-(4-(bis(4-Methoxyphenyl)amino)phenyl)-3-(4-methoxyphenyl)prop-2-en-1-one (**4b**)

Yellow solid; 62% yield; mp 85 ºC; IR (ATR) ν / cm⁻¹ 3039, 2932, 2835, 1653, 1586, 1503, 1449, 1336, 1284, 1249, 1032; ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* 8.8 Hz, 2H), 7.76 (d, 1H), 7.58 (d, *J* 8.7 Hz, 2H), 7.40 (d, 1H), 7.17-7.07 (m, 4H), 6.89 (m, 8H), 3.85 (s, 3H), 3.82 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 188.0, 161.3, 157.0, 152.7, 143.0, 139.3, 130.1, 130.0, 129.3, 128.1, 127.8, 119.7, 117.2, 115.0, 114.3, 65.9, 55.5; HRMS (ESI) *m/z* calcd. for C₃₀H₂₈NO₄ [M + H]⁺: 466.2018; found: 466.2031.

(*E*)-1-(4-(bis(4-Methoxyphenyl)amino)phenyl)-3-(4-(dimethylamino)phenyl)prop-2-en-1-one (**4c**)

Reddish-brown solid; 40% yield; mp 149-151 ºC; IR (ATR) ν / cm⁻¹ 3027, 2906, 2836, 1645, 1590, 1500, 1432, 1338, 1229, 1028; ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* 8.9 Hz, 2H), 7.77 (d, *J* 15.4 Hz, 1H), 7.53 (d, *J* 8.9 Hz, 2H), 7.34 (d, *J* 15.5 Hz, 1H), 7.12 (d, *J* 8.9 Hz, 4H), 6.89-6.86 (m, 6H), 6.69 (d, *J* 8.9 Hz, 2H), 3.82 (s, 6H), 3.03 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 188.3, 156.9, 152.4, 151.8, 144.1, 139.5, 130.1, 130.0, 127.7, 123.1, 117.3, 116.8, 114.9, 111.9, 55.5, 40.2.

(*E*)-1-(4-(bis(4-Methoxyphenyl)amino)phenyl)-3-(4-nitrophenyl)prop-2-en-1-one (**4d**)

Reddish-brown solid; 38% yield; mp 106-108 ºC; IR (ATR) ν / cm⁻¹ 2929, 2837, 1655, 1586, 1505, 1339, 1241; ¹H NMR (400 MHz, CDCl₃) δ 8.26 (d, *J* 8.9 Hz, 2H), 7.87 (d, *J* 8.9 Hz, 2H), 7.78 (d, *J* 15.8 Hz, 1H), 7.75 (d, *J* 11.9 Hz, 2H), 7.63 (d, *J* 15.8 Hz, 1H), 7.14 (d, *J* 8.9 Hz, 4H), 6.91-6.85 (m, 6H), 3.82 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 186.8, 157.3, 153.3, 148.3, 141.6, 140.1, 138.9, 130.5, 128.7, 128.2, 128.0, 125.9, 124.2, 116.8, 115.0, 55.5; HRMS (ESI) *m/z* calcd. for C₂₉H₂₅N₂O₅ [M + H]⁺: 481.1763; found: 481.1785.

(*E*)-1-(4-(bis(4-Methoxyphenyl)amino)phenyl)-3-(4-(9*H*-carbazol-9-yl)phenyl)prop-2-en-1-one (**9**)

Yellow solid; 44% yield; mp 173-175 ºC; IR (ATR) ν / cm⁻¹ 2931, 2836, 1652, 1595, 1505, 1450, 1335, 1241,

1225, 1171, 1028; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.15 (d, *J* 7.7 Hz, 2H), 7.92 (d, *J* 8.9 Hz, 2H), 7.88-7.84 (m, 2H), 7.66-7.58 (m, 3H), 7.49-7.41 (m, 4H), 7.35-7.28 (m, 2H), 7.15 (d, *J* 8.9 Hz, 2H), 6.95-6.82 (m, 6H), 3.83 (s, 6H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 187.7, 157.1, 153.0, 142.0, 140.5, 139.2, 139.2, 134.2, 130.3, 129.7, 128.9, 127.9, 127.1, 126.1, 123.6, 122.5, 120.4, 120.3, 117.0, 115.0, 109.8, 55.5; HRMS (ESI) *m/z* calcd. for C$_{41}$H$_{33}$N$_2$O$_3$ [M + H]$^+$: 601.2491; found: 601.2499.

Typical procedure for the synthesis of β-arylchalcones **5a** and **5b**

An oven-dried resealable Schlenk flask was filled with **4b** or **4c** (1.0 mmol), Pd(OAc)$_2$ (4.4 mg, 0.02 mmol) and P(*o*-Tol)$_3$ (12.2 mg, 0.04 mmol), evacuated and back-filled with nitrogen. Then, aryl iodide (1.5 mmol), K$_2$CO$_3$ (276 mg, 2.0 mmol) and DMF (4 mL) were added and the reaction was stirred at 120 °C for 24 h. After, the mixture was allowed to attain room temperature, water (15 mL) was added and the product was extracted with ethyl acetate (3 × 15 mL). The combined organic layers were dried over sodium sulfate, filtered and concentrated in rotatory evaporator. The crude product was purified through column chromatography in silica gel (hexane/ethyl acetate) providing the β-arylchalcones **5a** and **5b** in 48 and 77% yields, respectively.

1-(4-(bis(4-Methoxyphenyl)amino)phenyl)-3,3-diphenylprop-2-en-1-one (**5a**)

Orange oil; 48% yield; IR (ATR) ν / cm^{-1} 2932, 2835, 1647, 1588, 1502, 1443, 1329, 1267, 1239, 1163; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.72 (d, *J* 8.9 Hz, 2H), 7.35 (s, 5H), 7.28 (d, *J* 7.2 Hz, 3H), 7.21-7.16 (m, 2H), 7.10-7.04 (m, 5H), 6.86 (d, *J* 9.0 Hz, 4H), 6.75 (d, *J* 8.9 Hz, 2H), 3.80 (s, 6H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 190.8, 157.0, 152.9, 152.7, 141.8, 139.4, 139.3, 130.5, 129.8, 129.3, 129.0, 128.5, 128.4, 128.1, 128.0, 127.7, 124.8, 117.1, 114.9, 55.5; HRMS (ESI) *m/z* calcd. for C$_{35}$H$_{30}$NO$_3$ [M + H]$^+$: 512.2226; found: 512.2245.

1-(4-(bis(4-Methoxyphenyl)amino)phenyl)-3,3-bis(4-methoxyphenyl)prop-2-en-1-one (**5b**)

Orange oil; 77% yield; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.72 (d, *J* 8.9 Hz, 2H), 7.33-7.28 (m, 2H), 7.14-7.09 (m, 2H), 7.09-7.04 (m, 4H), 6.93 (s, 1H), 6.89-6.83 (m, 5H), 6.82-6.78 (m, 2H), 6.75 (d, *J* 8.9 Hz, 2H), 3.83 (s, 6H), 3.81 (s, 6H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 190.9, 160.5, 159.6, 156.9, 153.2, 152.4, 139.5, 134.7, 131.9, 131.4, 130.4, 130.1, 129.8, 127.6, 122.3, 117.2, 114.9, 113.7, 113.3, 55.5, 55.4, 55.2; HRMS (ESI) *m/z* calcd. for C$_{37}$H$_{34}$NO$_5$ [M + H]$^+$: 572.2437; found: 572.2410.

Theoretical calculation software

Theoretical calculations were performed using ORCA 3.0.3 program package.[23] Structures optimization were carried out by the DFT method using B3LYP exchange-correlation functional with the 6-31G** basis set.[22] Solvent effect (cyclohexane) was taken into account via the COSMO solvation method (ORCA package).

Determination of fluorescence quantum yields

The fluorescence quantum yield of chalcones were determined by a standard comparative method[19] using equation 1. All chalcone solutions were prepared in cyclohexane at a concentration range between 3.0×10^{-7}-1.1×10^{-6} mol L^{-1}. Fluorescein sodium salt solution was prepared in NaOH (0.1 mol L^{-1}) and employed as the standard solution with fluorescence quantum efficiency (ϕ_{st}) of 0.93.[20]

$$\phi_{ch} = \phi_{st} \frac{f_{st}(\lambda_{ex})}{f_{ch}(\lambda_{ex})} \frac{\int_{\lambda_{em}} F_{ch}(\lambda_{em})}{\int_{\lambda_{em}} F_{st}(\lambda_{em})} \frac{n_{ch}^2}{n_{st}^2} \qquad (1)$$

where $f_x(\lambda_{ex}) = 1 - 10^{-Ax(\lambda ex)}$ and $\int_{\lambda_{em}} F_x(\lambda_{em})$ is the integrated area of the fluorescence spectra of standard (x = st) or chalcone (x = ch) and n is the refractive index of solvents.

Cyclic voltammetry

Cyclic voltammetry was performed on an Ivium Compact Stat potentiostat. The measurements were performed in a system of three-electrode setup: (*i*) a glassy carbon working electrode; (*ii*) an Ag/AgCl(KCl$_{(sat)}$) reference electrode; and (*iii*) a Pt auxiliary electrode. Solutions of the compounds **4a-d** and **5a** with concentration of 2×10^{-3} mol L^{-1} were prepared in dichloromethane. TBAPF$_6$ was used as supporting electrolyte.[25] An electrochemical cell without the chalcone derivatives was used for reference and the pair ferrocene/ferrocenium was used for calibration.[26] The cyclic voltammetry experiments were performed in a range of 0 to 2.0 V with a step of 50 mV s^{-1} and these measurements were repeated 5 times. The HOMO energy levels were obtained through the equation $E_{HOMO} = -\left(E_{onset} - E_{\frac{FC}{FC^+}} + 4.8 \right)$ eV.

Supplementary Information

Supplementary information is available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgments

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