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A Combined Theoretical and Experimental Study on Intramolecular Charge Transfer Processes in Star-Shaped Conjugated Molecules

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ABSTRACT

In this work, 1,3,5-tristyrylbenzene (**1**) and 1,3,5-tristyryl-*s*-triazine (**2**) derivatives decorated with carbazole moieties have been synthesized for the first time. Their photophysical properties and the nature of their low-lying electronic excited state were investigated combining steady-state and time-resolved fluorescence spectroscopy, along with TD-DFT calculations. We found that the fluorescence emission of these compounds is highly sensitive to the polarity of the solvent, particularly for the *s*-triazine derivative whose color varies from blue to green or yellow depending on it. This behavior was associated to pronounced intramolecular charge transfer (ICT) processes from the

periphery of the molecule to the π -conjugated core. These ICT processes involve large changes in the dipole moment and geometry, the latter especially localized in a single branch of the molecule and not along the entire π -conjugated core. The higher quantum yields determined for 1,3,5-tristyrylbenzene derivative (**1**) were associated to higher radiative decay rates. On the contrary, the smaller radiative decay rates determined for 1,3,5-tristyryl-*s*-triazine derivative (**2**) became comparable to the non-radiative decay rates.

INTRODUCTION

Fluorescent π -conjugated molecules have attracted a great deal of attention, initially because their potential application in organic and molecular electronic devices¹ and, more recently, as fluorescent labels for biomolecules or as analytical and biological sensors.^{2,3} They still remain as contemporary targets since recent optical processes rise with new potential application. Aggregation-induced emission (AIE) effect, aggregation-induced enhanced emission (AIEE) or aggregation caused quenching (ACQ) are examples of such fluorescent process and a better understanding of them is needed.⁴ It has been estimated that by 2025 solid-state lighting in form of light emitting diodes (LEDs) could reduce the global amount of electricity consumed for lighting by around 35%⁵ and dye-sensitized solar cells (DSSCs) are postulated as one of the most powerful alternatives to reduce the carbon footprint caused by fossil fuels.⁶ In the last years, light-emitting devices based on organic compounds are becoming very popular. These compounds not necessarily exceed the level of performance of inorganic counterparts, though organic materials allow the production of cost-effective, large-area, and mechanically flexible electronic devices via solution-based high-throughput patterning techniques.^{7,8}

Different families of π -conjugated compounds are employed in the fabrication of fluorescent materials. They are typically constructed by combination of electron donating and electro withdrawing groups jointed by a π -bridge to tune the HOMO and LUMO orbitals and optimizing the optical properties. The electron donor carbazole-based π -electron system has shown good properties as light emitting, carrier transporting and photorefractive behaviour^{9,10} and specifically (9H-carbazol-9-yl)styryl derivatives has previously shown very good photoluminescence properties,¹¹⁻¹⁴ although they strongly depend on the molecular architecture, e.g. the π -bridge, the linkers between moieties and/or other substituents, and the whole molecular orientation.¹⁵

Note that light-emitting properties of tristyrylbenzene derivatives in solution or solid state, would strongly depend on supramolecular aggregation, thus modulating their possible technological and sensing applications as it has been recently disclosed in last years.¹⁶⁻¹⁹ Concurrently, Coya *et al.* demonstrated that tristyrylbenzene derivatives can be employed in the fabrication of OLEDs with satisfactory performance.^{20,21} In this work, we have thus synthesized two novel molecules based on the (9H-carbazol-9-yl)styryl moieties connected to benzene, an electron donating core, and to *s*-triazine, a strong withdrawing core, compounds **1** and **2** in Scheme 1, with the aim of study their photophysical properties when a π -bridge is preserved as *meta*-arrangement and the nature of the core is changed. As far as we know, this is the first time that these compounds have been synthesized and their optical and photophysical properties thoroughly studied, which intends to shed light on the molecular engineering strategies to create new molecules with tailored properties for light-emitting applications.

Scheme 1. Chemical structure of compounds **1** and **2**, along with two reference compounds (**3a**, **3b** and **4**)

MATERIAL AND METHODS

General. All reagents were used as received and without further purification. Toluene (Tol), tetrahydrofuran (THF), dichloromethane (DCM) and acetonitrile (ACN) were used as CHROMASOLV quality.

Synthesis. Formation of the double bonds in both structures was performed by the reaction of the commercial aldehyde **5** with the corresponding core in the presence of potassium *tert*-butoxyde, a standard methodology for the Horner-Wadsworth-Emmons (reaction that also works for the deprotonation and subsequent coupling of triazine

(scheme 2)).¹⁸ Specific details concerning preparation of **1** and **2** and their characterization are provided in the Supporting Information (SI).

Scheme 2. Synthesis of compounds **1** and **2**.

Spectroscopy. Unless otherwise stated, spectra were acquired in different solvents at 20°C and sample concentration of 1 μM . Quartz cuvettes (Hellma Analytics) of 10 mm were employed for all the absorption and emission measurements of liquid samples.

UV-Vis absorption spectra were acquired in a V-650 (Jasco) spectrophotometer and with a scan rate of 600 nm min^{-1} . A Peltier accessory was employed to control the temperature of the spectrophotometer measuring cell.

Steady-state emission spectra were acquired in a FS5 (Edinburgh Instruments) spectrofluorometer equipped with a Xe lamp of 150 W as light source, a TCSPC detector and an integrating sphere. The quantum yields, Φ_F , in solution and in solid state were measured using the integrating sphere. Experimental conditions are indicated in the corresponding tables and in the supporting information. In liquid samples, reabsorption was corrected through the following equation

$$\Phi_F^{corr} = \frac{\Phi_F^{obs}}{1 - a + \frac{a \Phi_F^{obs}}{100}} \quad (1)$$

where Φ_F^{obs} is the fluorescence quantum yield directly measured in the integrating sphere, and Φ_F^{corr} is the corrected quantum yield with a , the re-absorbed area calculated as the quotient between the areas of the emission band recorded using and not the integrating sphere, respectively. Chromaticity calculations of the emission spectra were done using the F980 Software of Edinburgh Instruments.

Fluorescence decay profiles were collected at the wavelength of maximum emission using a FLS920 spectrofluorometer (Edinburgh Instruments) equipped with a TCSPC detector. A sub-nanosecond pulsed Light-Emitting Diode, EPLED-360 (Edinburgh Photonics) was employed as light source at 368 nm for time-resolved fluorescence experiments. The fluorescence intensity decay, $I(t)$, was fitted to the following multiexponential function (using the “exponential reconvolution fit” implemented in the software F980 from Edinburgh Instruments)

$$I(t) = \sum_{i=1}^n \alpha_i \exp(-t/\tau_i) \quad (2)$$

where α_i and τ_i are the amplitude and lifetime for each i -th term. The number of i -th terms used in that fitting was the minimum needed to get a homogeneous distribution of the weighted residuals and a value of χ^2 near unity. The mean lifetime of the decay was then calculated as

$$\langle \tau \rangle = \frac{\sum_{i=1}^n \alpha_i \tau_i^2}{\sum_{i=1}^n \alpha_i \tau_i} \quad (3)$$

The temperature of the experiments was controlled using a Peltier accessory (temperature-controlled cuvette holder, TLC 50, Quantum Northwest).

FTIR measurements were carried out at room temperature using a 640-IR (Varian) spectrophotometer equipped with an attenuated total reflection (ATR) accessory. The spectra were recorded with resolution of 4 cm⁻¹ and 64 scans.

Computational Details. All the calculations were performed with the Gaussian09 (revision D.01) suite of programs.²² Three different flavors of Density Functional Theory (DFT) hybrid functionals have been employed; i.e., the Becke-Lee-Yang-Parr three-parameter B3LYP,²³ the Perdew–Burke–Erzenrhof PBE0,^{24,25} and the Truhlar’s Minnesota functional M06-2X,²⁶ together with basis sets 6-31G* and 6-31+G*, the latter incorporating diffuse functions which are particularly recommended in excited-state calculations.²⁷

It should be noted that the use of a set of functionals differing in their proportion of exact-like exchange, 20% for B3LYP, 25% for PBE0, and 54% for M06-2X, would allow us to better bracket the accuracy of the results. First of all, due to the conformational disorder of the branches, a previous thorough gas-phase conformational scan was carried out. For that purpose, the lowest energy conformers obtained from a random conformational search employing Molecular Mechanics (Avogadro software, MMFF94 force field)²⁸ were optimized at the B3LYP/6-31G* level of theory, and the lowest energy conformer was reoptimized with the rest of methods and basis sets. The nature of the stationary points was assessed by means of the frequencies (all-positive) calculated analytically from the second derivatives of the energy. Wavenumbers were quantitatively corrected employing a scaling factor.²⁹ To systematically analyze the molecular structure of both derivatives, we have made use of the ‘Bond Length Alternation’ (BLA) values. This parameter, widely employed in the literature, is defined as the difference between the average length of the carbon-carbon single and double bonds.^{30,31} Here, this parameter was calculated for all the phenyl-vinylene branches involving the carbon atoms 1 – 6 shown in Figure 1.

Vertical electronic transitions were computed at the Time-Dependent (TD)-DFT level for the solvated molecule within the Polarizable Continuum Model (PCM)

methodology.^{32,33} The absorption energy was calculated as $E_{ab}(S_n) = E_{S_n}(G_{S_0}) - E_{S_0}(G_{S_0})$, where $E_{S_0}(G_{S_0})$ is the energy of the S_0 state at its equilibrium geometry (G_{S_0}) while $E_{S_n}(G_{S_0})$ is the energy of the S_n state at the ground-state geometry. ICT character of the lowest-energy electronic transitions was evaluated through the integral of overlap of hole-electron distribution (S_{he}), the distance between centroid of hole and electron (d_{he}), and Δr index.³⁴ Those magnitudes were calculated employing the Multiwfn 3.3.6 code.³⁵ The fluorescence emission energy from the first excited state was calculated as $E_{em}(S_1) = E_{S_1}(G_{S_1}) - E_{S_0}(G_{S_1})$, where $E_{S_1}(G_{S_1})$ is the energy of the S_1 state at its equilibrium geometry (G_{S_1}), in the State-Specific solvation approach,³⁶ while $E_{S_0}(G_{S_1})$ corresponds to the energy of the S_0 state at the S_1 state geometry (G_{S_1}) and with the static solvation from the excited state.³⁷

Finally, the vertical singlet–triplet gap (ΔE_{ST}) was calculated and used as a key energy magnitude for the analysis of the time-resolved fluorescence experiments and the discussion of the radiative and non-radiative mechanisms involved in the relaxation of the S_1 state. This energy difference was obtained as $\Delta E_{ST} = E_{ab}(S_1) - E_{ab}(T_1)$, where $E_{ab}(T_1)$ is the vertical excitation energy for absorption to the T_1 excited state. For this specific case, both $E_{ab}(S_1)$ and $E_{ab}(T_1)$ were obtained using the TD-PBE0 method,^{24,25} along with the def2-TZVP basis sets (S_0 state was previously optimized at the PBE0-D3(BJ)/def2-TZVP level of theory, including the D3(BJ) correction for intra-molecular dispersion effects³⁸⁻⁴⁰). Also, in this approach, both vertical transitions were calculated in gas phase using the Tamm–Dancoff approximation.⁴⁰ In previous work, this methodology has been demonstrated to significantly and systematically improves the accuracy of triplet energies in case of pronounced ICT excitations and, hence, was chosen for the calculation of ΔE_{ST} for the studied molecules.⁴²⁻⁴⁵

RESULTS AND DISCUSSION

Molecular Structure. Figure 1 and Table 1 show the molecular structure calculated, together with some selected geometrical parameters for the studied compounds, respectively. It was found that 1,3,5-tristyrylbenzene and 1,3,5-tristyryl-*s*-triazine cores are near-planar but there exist some differences for the dihedral angles of the different branches of each molecule. In addition, a more effective conjugation (i.e. BLA values of 0.124 – 0.126 and 0.128 – 0.129 Å, respectively) was observed for 1,3,5-tristyryl-*s*-triazine core with respect to 1,3,5-tristyrylbenzene. In general, dihedral angles τ_1 and τ_3 are also smaller for compound **2** than for compound **1**, except in polar solvents (dichloromethane and acetonitrile) where τ_3 reaches $\sim 10^\circ$ in one single branch while the rest of branches remain near planar ($\tau_3 \leq 3^\circ$). In both compounds, carbazole moieties are largely twisted ($\tau_4 \geq 52^\circ$ with respect to the rest of the molecule and the variation of the polarity of the solvent does not significantly modify this parameter. Fairly similar FTIR spectra were recorded for both compounds showing the two characteristic bands of 9-phenylcarbazole at ~ 1500 and ~ 1450 cm^{-1} , corresponding to rocking and stretching modes in the carbazole moiety (FTIR spectra are shown in Figure S3 and the corresponding vibrational assignment in Table S1).⁴⁶ Other intense bands associated to C-H wagging modes in carbazole moieties appear at ~ 740 and ~ 720 cm^{-1} .

Figure 1. Molecular structure of compounds 1 and 2 calculated at the M06-2X/6-31+G* level of theory, using dichloromethane as solvent. The numbering and dihedral angles $\tau_1 - \tau_4$ used in Table 1 are shown.

Table 1. Some Selected Geometrical Parameters Calculated for the S_0 and S_1 States of Compounds 1 and 2 in Different Solvents. BLA (Bond Length Alternation) Was Calculated between the Atoms 1 and 6 Shown in Figure 1. Atoms Involved in Dihedral Angles τ_1 and τ_2 Are also Shown in Figure 1. Calculations Were Carried out at the M06-2X/6-31+G* Level of Theory.

Comp.	Solv. ^a	Branch	BLA		τ_1 (deg.)		τ_2 (deg.)		τ_3 (deg.)		τ_4 (deg.)	
			S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
1	Tol ^b	1	0.129	–	5.5	–	-179.0	–	-2.6	–	53.9	–
		2	0.128	–	1.4	–	-179.3	–	-8.1	–	54.4	–
		3	0.129	–	-7.5	–	-180.0	–	4.4	–	-55.5	–
	THF	1	0.129	0.125	2.8	0.5	-179.4	-179.5	-1.2	-0.1	53.7	53.6
		2	0.128	0.124	4.9	0.3	-179.6	179.7	-6.1	0.3	55.1	54.5
		3	0.129	0.004	-5.6	-0.7	179.9	178.9	3.4	-0.3	-55.6	-43.6
	DCM	1	0.129	0.125	2.8	1.0	-179.4	-179.5	-1.3	0.0	53.7	53.5
		2	0.128	0.124	4.9	-6.4	-179.6	179.1	-6.1	-12.3	55.0	55.2
		3	0.129	0.005	-5.5	-1.0	179.9	178.9	3.3	-0.6	-55.6	-43.6
	ACN	1	0.129	0.126	2.7	0.7	-179.4	-179.6	-1.2	0.2	53.4	53.2
		2	0.128	0.124	4.4	-6.3	-179.6	179.1	-6.2	-12.1	54.8	55.0
		3	0.129	0.008	-5.5	-0.9	179.9	178.8	3.4	-0.5	-55.3	-43.3
	2 Tol	1	0.126	0.127	0.2	2.0	-178.9	179.7	0.5	-4.9	52.8	54.0
		2	0.124	0.021	0.1	1.7	-179.6	179.0	2.6	-2.9	54.2	38.9
		3	0.125	0.117	0.2	0.6	178.7	179.5	2.5	2.3	-53.0	-52.9

^a Tol, THF, DCM and ACN correspond to the solvents: toluene, tetrahydrofuran, dichloromethane and acetonitrile, respectively.

^b Excited state calculations failed due to severe convergence problems.

UV-Vis Absorption Spectroscopy. Figure 2 shows the absorption spectra of compounds **1** and **2** in different solvents. Two intense bands can be distinguished in all the spectra. Detailed information on the maximum absorption wavelengths and their corresponding molar absorption coefficients is collected in Table 2 and Table S2 (see SI). The lowest-energy absorption band is not very sensitive to the polarity of the solvent both for compound **1** and **2**. In dichloromethane, this is centered at 3.65 eV for compound **1**, and 0.36 eV red-shifted for compound **2**. Likewise, a difference of 0.12 eV can also be observed when the lowest absorption bands of reference compounds **3a** and **4** are compared (see Table 2). This behavior can be associated to an energy stabilization of the frontier molecular orbitals, particularly LUMO, due to the presence of nitrogen atoms in

the molecular core (LUMO energy is -1.41 and -1.90 eV for compounds **1** and **2**, respectively; while HOMO energy is -6.79 and -6.94 eV for compounds **1** and **2**, respectively, in dichloromethane solution). A similar result was reported in a previous work in which it was observed that LUMO energy gradually decreases from *p*-terphenyl to diphenyl-*s*-tetrazine upon the increase of the number of nitrogen atoms in the central ring.⁴⁷ In addition, carbazole substitution also leads to large red-shifts of 0.31 eV for compound **1** and 0.55 eV for compound **2** with respect to reference compounds **3b** and **4**, respectively (in dichloromethane solution).^{48,49}

Table 2. Experimental Maximum Absorption Energy (E_{ab}^{exp}) and Calculated Lowest Energy Transitions (E_{ab}^{calc}), along with their Molar Absorption Coefficients (ϵ) in Different Solvents and the Oscillator Strength (f) and Orbital Contributions for these Transitions. Calculations Were Carried out at the TD-M06-2X/6-31+G* Level of Theory. Tol, THF, DCM and ACN Correspond to Toluene, Tetrahydrofuran, Dichloromethane and Acetonitrile, respectively.

Compound (solvent)	E_{ab}^{exp} (eV [nm])	$\epsilon \pm 2\sigma$ (cm L mol ⁻¹)	E_{ab}^{calc} (eV [nm])	f	States	Main component of the transition (% contribution)
1 (Tol)	3.59 [345]	97.8±9.7	3.63 [341]	1.476	S ₀ →S ₁	HOMO-1→LUMO (43%)
			3.70 [335]	2.020	S ₀ →S ₂	HOMO→LUMO (34%)
1 (THF)	3.61 [343]	150±9	3.65 [340]	1.457	S ₀ →S ₁	HOMO-1→LUMO (46%)
			3.73 [332]	2.025	S ₀ →S ₂	HOMO→LUMO (34%)
1 (DCM)	3.60 [344]	40.3±3.4	3.65 [340]	1.461	S ₀ →S ₁	HOMO-1→LUMO (46%)
			3.73 [332]	2.031	S ₀ →S ₂	HOMO→LUMO (34%)
1 (ACN)	3.60 [344]	14.7±0.4	3.66 [339]	1.442	S ₀ →S ₁	HOMO-1→LUMO (48%)
			3.74 [331]	2.024	S ₀ →S ₂	HOMO→LUMO (34%)
2 (Tol)	3.19 [389]	116±11	3.52 [352]	1.962	S ₀ →S ₁	HOMO→LUMO (55%)
			3.54 [350]	1.219	S ₀ →S ₂	HOMO→LUMO+1 (24%)
						HOMO-2→LUMO (19%)
2 (THF)	3.25 [381]	48.1±5.8	3.54 [351]	1.989	S ₀ →S ₁	HOMO→LUMO (45%)
			3.55 [349]	1.235	S ₀ →S ₂	HOMO-2→LUMO (27%)
						HOMO-1→LUMO+1 (19%)
2 (DCM)	3.24 [383]	91.2±11.6	3.54 [350]	1.952	S ₀ →S ₁	HOMO→LUMO (43%)
			3.56 [349]	1.292	S ₀ →S ₂	HOMO-2→LUMO (26%)
						HOMO→LUMO+1 (20%)
2 (ACN)	3.30 [376]	9.25±0.51	3.54 [350]	1.951	S ₀ →S ₁	HOMO→LUMO (30%)
						HOMO-1→LUMO (22%)
			3.56 [348]	1.296	S ₀ →S ₂	HOMO→LUMO+1 (29%)
3a (DCM) ^a	3.91 [317]	91.2				HOMO-2→LUMO (21%)
4 (DCM) ^b	3.79 [327]					

^a References ^{48,50}; ^b Reference ⁴⁹

a)

b)

Figure 2. Absorption spectra of **1** (a) and **2** (b) in different solvents (sample concentrations were 1 μ M)

Different TD-DFT methods (TD-B3LYP, TD-PBE0 and TD-M06-2X) and basis sets (6-31G* and 6-31+G*) were employed to calculate the lowest-energy electronic transitions of both molecules in the chosen solvents (see Table S3 in SI). High oscillator strengths were found for these transitions ($f \geq 1.2$; see Table 2) in agreement to the previous observations reported for compound **3b**, other related phenylenevinylenes and, in general, systems with large number of conjugated rings such as coumarins, porphyrins, phthalocyanines and graphene nanoribbons, among others.^{17,52-57} The combination of TD-M06-2X and 6-31+G* yielded the best match between calculated and experimental values. The higher percentage of HF-like exchange in M06-2X, compared to B3LYP and PBE0, reduces any possible underestimation in the calculation of the excited-state energies, in agreement with previous works.^{17,50,58} According to the findings obtained with TD-M06-2X/6-31+G*, the lowest energy absorption band of compound **1** corresponds to two π - π^* electronic transitions whose main components are HOMO-1 $\rightarrow$ LUMO and HOMO $\rightarrow$ LUMO electronic excitations (see Table 2). As shown in Figure 3, HOMO and HOMO-1 are mainly localized on the external part of the molecule, involving the carbazole groups, while LUMO is particularly located on the central core. Consequently, these electronic transitions should imply an intramolecular charge transfer (ICT) process from the outer part to the inner part of the molecular backbone.

The ICT phenomenon is even clearer for compound **2**, with occupied orbitals HOMO-2, HOMO-1 and HOMO localized on single branches of the molecule, particularly on the carbazole moiety. On the contrary, LUMO and LUMO+1 are localized on the core of the molecule and the electron-withdrawing *s*-triazine ring. The lowest energy absorption band mainly involves two π - π^* transitions which consequently imply that the charge is transferred from the carbazole moieties to the *s*-triazine core. The

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2
3 integral of overlap of hole-electron distribution (S_{he}), the distance between centroid of
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5 hole and electron (d_{he}), and Δr index are molecular descriptors typically employed to
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7 quantitatively analyze the ICT character of an electronic transition. They were calculated,
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9 in gas phase, at the TD-M06-2X/6-31+G* level of theory and using the Tamm–Dancoff
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11 approximation (TDA). As shown in Figure 4, a lower S_{he} and higher lower d_{he} were found
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13 for compound **2**, with respect to **1**, indicating that the charge transfer must be more
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15 efficient for the *s*-triaziazine derivative. In this sense, a significantly higher Δr value was
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17 also calculated for compound **2** with respect to **1**. In the next section, we will discuss the
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19 associated changes in the molecular structure and dipole moment upon the electronic
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21 excitation, as well as the effect of the polarity of the solvent on the light-emitting
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23 properties.
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Figure 3. Isocontour plots (0.02 a.u.) of some selected frontier MOs of compound **1** and **2** computed at the M06-2X/6-31+G* level of theory in gas phase.

Figure 4. Charge density distribution (CDD; hole in purple; electron in green), integral of overlap of hole-electron distribution (S_{he}), distance between centroid of hole and electron (d_{he}), and Δr index calculated for molecules **1** and **2** at the TD-M06-2X/6-31+G* level of theory (in gas phase and using TDA).

Fluorescence Spectroscopy. Steady-state emission spectra of compounds **1** and **2** in different solvents are shown in Figure 5. Two main differences between both compounds were observed both in the shape of the spectra and in the spectral shifts as a function of the polarity of the solvent. Regarding the shape of the emission spectra, fine vibronic structure is only partially observed for compound **1** in the least polar solvents used (toluene and tetrahydrofuran; the solvents are ordered on the basis of their dielectric constants in Table 4) indicating that the excited state of this compound must adopt a more planar and symmetric molecular structure than **2**. In tetrahydrofuran solution, the main structural differences between both compounds in the S_1 state were found in the dihedral angle $|\tau_3|$, which is $\leq 0.3^\circ$ for **1**, and reaches values between 0.2° and 2.1° for the *s*-triazine derivative (see Table 1). In general, an increase of the maximum values reached for dihedral angles $|\tau_1|$ and $|\tau_3|$ of the S_1 state is observed in more polar solutions (dichloromethane and acetonitrile). In addition, carbazole moieties seem to produce a certain distortion of the molecular structure of the excited state in comparison to the reference compound **3b**. In this sense, the vibronic structure of **3b** was observed both in

non-polar solvents as *n*-hexane and in polar solvents as acetonitrile and the fluorescence emission was not sensitive to the polarity of the solvent.¹⁷

The second interesting feature observed in Figure 5 is the strong sensitivity of the fluorescence emission wavelength ($\lambda_{\text{em}}^{\text{max}}$) to the solvent polarity and the large Stokes shifts found, especially for compound **2**. This large Stokes shift observed for compound **2** was also predicted by the calculations carried out at the TD-M06-2X/6-31+G* level of theory (see Table 4). Figure 6 shows a CIE1976 chromaticity diagram of both compounds in different solvents. Although the fluorescence emission color is always blue for compound **1**, the emission color can be tuned in **2** from blue to green or yellow depending on the polarity of the solvent. In that sense, some carbazole-*s*-triazine derivatives have been used in opto-electronic applications such as blue or green phosphorescent emitters for OLEDs,⁵⁹⁻⁶¹ and as emitters in Thermally Activated Delayed Fluorescence (TADF) applications.^{62,63} To explain these large Stokes shifts observed, the shape and distribution of the frontier molecular orbitals of compounds **1** and **2** were compared with that from the reference compound **3b**. HOMO and LUMO are delocalized on the whole π -conjugated core of **3b**, and it is hence expected that the structural changes upon electronic excitation affect similarly all the branches of the core.¹⁷ On the contrary, frontier orbitals of compound **1** and, particularly, **2** are localized on certain branches of the core (see Figure 3). Thus, electronic excitation could provoke non-homogeneous structural distortions in the different branches of molecules **1** and **2**. Accordingly, Table 1 shows how the geometrical changes upon the electronic excitation mainly takes place in one single branch that undergoes a certain planarization. BLA of that styrylbenzene branch decreases from 0.124 – 0.129 angstroms in S_0 state up to 0.004 – 0.021 angstroms in S_1 state while the BLA of the rest of the branches only a show slight variation. In the branch where LUMO is mainly localized, the dihedral angle of the linkage phenyl-carbozole (τ_4

in Table 1) also undergoes a planarization of $10^\circ - 15^\circ$. These geometric distortion upon excitation should lead to modifications in the dipole moment of the molecule. The Lippert-Mataga equation⁶⁴⁻⁶⁶ was employed to study the influence of solvent on the emission spectra and the change in the dipole moment upon excitation:

$$\Delta\nu = \nu_{ab} - \nu_{em} = \frac{2(\mu_E - \mu_G)^2}{h c a^3} \Delta f + constant \quad (4)$$

where $\Delta\nu$ is the Stokes shift (in cm^{-1}); ν_{ab} and ν_{em} are the wavenumbers corresponding to spectral maxima in absorption and fluorescence spectra, respectively (in cm^{-1}); μ_E and μ_G are the dipole moments of the compound in solution in excited and ground states, respectively (in $\text{D} = 1 \times 10^{-18} \text{ cm}^{5/2} \text{ g}^{1/2} \text{ s}^{-1}$); h is the Planck constant ($h = 6.626 \times 10^{-27} \text{ erg s}$); c is the speed of light in vacuum ($c = 2.998 \times 10^{10} \text{ cm s}^{-1}$); a is the effective radius of Onsager cavity (in cm); and Δf is Lippert-Mataga solvent polarity parameter.^{66,67} Figure 7 shows the dependence of the Stokes shift versus Δf and Table 4 collects the value of the parameters employed for the fitting of the Lippert-Mataga equation. The change in the dipole moment upon the excitation, $\Delta\mu = \mu_E - \mu_G$, is comparable to other compounds in which ITC processes have been reported such as 4-styryl-1,8-naphthalimides, 2,4,6-tri(5-aryl-2-thienyl)pyrimidines and boradiazaindacenes, among others.⁶⁷⁻⁶⁹ As expected, $\Delta\mu$ is especially high in compound **2** and it can be associated to a strong deformation of the excited state.

The kinetics rate constants for the radiative deactivation k_F and non-radiative deactivation via internal conversion, k_{ISC} , were estimated from the mean lifetime and fluorescence quantum yields

$$k_F = \frac{\Phi}{\langle \tau \rangle} \quad (5)$$

$$k_{ISC} = \frac{1}{\langle \tau \rangle} - k_F \quad (6)$$

and their values are shown in Table 3. Mean fluorescence lifetimes, $\langle\tau\rangle$, were obtained through eq. (2) and (3); some examples of fluorescence intensity decays reordered for compounds **1** and **2** are shown in Figure S4. Intersystem crossing, ISC, from S_1 to T_1 state was neglected because the energy gap between both states (ΔE_{ST}) is too high in comparison with compounds that exhibit efficient ISC, within the order of 0.1 – 0.2 eV ($\Delta E_{ST} = 0.86$ and 0.54 eV for compounds **1** and **2**, respectively).⁷⁰ Similar k_F values within 0.17 – 0.22 ns⁻¹ were obtained for compound **1** in the different solvents indicating that the solvent properties do not strongly affect the radiative deactivation of this compound. For this compound, radiative deactivation is favored with respect the compound **2**. Higher k_{ISC} values were calculated for **2**, which became comparable to k_F . The stronger deformation of **2** in the excited state and the stabilization of its high dipole moment in polar solvents could favor the non-radiative relaxation. This fact could explain the lower quantum yields found for compound **2** than for its counterpart.

In summary, the observations made here are expected to impact on the design of efficient light emitters based on star-shaped conjugated molecules. In addition, the emission color can be tuned by means of ICT processes, combining electron-donating and withdrawing groups in the core and the periphery of the molecule.

1)

2)

Figure 5. Fluorescence emission spectra of **1** and **2** in different solvents (sample concentrations were 1 μ M)

(a)

(b)

Figure 6. (a) Photographs and (b) CIE1976 chromaticity diagram of solutions of the compounds **1** and **2** in different solvents.

Figure 7. Stokes shift ($\Delta\nu$) vs. Lippert-Mataga solvent polarity parameter (Δf) for compounds **1** (black) and **2** (red)

Table 3. Maximum Excitation and Emission (Experimental and Calculated at the TD-M06-2X/6-31+G* Level of Theory) Wavelengths/Energies ($\lambda_{\text{ex}}^{\text{max}}/E_{\text{ex}}$ and $\lambda_{\text{em}}^{\text{max}}/E_{\text{em}}$) and Mean Fluorescence Lifetime ($\langle\tau\rangle$) Determined for Compounds **1** and **2** in Various Solvents at 298 K. k_F and k_{ISC} Correspond to the Fluorescence and Intersystem Crossing Rate Constants, respectively.

Compound (solvent) ^a	$E_{\text{ex}}[\lambda_{\text{ex}}^{\text{max}}]$ (ev [nm])	$E_{\text{em}}[\lambda_{\text{em}}^{\text{max}}]$ (ev [nm]) exp.	$E_{\text{em}}(S_1)[\lambda_{\text{em}}^{\text{max}}]$ (ev [nm]) calc.	Φ (%)	$\langle\tau\rangle$ (ns)	k_F (ns ⁻¹)	k_{ISC} (ns ⁻¹)
1 (Tol) ^b	3.57 [347]	3.09 [401]	—	59	3.41	0.17	0.12
1 (THF)	3.61 [343]	3.08 [403]	2.94 [422]	80	4.56	0.18	0.04
1 (DCM)	3.59 [345]	2.96 [419]	2.93 [423]	75	3.39	0.22	0.07
1 (ACN)	3.64 [341]	2.89 [429]	2.86 [433]	83	3.84	0.22	0.04
2 (Tol)	3.13 [396]	2.74 [453]	2.78 [445]	55	3.87	0.14	0.12
2 (THF)	3.26 [380]	2.48 [500]	2.41 [514]	17	3.31	0.05	0.25
2 (DCM)	3.25 [381]	2.36 [526]	2.38 [521]	73	4.03	0.18	0.07
2 (ACN)	3.29 [377]	2.16 [574]	2.24 [554]	16	2.03	0.08	0.41

^a Tol, THF, DCM and ACN are the used solvents: toluene, tetrahydrofuran, dichloromethane and acetonitrile, respectively.

^b These calculations failed due to severe convergence problems.

Table 4. Stokes Shifts ($\Delta\nu$) along with Lippert-Mataga Polarity Parameters (Δf), Dielectric Constants (ϵ) and Refractive Indexes of the Chosen Solvents. Slopes Were Obtained from the Linear Fits of Figure 7. The Change in the Dipole Moment from the Ground to the Excited State, $\mu_E - \mu_G$, Was Calculated by Using of Eq. (4). (Tol, THF, DCM and ACN Correspond to Toluene, Tetrahydrofuran, Dichloromethane and Acetonitrile, respectively).

Solvent	ϵ	n	Δf^a	$\Delta\nu$ ($10^3 \times \text{cm}^{-1}$)		a (Å)		Slope ($10^3 \times \text{cm}^{-1}$)		$\mu_E - \mu_G$ (D)	
				1	2	1	2	1	2	1	2
Tol	2.38	1.496	0.01350	4.05	3.63						
THF	7.58	1.407	0.20964	4.34	6.25	7.19	7.56	5.39	18.03	14.1	27.8
DCM	10.36	1.445	0.22073	5.20	7.10						
ACN	37.50	1.339	0.30736	5.76	9.17						

^a Lippert-Mataga solvent polarity parameter, $\Delta f = [(\epsilon - 1)/(2\epsilon + 1)] - [(n^2 - 1)/(2n^2 + 1)]$

CONCLUSIONS

In this work, a 1,3,5-tristyrylbenzene (**1**) and a 1,3,5-tristyryl-*s*-triazine (**2**) derivatives possessing carbazole moieties have been synthesized and spectroscopically and theoretically characterized. We have found that the fluorescence emission of these compounds is sensitive to the polarity of the solvent, particularly for compound **2**. This behavior has been associated to ICT processes from the periphery of the molecule, involving the carbazole rings, to the π -conjugated core. In contrast to the reference compound **4**, the frontier molecular orbitals of **1** and **2** are not fully delocalized over the entire molecule, i.e. occupied orbitals are mainly localized on the branches and virtual orbitals on the π -conjugated core.

As commonly described for ICT compounds, the effect of the solvent polarity on the Stokes shifts was studied through the Lippert-Mataga equation. Large changes in the dipole moment upon excitation were found, particularly for compound **2**, where the fluorescence emission color can be tuned from blue to green or yellow depending on the polarity of the solvent. The strong changes in the dipole moment upon excitation were attributed to the structural deformations that the excited electronic state undergoes. TD-DFT calculations indicated that the main geometrical changes in the excited state involve a certain planarization of a single branch of the molecule.

The highest radiative decay rates were determined for compound **1**. The smaller radiative decay rates determined for compound **2** became comparable to the non-radiative decay rates. This fact can be related to the higher quantum yields found for compound **1**. The stronger deformation of **2** in the excited state and the stabilization of its high dipole moment in polar solvents could favor the non-radiative relaxation.

SUPPORTING INFORMATION

Procedures for the synthesis and chemical characterization of the studied compounds. Detailed information on the calculations of vertical electronic transitions with different TD-DFT methods and vibrational assignment of the most representative bands found in the FTIR spectra. Detailed information on UV-Vis absorption spectra, fluorescence quantum yields and CIE1976 chromaticity coordinates measured for the studied compounds. FTIR spectra and fluorescence intensity decays.

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