Novel easy to synthesize benzonitrile compounds with mixed carbazole and phenoxazine substituents exhibiting dual emission and TADF properties.

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ABSTRACT

The photophysical and electrochemical properties of a new class of fluorinated benzonitrile compounds substituted with mixed phenoxazine and carbazole units have been investigated. While absorbing in a large range of the UV-vis spectrum due to both localized and charge transfer absorption, these compounds show dual broad emission in solution and intense emission in PMMA films, with photoluminescence quantum yields changing from a few percent in solution to 18% in more rigid environment. The compounds also exhibit thermally activated delayed fluorescence demonstrated by the role of oxygen in the quenching of delayed fluorescence and by time-resolved luminescence studies, with an efficiency directly related to the number of phenoxazine substituents. The electrochemistry reveals dramatic changes in the reduction mechanisms according to the number of remaining fluorine atoms on the benzonitrile core. All these results demonstrate how it is possible to tune the photophysical and electrochemical properties of easily synthesizable derivatives by controlling the nature and relative number of the substituents on a simple aromatic platform.

INTRODUCTION

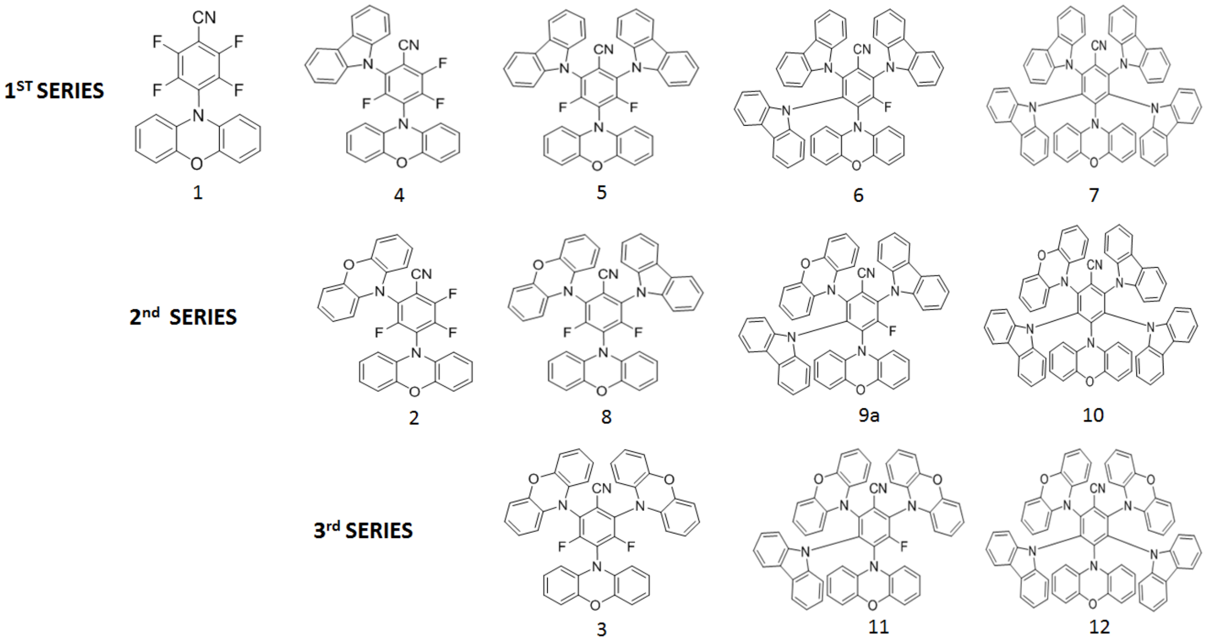
Nowadays there is a growing demand for efficient white-light-emitting organic molecules due to their applications in lighting and display technologies. In order to achieve natural illumination properties, resembling daylight, a key factor is to cover the entire visible emission range, i.e. 400-700 nm[1-2]. The most common reported white-light organic emitters consist in a combination of different compounds that emit in a different range of wavelengths. However, the replacement of multicomponent emitters with a single white-light-emitting molecule would be advantageous in several aspects, *e.g.* improved stability and reproducibility, and simpler fabrication process[3-4].

Efficient thermally activated delayed fluorescence (TADF) emitters with donor−acceptor (D−A) architectures are considered to date among the most promising materials in lighting applications due to their free-metal efficient triplet harvesting properties. The photoluminescence (PL) spectra originating from intramolecular charge transfer (ICT) excited states typical of these materials, are significantly broadened in respect to the well-structured and narrowband emission from localized states (LE) in typical non-ICT fluorescent materials. Moreover, D-A design is crucial for facilitating a very small singlet-triplet (^{1}CT-^{3}CT-^{3}LE) energy gap[5-7]. This ensures an efficient triplet to singlet reverse intersystem crossing (RISC) interconversion that is fundamental to achieve a highly efficient TADF process[8-10]. Another characteristic of TADF active D-A systems is their ability of tuning the emission properties by changing the position or the number of substituents[9, 11]. Based on these design principles, various purely organic TADF emitters have been developed. However, to date, one of the most promising strategies to achieve a broadband TADF emission, sufficient to cover the entire visible range, is to take advantage of intermolecular CT exciplex states[12-13]. Nevertheless, even if exciplexes are considered good candidates for lighting application the use of a single emitter is more advantageous than two or more, as required in exciplexes. Moreover, in some cases, exciplex systems facilitate triplet-triplet annihilation (TTA)[14] leading to triplet harvesting losses. It results that despite TADF molecules are considered to be the next-generation luminescent materials, the research for single-component white-light TADF materials remains a true challenge.

In this work, we designed and studied the photophysical properties of several new benzonitrile derivatives substituted by carbazole (Cz) and phenoxazine (PhOx) units. (**Scheme 1**). All the molecules are based on a central benzonitrile (BzN) core decorated with a variable number of PhOx and Cz donor substituents, and fluorine atoms in the remaining positions. Three series are considered according to the number of PhOx substituents which varies from 1 (Series 1) to 3 (Series 3).

The use of the electron-deficient benzonitrile core as the acceptor was motivated by the good photophysical properties and the simple synthetic protocols making benzonitrile one of the most popular electron-acceptor for constructing TADF molecules since their introduction in the field[15-22]. On the side of donors, carbazole was chosen due to its weak donor properties and a relatively low-lying HOMO level, which is a necessary prerequisite for the design of deep-blue TADF emitters[23]. On the contrary, phenoxazines possess a strong electron donor character, due to the presence of two heteroatoms (N and O) that are electron-rich and contribute to the HOMO with their non-bonding electrons. This results in a low ionization potential that allows obtaining red-shifted emission.

The use of the benzonitrile core as an acceptor and the mixing of two donor groups in different proportions in the same molecule results in an original molecular design for novel D-A derivatives. Only a few examples of D^1-A-D^2 TADF compounds have already been reported in the literature[24-30] and therefore we consider it interesting to explore in deep the characteristics of these systems. Our study presents the crystallographic, electrochemical and photophysical properties of the three series of compounds. The manuscript is mainly focused on the behaviour of the 1st series, while the results concerning the 2nd and 3rd series are reported in ESI.



Scheme 1: The three series of polysubstituted fluorobenzonitrile derivatives studied with one (1st series), two (2nd series) and three (3rd series) phenoxazine units and a variable number of carbazole moieties.

METHODS

Synthesis and characterization

All chemicals were received from commercial sources and used without further purification. Thin layer chromatography (TLC) was performed on silica gel. Column chromatography was performed with SDS 0.040–0.063 mm silica gel. All mixtures of solvents are given in v/v ratio. NMR spectra were recorded on a JEOL ECS (400 MHz) spectrometer. ^{13}C NMR spectra were proton decoupled. HRMS spectra were measured either on an UPLC/ESI-HRMS device (Acquity Waters UPLC system coupled to a Waters LCT Premier XE mass spectrometer equipped with an electrospray ion source), or a Q-TOF mass spectrometer (Q-TOF 6540, Agilent) equipped with an APPI ion source.

Electrochemistry

The electrochemical cell is composed of a platinum electrode with a Pt of 2 mm diameter as a working electrode, an Ag|Ag$^+$ electrode as a reference electrode and a platinum coil as an auxiliary electrode. Measurements were conducted at room temperature at a potential scan rate of 50 mV/s and were calibrated against a ferrocene/ferrocenium redox couple. Electrochemical measurements were conducted with a CHI600B potentiostat device, in 1.0 mM concentration of all compounds with 0.1 M solutions of Bu_4NPF_6, 99% (Sigma Aldrich) added in dichloromethane (DCM) CHROMASOLV®, 99.9% (Sigma Aldrich).

Quantum chemical calculations

Ground state geometries were optimized at the B3LYP/6-31+g(d) level of calculation followed by a frequency calculation. TDDFT on these geometries were done at the M06-2X/6-311+g(d,p) level of theory looking for both singlets and triplets levels in vacuo and including toluene solvent effect with IEFPCM model. Then first singlet excited state geometries were optimized at the M06-2X /6-31+g(d) level followed by a frequency calculation at the same level. Finally, a TDDFT calculation was done on these S1 optimized geometries at the M06-2X /6-311+g(d,p) level of theory looking for both singlets and triplets levels in vacuo and including toluene solvent effect with IEFPCM model. In parallel first triplet excited state geometries were optimized at the M06-2X /6-31+g(d) level followed by a frequency calculation at the same level and by a TDDFT calculation on these T1 optimized geometries at the M06-2X /6-311+g(d,p) level of theory. All calculations were done with Gaussian 16 (Revision B.01) software[46]. Data were analyzed with GaussView 6.0, PyMOL (The PyMOL Molecular Graphics System, Version 2.1.1 Schrödinger, LLC), Mercury 4.1.0 and GaussSum3.0[47] softwares. Calculated absorption spectra were obtained by a convolution of Gaussian functions with a 3000cm^{-1} (0.37eV) FWHM.

Film processing

All blends were obtained by drop-casting DCM solutions (0.05 g/L) of the compounds at room temperature on quartz slides followed by slow (1 night) evaporation in solvent saturated conditions. Concentration of the fluorophore in the film is reported in weight percentage (w/w) relative to the polymer mass in the solution. All blends formed clear, glassy, transparent solid films.

Photophysical studies

UV-vis absorption measurements (scan mode) were collected using a Cary 4000 double beam spectrophotometer (Agilent) using rectangular 10 mm path length quartz cuvettes from Hellma, at 25 °C. The absorption spectra were recorded with concentrations in the range 5.6-2.0 µM (total volume = 10 mL volumetric flask). For all the solvents, dilutions were made from a stock solution in chloroform at 1 mg/5mL. Fluorescence spectroscopic studies were performed with a FluoroLog3 fluorescence spectrometer (Horiba Jobin Yvon) at 25°C, with rectangular 10 mm path length quartz cuvettes from Hellma. The emission and excitation spectra were recorded with a diluted solution with absorbance lower than 0.1. For the excitation and emission spectra, the slits widths were adjusted between 2-5 nm, integration time = 0.1 s, 1 nm step. All fluorescence spectra were corrected from the lamp fluctuations and the apparatus response fluctuations.

The relative photoluminescence quantum yields (QY) in solution were determined[48] at 25 °C, from corrected emission spectra using quinine sulphate in 0.1 M $HClO_4$ as standard. For each QY measurements, slit width, excitation wavelength, scan rate, integration time and emission range were kept identical for the reference and the sample. The fluorescence QY was determined thanks to the following formula:

$$\Phi_S = \Phi_R \bullet \left(\frac{Abs_R}{Abs_S}\right) \bullet \left(\frac{\eta_S^2}{\eta_R^2}\right) \bullet \left(\frac{I_S}{I_R}\right)$$

Where:

- Φ = Fluorescence quantum yield
- *Abs* = absorbance of the solution
- η = refractive index of the solvent
- *I* =Integrated fluorescence intensity of the emitted light
- Subscripts ‘R’ and ‘S’ refer to the reference and sample respectively

Lifetime experiments were done using 10 mm path length quartz cuvettes:

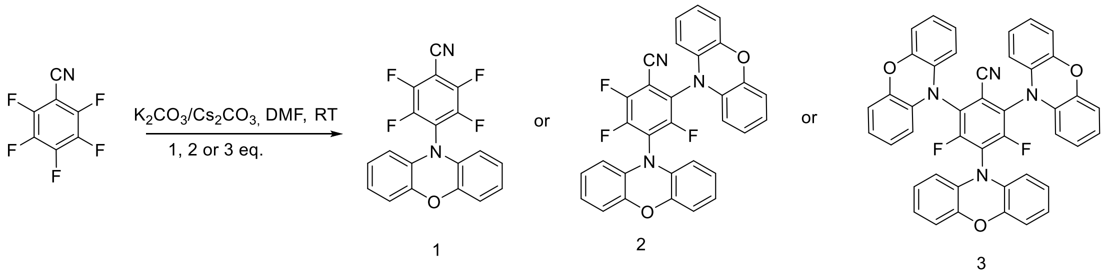
The **ns** fluorescence decay curves in solution, were obtained by the time-correlated single-photon counting (TCSPC) method with a femtosecond laser excitation composed of a Titanium Sapphire laser (Tsunami, Spectra-Physics) pumped by a doubled Nd:YVO_4 laser (Millennia Xs, Spectra-Physics). The fluorescence data were analyzed using the Globals software package developed at the Laboratory for Fluorescence Dynamics at the University of Illinois at Urbana-Champaign, which includes reconvolution analysis and global non-linear least-squares minimization method. The quality of the fit was estimated by visual inspection of the weighted residuals and calculation of χ^2

The **µs** fluorescence decay curves in solution were obtained using an Edinburgh instrument LP920 laser flash photolysis spectrometer combined with a Nd:YAG laser (Continuum) tripled at 355 nm via non-linear crystals. The Levenberg Marquardt algorithm was used for non-linear least square fit (tail fit) as implemented in the L900 software (Edinburgh instrument). The quality of the fit was estimated by visual inspection of the weighted residuals and calculation of χ^2.

RESULTS AND DISCUSSION

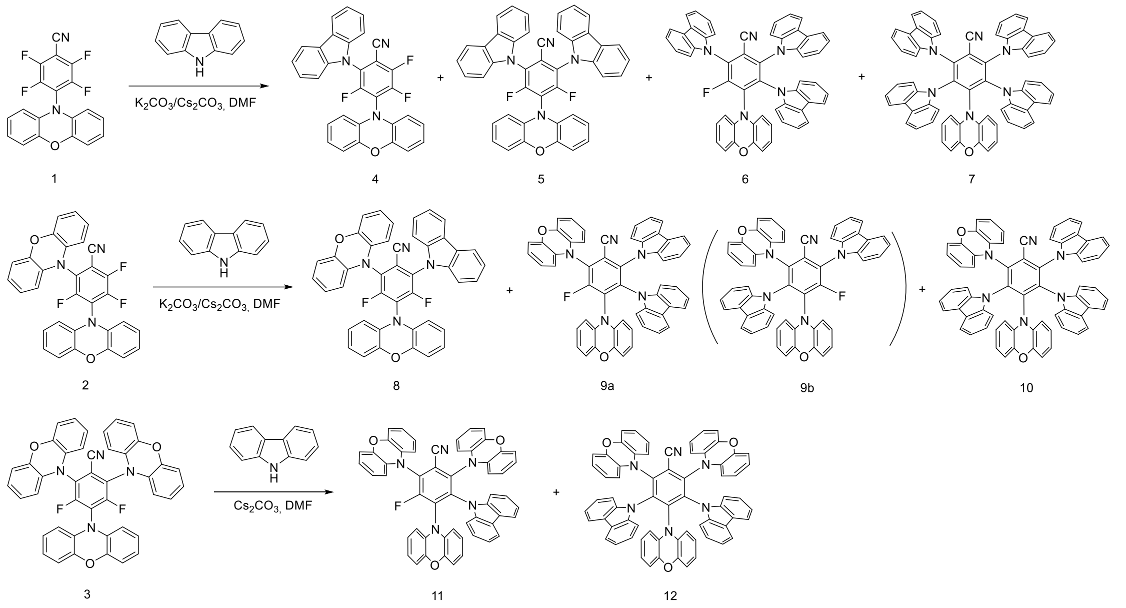
1. Synthesis

Scheme 2 summarizes the first synthetic steps for these new compounds. The different reactivity of the five fluorine atoms on pentafluorobenzonitrile (PFBN) towards nucleophilic substitution offers a special advantage to prepare various symmetrically and unsymmetrically substituted benzonitrile derivatives in a facile manner. The *para* fluorine atom, and to a lesser extent the *ortho* ones, of PFBN readily undergo nucleophilic substitution selectively in a dipolar aprotic solvent (DMF) and the presence of a weak base (K_2CO_3) at room temperature, with the moderate nucleophilic anion issued from the PhOx. This way, compounds **1**, **2**, and **3** were easily synthesized by sequential nucleophilic displacement of the *para*, *ortho* and *ortho'* fluorine atoms on PFBN using 1, 2 or 3 eq. of PhOx, respectively, giving in each case quantitatively the targeted compound.



Scheme 2: Substitution of fluorine atoms on PFBN with 1, 2 or 3 eq. of phenoxazine anion.

The *meta* and *meta'* fluorine atoms can be substituted as well but by stronger nucleophiles, which provides a possible opportunity for the synthesis of hetero-substituted compounds. In this work we decided to use carbazolyl anion as such nucleophile. Compounds **4-12** were successfully prepared by further reaction of compounds **1, 2** and **3** with the nucleophile. The remaining fluorine atoms were displaced sequentially with various equivalents of Cz in the presence of K_2CO_3 or Cs_2CO_3 at room temperature or at 60°C-80°C, according to the reactivity of the compounds. We link the latter to the steric hindrance generated by the PhOx already connected to the benzonitrile core in addition to the intrinsic reactivity of the fluorine atoms as a function of their position on PFBN (**Scheme 3**). This difference in reactivity between the PhOx and Cz anions allowed us to prepare most of the mixed, partially and fully substituted benzonitriles reported here.



Scheme 3: Synthesis of the various heterosubstituted compounds by displacement of fluorine by carbazole.

As long as the reaction conditions are carefully controlled, the sequential substitution reactions proceed smoothly resulting in the target substituted compound as the main product, with only small amount of side products featuring other substitutions. In the case of compound **9**, **9b** was always obtained in ca. 10% amount, along with the major isomer **9a**. All products were purified by column chromatography, and characterized by ^{19}F, ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry (see experimental section and ESI for details).

2. X-ray diffraction analysis

Geometries of the selected benzonitrile derivatives were obtained from single crystal X-ray diffraction (XRD). Only crystal structures of **1** and **4-7** were obtained and are presented in **Figure 1A** (see all crystallographic data reported in **Table S1**). All the molecules show large twisting angles between the donor and acceptor moieties, a beneficial situation to get spatial separation of the HOMO and LUMO and a small singlet-triplet energy gap which is a necessary condition to obtain TADF properties. The D-A dihedral angles tend to decrease with the increasing number of donor moieties on the benzonitrile core (see **Table S2**). Moreover, the dihedral angles between PhOx and the acceptor unit are in general larger than those involving Cz.

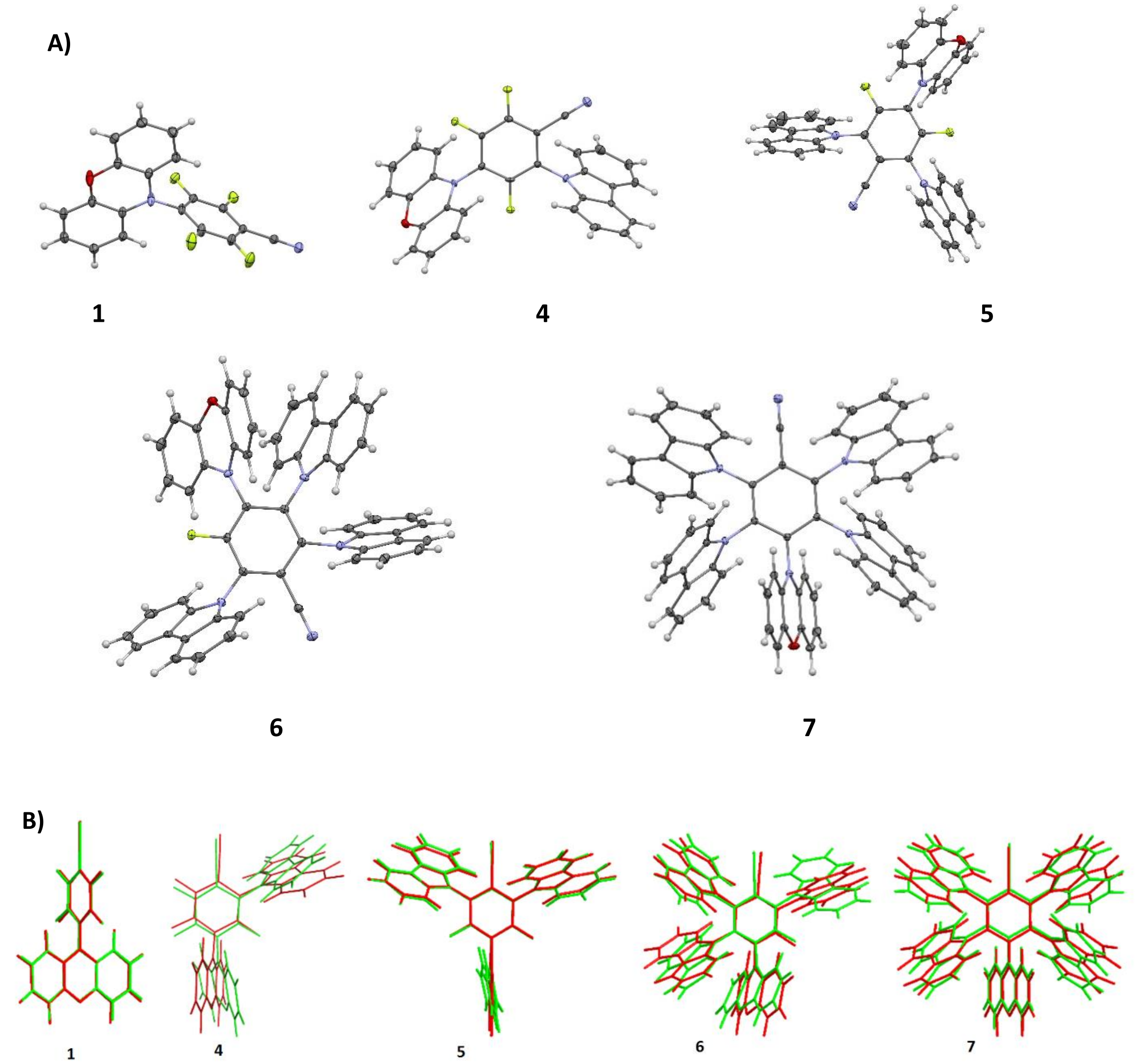


Figure 1: A): ORTEP drawing of compounds **1**, **4-7**. Thermal ellipsoids are shown at the 30% level. For the sake of clarity, solvent molecule is omitted and only one molecule of the asymmetric unit in **5** is shown. **B)**: Overlap between ground state calculated (red) and XRD structures (green) for molecules **1** and **4-7**.

DFT calculations have been performed on compounds **1**-**12** to predict the optimized geometries of these molecules. **Figure 1B** shows the overlap of crystal structures and calculated ground state geometries. The angles between the main planes of Cz and PhOx obtained from XRD structures match quite well the calculated ones in the ground state (**Table S2**), especially for the molecules with the lower number of substituents (**1, 4, 5**).

3. Energy levels, molecular orbitals and electrochemistry

The calculated energies of the molecular orbitals in **1** and **4**-**7** are presented in **Figure 2**. The HOMO level gradually increases with the number of Cz units, as expected due to its donor character. The LUMO level increases as well in the same order leading to a small variation of the HOMO-LUMO gap in the series. The HOMO-LUMO gap is however smaller in **7** than in **1**. A similar trend is observed for the second series while the HOMO and LUMO levels remain fairly constant in the third series. (**Figure S1**).

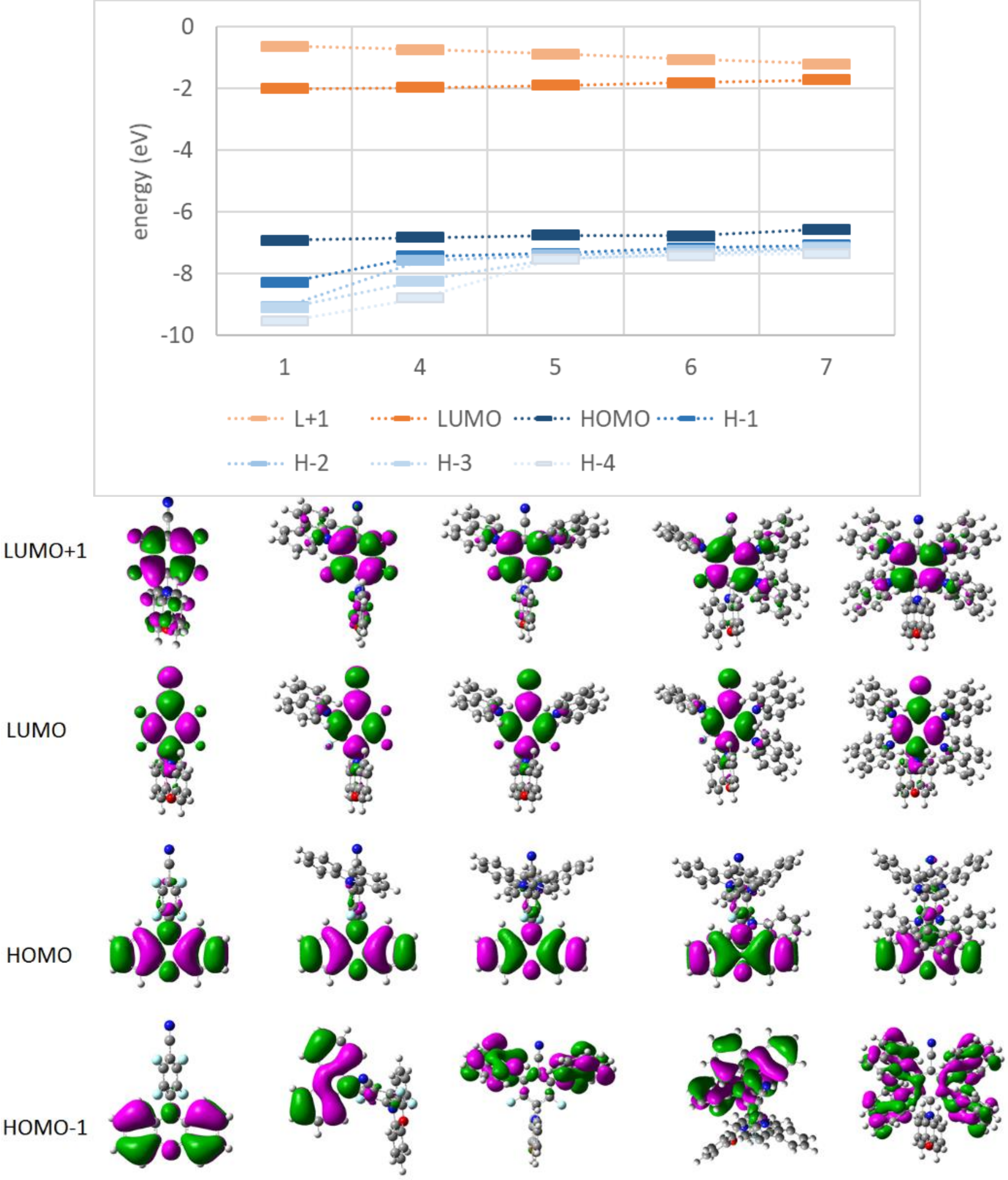


Figure 2: Energy levels and molecular orbital contours of HOMO-1, HOMO, LUMO and LUMO+1, for **1** and **4**-**7** (from left to right).

Figure 2 also shows the frontier orbital contours of **1** and **4**-**7**. It is clear that the two highest occupied molecular orbitals (HOMO and HOMO-1) are centered on phenoxazine and carbazole substituents, while the two lowest unoccupied orbitals (LUMO and LUMO-1) are centered on the benzonitrile. This confirms that donor (D) and acceptor (A) subunits are actually electronically independent in all compounds of the first series. In a more detailed view, one can see that HOMOs are centered on PhOx and (HOMO-1)s on Cz. One can thus expect the first oxidation to involve PhOx and the second one Cz which will be indeed confirmed by the electrochemical study (see below). The reduction process should mainly concern the benzonitrile core since it is where LUMO is mainly localized.

Cyclic voltammetry (CV) experiments have been performed on all molecules **1-12** and the results are displayed in **Figure 3** for the 1st series and in **Figure S3** for the two others.

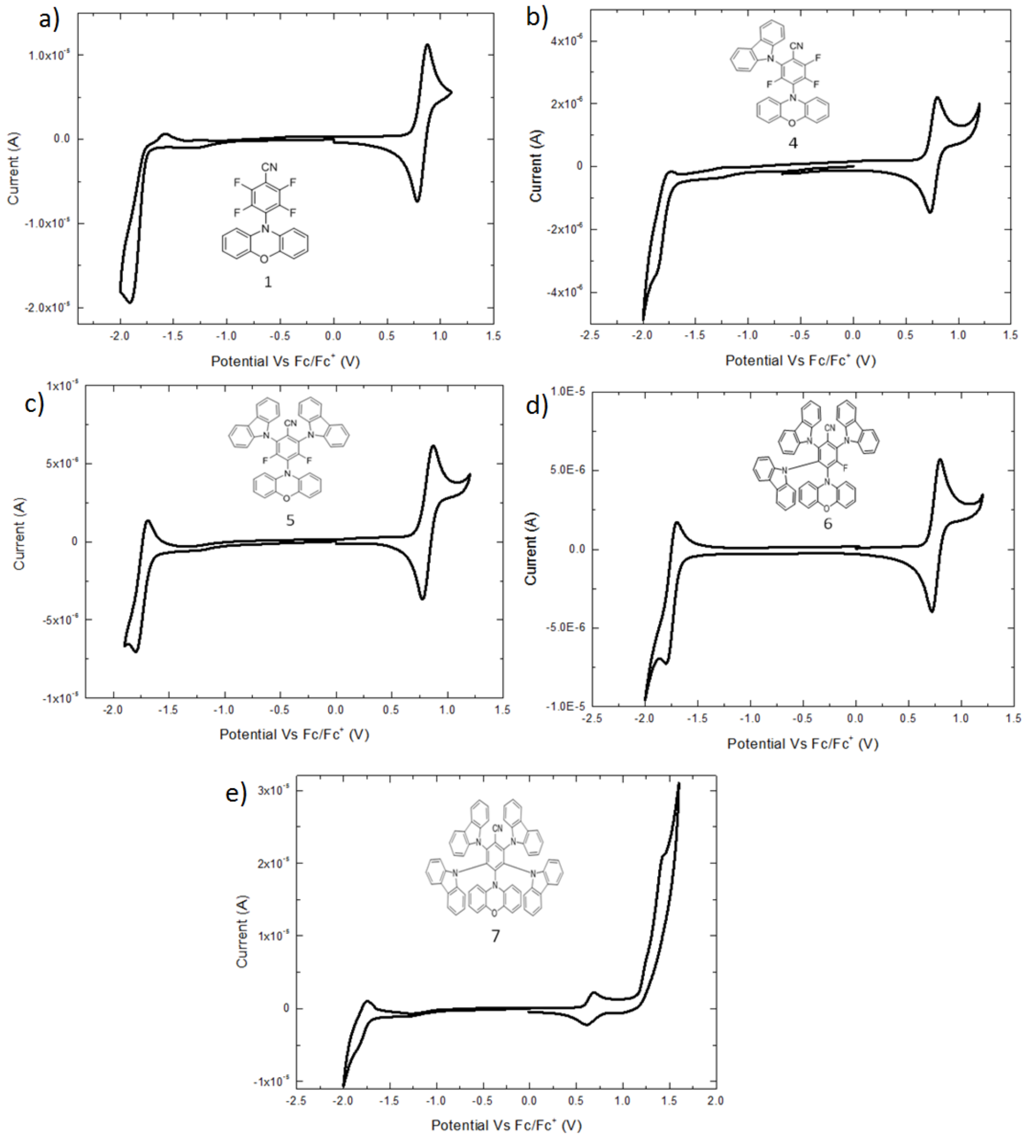


Figure 3: CV traces of compounds **1, 4-7** in DCM containing 0.1 M TBAPF$_6$. Scan rate: 50 mV/s.

All CVs feature a cathodic peak which can be assigned to the benzonitrile core reduction and one or more oxidation peaks assigned to the peripheral donor moieties (Cz or PhOx). It is important to note that PhOx is reversibly oxidized, while the oxidation of unsubstituted Cz is usually irreversible[31], sometimes leading to electropolymerization (see **Figure S4** for **5**). Therefore, compounds **1-3** show a single reversible oxidation assigned unambiguously to PhOx. For the other heterosubstituted benzonitrile compounds, only the first oxidation waves are reversible, because the more electron-rich PhOx are always oxidized before the Cz unit.

Interestingly, the reduction of the benzonitrile core gives an irreversible peak for some derivatives and a reversible one for others. A clear trend is visible in **Figure 3**, where the reversibility gradually appears and increases as the number of fluorine atoms decreases. We can reasonably assume that the lack of reversibility is related to a chemical reaction associated with the electron uptake. When the number of fluorine decreases, the reversibility increases suggesting that fluorine plays the role of a leaving group in the electrochemical reduction process. Besides, the peak current ratio calculated between the first oxidation and the first reduction varies from about 0.6 to 1 in the first series (see **Table 1**). As the first anodic peak corresponds to the one-electron oxidation of PhOx, one can deduce that the reduction of benzonitrile involves either two electrons (e.g. for **1**) or only one (e.g. for **7**). A confirmation of this change in the number of electrons exchanged upon reduction according to the number of fluorine on the benzonitrile core is given in **Figure S2** by looking at compound **2**, for which the peak ratio is close to 1: because the first oxidation involves this time two electrons (one per PhOx, each behaving independently), the reduction of **2** is thus bielectronic again, as for **1**. To be consistent with a bielectronic reduction, the reduction mechanism should lead to either the substitution of fluorine by hydrogen through an ECEC mechanism[32] or to a dimer through an EC_2 mechanism[33], both mechanisms starting by the formation of an intermediate anion radical of fluorobenzonitrile[34] (see **figure S5**). In absence of fluorine (compound **7**), no leaving group can be removed after the first monoelectronic reduction and the reduction stops at the anion radical level. Interestingly, this is also the case for **6** despite it contains one fluorine. We can thus infer that the preferred mechanism is the dimerization, which is hampered in **6** due to steric hindrance. It is worth mentioning that the same behavior is observed in the two other series with an irreversible reduction for **2**, a partially reversible for **3** and a fully reversible for **9-10** and **11-12**.

It is possible also to notice that the reduction potential shifts slightly towards more positive values when substituting fluorine by Cz, especially in the first series (**Table 1**). This is not in agreement with the electron donor effect of Cz compared to the attracting inductive effect of fluorine, nor with the variation of the LUMO energies in the first series (**Figure 2**), but one must consider the role of the chemical reaction following the first electron transfer, which facilitates the reduction and thus tends to shift the potential towards more positive values. The fact that the more substituted compounds in a series are more easily reduced does not allow to discriminate between the two mechanisms. Indeed, the elimination of fluoride in the ECEC mechanism should be favored in presence of donor substituents like Cz or PhOx when those substitute the fluorine and thus would lead to the observed positive shift of the reduction potential. However, a strong argument to support the dimerization mechanism as the first reduction step, is that non-activated fluoride elimination from a negatively charged species (typically a carbanion) is usually a (very) slow process in organic chemistry, and sometimes cannot occur at all (CF_3^- is quasi-stable)[35]. Therefore, it is highly probable that elimination is extremely slow on the polyfluorinated anion-radical, and can only occur after the dimerization step, because at this point it allows to restore the aromatic character of the biphenyl ring. The dimerization process is however not possible for compounds bearing only one fluorine (**6**, **9**, **11**) because of steric hindrance and even those bearing two fluorines (**5**, **8**, **3**) show a partial reversibility, indicating that dimerization as well as ECEC are both slowed down albeit for different reasons.

Regarding the oxidation of the investigated compounds, the first oxidation potential varies slightly in the first series, decreasing from **4** to **7**, in agreement with the opposite variation of the HOMO energies (**Figure 2**). When the investigated compounds involve more than two PhOx, the oxidation wave splits into two or three peaks, due to coulombic repulsion between the injected positive charges. The presence of electron-rich Cz on the BzN core tends to slightly diminish the oxidation potential of PhOx (see **7, 10, 12** compared to **1, 2** in **Table 1**). Each PhOx behaves as a more or less independent redox unit, and one can also emphasize the generation of a very stable cation-radical related to the anti-aromatic character of the neutral form for this family of compounds.

Table 1: Electrochemical data of **1-12**: first peak oxidation and first peak reduction potentials, first anodic *vs*. cathodic peak current ratios, HOMO and LUMO energies derived from CV.

Compound	**E_{ox} vs Fc/Fc^{+} (V)(a)**	**E_{red} vs Fc/Fc^{+}(V)(a)**	**Red vs. Ox peak current ratio**	**HOMO (eV)(b)**	**LUMO (eV)(c)**	**HOMO-LUMO gap (eV)**
1	0.56	-1.95	0.6	-5.66	-3.16	2.50
2	0.56	-1.85	1.2	-5.66	-3.25	2.41
3	0.57	-1.80	1.3	-5.67	-3.30	2.37
4	0.56	-1.87	0.7	-5.66	-3.23	2.43
5	0.57	-1.83	0.9	-5.67	-3.27	2.40
6	0.52	-1.78	0.8	-5.62	-3.32	2.30
7	0.40	-1.89	1.2	-5.50	-3.21	2.29
8	0.58	-1.81	1.4	-5.68	-3.29	2.39
9a	0.51	-1.84	1.3	-5.61	-3.26	2.35
10	0.42	-1.87	0.9	-5.52	-3.23	2.29
11	0.49	-1.81	1.4	-5.59	-3.29	2.36
12	0.39	-1.83	0.9	-5.49	-3.27	2.29

(a) Measured in DCM at room temperature by cyclic voltammetry; (b) Estimated from the oxidation potential in DCM, HOMO(/eV) = -Eox (/V) –5.1; (c) Estimated from the reduction potential in DCM, LUMO(/eV) = -Ered(/V) – 5.1.

4. UV-Vis absorption properties

We first show the results of calculated absorption spectra for the first series obtained from TDDFT (**Figure 4** and **Table S3**). Three main absorption bands can be observed in each spectrum that can be assigned to either locally excited (LE) or charge transfer (CT) excitations. The transitions at lower energy present a CT character. In particular, the lowest energy transition can be assigned to the CT between PhOx and BzN in all cases and is reported further as "PhOx CT". When carbazole moieties are added, additional CT transitions involving Cz as donors appear in between ($\lambda \approx 300$-350 nm) and are reported further as "Cz CT". All the higher energy transitions show larger oscillator strengths and are assigned to π-π^* transitions (LE). All the transitions with their corresponding orbital contributions are listed in **Table S3**.

The calculated absorption spectra for compounds of the 2nd and 3rd series are shown in **figure S2** (TDDFT results in **table S3**). It can be noticed that **2** and **3** present only two distinct CT bands, while molecules **8**-**10** and **11**-**12** present three, with the same assignment as for the first series.

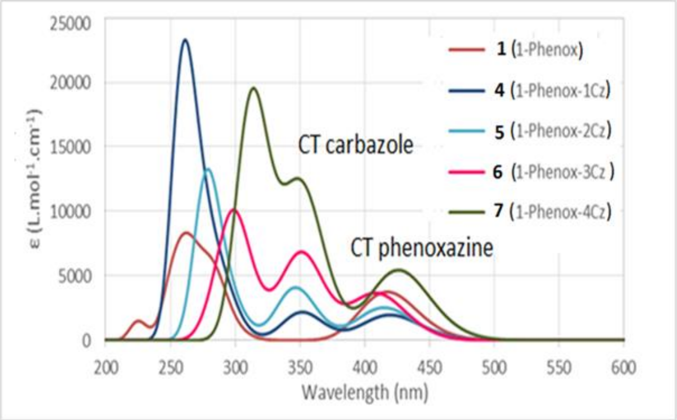


Figure 4: Calculated spectra (DFT) in toluene for the compounds of the 1st series.

Experimental absorption spectra have been recorded for the molecules either in solution (10^{-5} M) with solvents of various polarities or in a PMMA matrix (0.05 %wt). Absorption spectra of **1** and **4**-**7** in cyclohexane and PMMA are displayed in **Figure 5** and the absorption maximum wavelengths are reported in **Table 2**. The less intense bands at lower energy, in molecule **1** (421 nm) and **4**-**7** (370-470 nm), do not appear neither in the donor (phenoxazine[36] and carbazole[37]) nor in the acceptor (benzonitrile[38]) absorption spectra. Therefore, and in agreement with DFT calculations (**Figure 4**), they are assigned to the several singlet CT transitions occurring between the D and A moieties. More precisely we can assign the CT band at lower energy (between 421 and 467nm) to PhOx CT and the ones at higher energy (between 385 and 411 nm) to Cz CT. In compounds **5**, **6** and **7** containing additional Cz, it is possible to spot an additional shoulder (see **Table 2**) that can be assigned to the CT states resulting from the various Cz substituted at distinct positions on the BzN core. At higher energy (up to 360 nm), the absorption spectrum is almost entirely formed by superposition of the absorption of individual donors and acceptor. In particular, the absorption band at 287-289 nm, present only in compounds **4-7**, is assigned to the π-π* localized absorption of Cz[37]. The absorption bands between 324 and 330 nm are also associated with the localized absorption of Cz[37], while the other absorption bands are assigned to the localized absorption of PhOx[36].

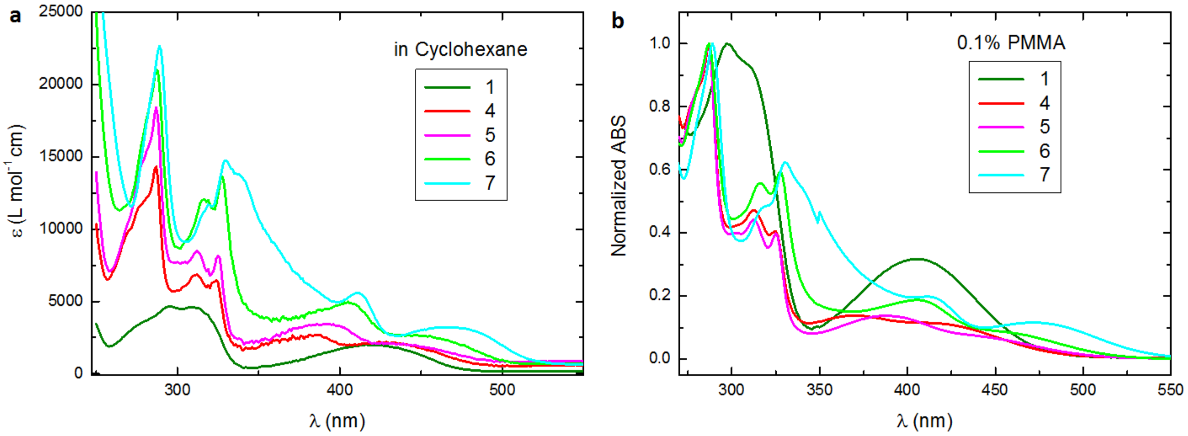


Figure 5: Absorption spectra of **1** and **4-7** in **a)** cyclohexane (10^{-5} M) and **b)** PMMA (0.1%wt). Absorption spectra in PMMA are normalized vs. the maximal absorbance value.

The absorption spectra of molecules of the 2nd and 3rd series in cyclohexane and PMMA are presented in **Figure S6.** These two series present a fully similar UV-Vis absorption behavior as their parent compounds of the first series.

Table 2: High and low energy absorption maximum wavelengths of **1** and **4-7** in cyclohexane (c=10^{-5} M).

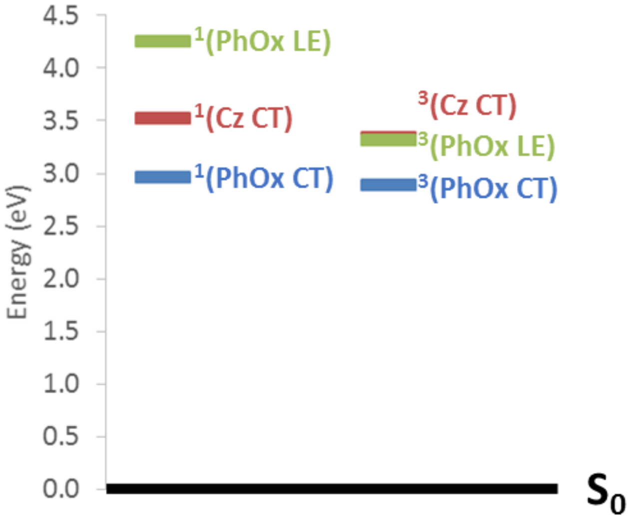
Compound	λ_{max}/ nm (LE)	λ_{max} /nm (CT)
1	312, 297, 280(s)	421
4	368(s), 324, 311, 301(s) 287, 277(s)	426, 385
5	325, 302, 312, 287, 278(s)	432, 391, 378(s)
6	327, 316, 304 (s), 287	440, 404, 388(s)
7	339, 330, 320, 289	467, 411, 373(s)

(s) = shoulder

5. Emission properties

5.1 Calculated excited states

A more detailed analysis of the TDDFT results done on both singlet and triplet states (**Table S4**) show the presence of several excited states close in energy. The lower excited states correspond to the PhOx CT for both spin multiplicities. The corresponding calculated singlet to triplet energy gaps $\Delta E_{S\text{-}T}$ for **1-12** are reported in **Table S5** and are typically small (0.04 to 0.20 eV) which should be beneficial for observing TADF. In the case of the compounds containing carbazole substituents, there is also a relatively low-lying Cz CT that is found approximately 0.5 eV above the PhOx CT for both spin multiplicities. The $\Delta E_{S\text{-}T}$ values for these Cz CT states (see **table S5** for compounds **4-7**) are slightly larger than for the PhOx CT states but still remaining rather small (0.16 to 0.20 eV). Finally, there are various LE states centered on either PhOx or BzN. In their singlet states they are found 1.2 eV above the Phox CT but the triplet state is highly stabilized and one this ^{3}LE state is typically found close to the ^{3}(Cz CT). This low lying triplet LE state should help the intersystem crossings (ISC and rISC). **Scheme 4** presents the calculated energy levels of the singlet and triplet LE and CT states of compound **4** as a representative example of the series.



Scheme 4: Calculated energy levels (left: singlets and right: triplets) involved in the emission properties of compound **4**.

5.2 Experimental emission spectra

The emission properties of the investigated compounds have been measured in solution and in PMMA films. The results are shown in **Figure 6** (full spectra) and **Figure S7** (high energy bands) and data reported in **Table 3** for the 1st series. Remarkably, a dual emission is particularly evident for the molecules of the 1st series in cyclohexane, an effect already reported by Karpiuk and Zhou[39-40] but not for TADF active compounds. In particular, **1** displays a very weak emission in the red region, assigned to the PhOx CT transition. The well-resolved emission in the blue region of **1** (387, 407, 425s), (**Figure S7a**), is assigned to PhOx LE[41]. For molecules **4-7** the emission band at low energy due to PhOx CT[41] becomes much more intense. On the other hand, in **4** and **5** the emission at higher energy appears only partially resolved. This is assigned to the sum of both PhOx LE and Cz CT contributions. With the increasing number of carbazoles (**6-7**), the emission at higher energy appears Gaussian without any vibronic resolution (**Figure S7a**). The remaining dual Gaussian emission can be associated exclusively to Cz CT (higher energy) and to PhOx CT (lower energy). From these observations we understand that up to 2 Cz units, both PhOx LE and Cz CT contribute to the high energy emission, while when the molecule is substituted with 3 or 4 Cz units, Cz CT becomes predominant. This behavior could depend on the occurrence of FRET between PhOx LE and Cz-BzN arms. Moreover, increasing the number of Cz leads to a stronger absorption of the Cz CT states, facilitating energy transfer from the PhOx LE which leads to emission from this latter completely disappearing.

Excitation spectra have been recorded and are reported in **Figure S8**. The excitation matches the absorption in all cases, allowing to confirm that dual emission does not involve impurities but are actually associated to excited states of the investigated compounds. Excitation spectra at emission wavelengths corresponding to PhOx and Cz CT states are also reported for compounds containing two different donors. Once again, these excitation spectra match pretty well the absorption ones.

In PMMA the PL band at low energy remains strong for all molecules (**Figure 6b**). On the contrary, the band at higher energy appears weak or even hardly visible, and drastically decreases with the increasing number of Cz (**Figure S7b**), indicating that most of the excitation goes directly to the PhOx CT state. The reason for this behavior might be related to the rigid environment of the polymer host that reduces the mobility of carbazole, which cannot rotate anymore to stabilize the Cz CT state[24].

In order to evaluate the single-component white-light properties, the chromaticity coordinates were calculated for PL spectra of **4**-**7** (**Figure S9a, Table S6**). The obtained color coordinates change from warm-white to cold-white light, and thus this class of molecules can be considered as potentially highly suitable for white-light display applications.

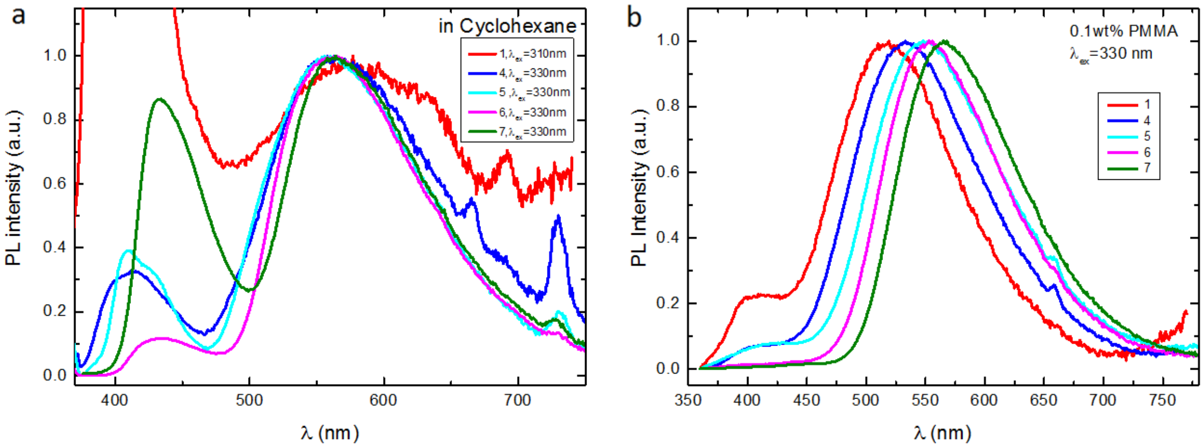


Figure 6: Normalized (to the maxima of the PhOX CT band) photoluminescence spectra of **1** and **4**-**7** in **a)** cyclohexane (c=10^{-5} M) and **b)** PMMA (0.1%wt). Excitation wavelength: 330 nm.

As regarding the emission properties of 2nd and 3rd series, they show a quite different behavior. The PL spectra are displayed in **Figure S10**. At lower energy (between 480 and 750 nm), all molecules present a strong emission arising from the PhOx CT, while at higher energy (between 350 and 500 nm) emission is hardly visible in most cases. In particular, the PhOx LE is visible in **2** (**Figure S10a**, **inset a**) and becomes stronger in **3** (**Figure S10c**). On the other hand, emission from Cz CT is intense only in **12** (**Figure S10c**) and barely visible in the other molecules (insets in **Figure S10a,c**). In our opinion, this is related to the higher number of phenoxazines present in the second and third series that favors the emission from the PhOx CT state, so that all the excitation energy is transferred on this low-lying energy state.

Table 3: Experimental photoluminescence (PL) emission wavelengths for the first series.

Compound	PL, λ_{max} /nm^{a}		PL, λ_{max}/nm^{b}
1	387, 407, 425(s)	577	578
4	404(s), 412	563	565
5	410, 423(s)	556	559
6	432	565	565
7	432	564	564

^{a} λ_{ex} = 300-330 nm, ^{b} λ_{ex} = 390-440 nm, (s)=shoulder

From the steady state absorption and emission properties, it is possible to conclude that in the three series, there is a gradual bathochromic shift of the CT absorption maximum with the increasing number of carbazoles (**Figures 5 and S5**). A bathochromic shift of the PL spectra occurs in PMMA for all three series, but only for the 2nd and 3rd series in solution (**Figures 7, S7, S10**). The bathochromic shift with the increasing number of Cz was already reported in literature[42-43], and is related to the delocalization of the CT state that increases with the number of donors.

We can also conclude that depending on the number of Cz and on the medium, emission can stem from either BzN-Cz or BzN-PhOx CT states.

5.3 Solvatochromism

The photophysical properties of **4**-**7** were also investigated in three solvents with increasing polarity: cyclohexane (ε=2.0, μ=~0.0D); toluene (ε=2.4, μ=0.36D) and dichloromethane (ε=8.9, μ=1.6D). Positive solvatochromism was observed for both CT emission bands of all molecules (**Figure 7**). This effect further confirms that the dual emission of **4**-**7** in cyclohexane originates from two different CT states. Positive solvatochromism of the lower energy PhOx CT band is present for all molecules of the 2nd and 3rd series (**Figure S11**). On the other hand, the band at higher energy clearly visible in **3** is not affected by the solvent polarity, as suggested by its assignment to the PhOx LE.

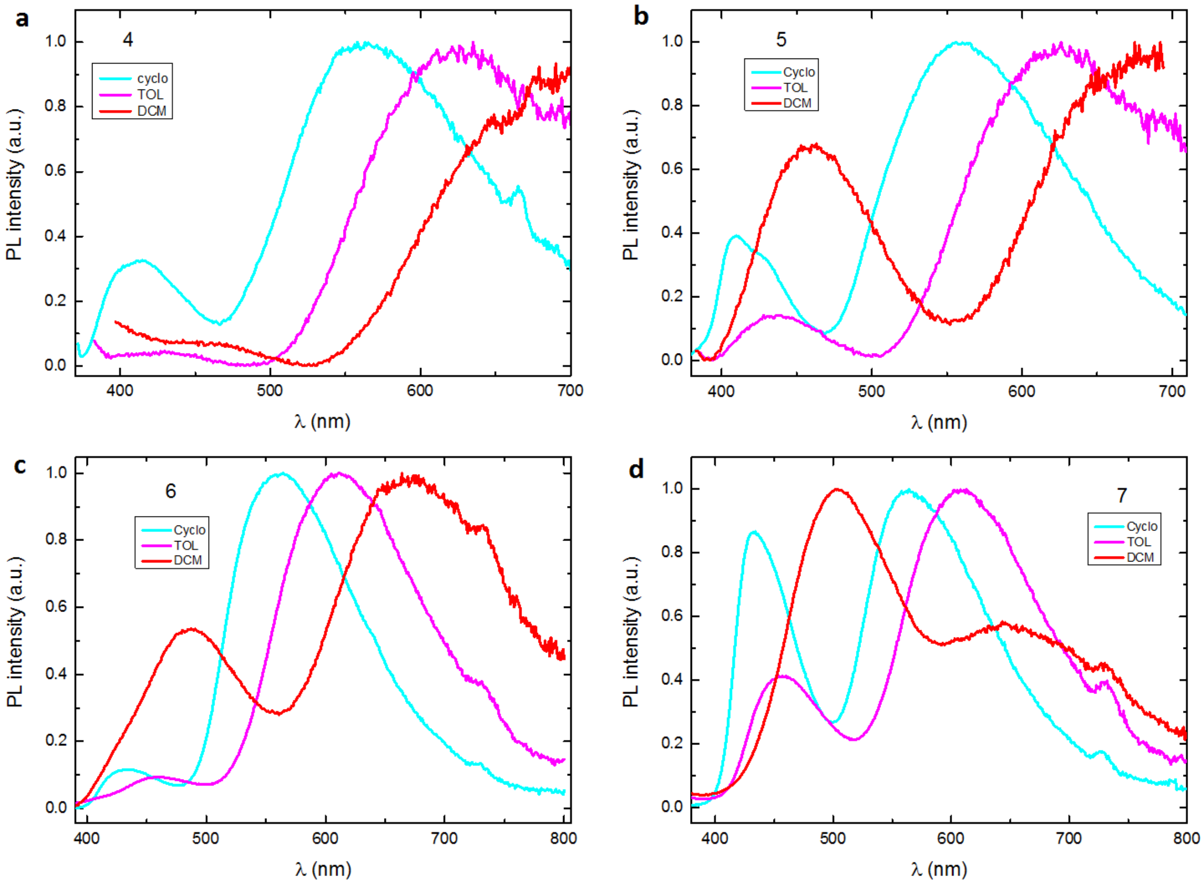


Figure 7: Normalized photoluminescence (PL) spectra in cyclohexane (10^{-5} M, cyan), toluene (10^{-5} M, pink), and DCM (10^{-5} M, red) of compounds **a) 4**, **b) 5**, **c) 6** and **d) 7.** Excitation wavelength: 330 nm.

5.4 Effect of oxygen on quantum yields and lifetimes

The photoluminescence quantum yields (PLQY, Φ_{PL}) in air-equilibrated and deoxygenated conditions were measured in cyclohexane, toluene, and PMMA (**Tables 4 and S7**). In cyclohexane, two different excitation wavelengths were used, one relative to the absorption region of the donor and acceptor moieties (λ_{ex}=300-330 nm), and the other relative to the CT states absorption (λ_{ex}=390-430 nm).

Table 4: Photoluminescence yield Φ_{PL} (%) of **1** and **4-7** in cyclohexane (CH), toluene and PMMA, with oxygen and after degassing. Delayed fluorescence (DF) vs. prompt fluorescence (PF) ratio values.

Compound	**CH^a**	**CH degas.^{a}**	**CH^b**	**CH degas.^{b}**	**Toluene^a**	**Toluene degas.^{a}**	**PMMA^c**	**PMMA degas.^{c}**
1	0.2	0.2	nd	nd	-	-	4.5	5.0
4	0.7	1.0	0.7	1.0	-	-	4.3	5.2
5	1.3	2.0	1.5	1.7	0.1	0.1	4.0	4.9
6	2.4	3.0	1.9	2.1	0.3	0.3	13.6	15.9
7	1.6	2.5	1.3	1.7	0.2	0.2	15.1	18.1

$^a\lambda_{ex}$=300-330 nm, $^b\lambda_{ex}$=390-430 nm, $^c\lambda_{ex}$=400 nm, nd: not detected (too weak)

Aerated PLQYs measured in cyclohexane increase with the number of substituents in the 1st and 2nd series, with the exception of the fully substituted compounds (**7**, **10**). Conversely, in the 3rd series the PLQYs decrease with the number of substituents. The observed trend results from a balance between, on one hand, the positive effect of the CT state stabilization and, on the other hand, the activation of roto-vibrational non-radiative pathways, both effects occurring when increasing the number of donors. Finally, for the fully substituted compounds the non-radiative pathways become dominant and over-compete the CT stabilization effect. In toluene PLQYs are always very low and are not further discussed since differences between them may be smaller than experimental errors. In PMMA, PLQYs tend to increase with the number of substituents except in the case of **1**, **4** and **5** where they remain similar. In a rigid matrix the roto-vibrational non-radiative pathways are less favorable and the more substituted compounds are the most emissive thanks to the CT state stabilization.

After degassing the samples, all molecules experience a moderate increase of the PLQY (**Tables 4** and **S7**) both in solution and PMMA films, which is indicative of a TADF activity. The PLQY of **4**-**7** in deoxygenated cyclohexane increases by a factor that depends on the excitation wavelength used, thus indicating that **4**-**7** present TADF properties from both CT states. The spectra (**Figure S12**) clearly show that both emission bands increase in intensity after solvent deoxygenation while maintaining the same shape and position. The clear peak inversion between Cz CT and PhOx CT emissions after deoxygenating the cyclohexane solution of **7** indicates that TADF is more intense in the former than in the latter. For the molecules of the 2nd and 3rd series (**Figure S13**), in all cases an increase of the PhOx CT emission intensity after degassing is observed. This confirms a TADF process associated to this transition. However, the PLQY obtained when exciting at 330 nm is similar to the one obtained at 400 nm (**Table S7**). This is in line with the fact that in the second and third series, the contribution of Cz CT to the total emission is weaker than in the first series.

Table 5: Delayed fluorescence (DF) vs. prompt fluorescence (PF) ratio values.

		DF/PF
1st series	**1**	-
	4	0.62
	5	0.68
	6	0.59
	7	0.67
2nd series	**2**	1.14
	8	0.93
	9a	1.17
	10	1.18
3rd series	**3**	1.21
	11	0.54
	12	0.91

Finally, the ratio of DF to PF could also be obtained from the emission PLQYs measured in air-saturated and degassed cyclohexane solutions (**Table 5**). We have estimated DF to PF ratio using steady-state experiment, owing to the fact that TADF is typically quenched by oxygen, while prompt is not. The small DF/PF obtained for the 1st series indicates a poor contribution of TADF in solution. On the contrary, the DF/PF values are larger in the 2nd and 3rd series which demonstrates that a higher number of PhOx units helps improving TADF properties in this class of materials. This is in line with the stronger donor effect of PhOx, which is generally used to improve the TADF properties of D-A compounds[44-45].

In order to further confirm the TADF properties of these compounds, PL decays were collected and lifetimes measured (**Table 6**). The decays comprise two to three characteristic lifetimes: one in the nanosecond regime attributed to the prompt fluorescence (PF) and one or two in the microsecond range due to TADF. It is interesting to note that the compounds displaying two long lifetimes are the same that present two emission bands.

Table 6: Luminescence lifetimes of molecules **1-12** in cyclohexane at RT recorded in absence of oxygen.

Series	Compound	$\tau 1_{av}$ (ns)	$\tau 2$(ns)	$\tau 3$(ns)	τ_{av} (µs)
1st	**1**	n.e.	n.e.	n.e.	n.e.
	4	14.7±0.10	384±2.8 (99%)	2162±40 (1%)	1.9
	5	8.9±0.06	1200±10 (96%)	8828±59 (4%)	8.6
	6	8.2±0.01	1599±12 (91%)	14403±61 (9%)	11.4
	7	17.8±0.10	1459±100 (87%)	24291±200 (13%)	23.7
2nd	**2**	17.2±0.30	715±21	-	0.7
	8	19.8±0.07	824±19	-	0.8
	9a	17.3±0.20	585±13	-	0.6
	10	13.74±0.30	343±1.8 (99%)	2330±4.5 (1%)	2.3
3rd	**3**	18.8±0.20	651±30	-	0.7
	11	11.7±0.10	673±5.3	-	0.7
	12	3.2±0.03	574±11 (99%)	1092±3.6 (1%)	1.0

n.e. not emissive

In order to better understand the origin of the two long lifetimes, the PL decays of **7** have been recorded at two different emission wavelengths corresponding to the maximum of the two emission bands (440 and 560 nm). The results are displayed in **Figure 8** and **Fig S14**. In addition to the expected PF short lifetime (17.8ns), two longer ones have been extracted, 24 µs (at 440 and 560 nm) and 1.5 µs (440nm) and 0.7 (560nm). In **Figure 8** it is possible to see that decays collected at different emission wavelengths present both two long components. However, when the decay is collected at 440 nm which corresponds to the emission maximum of Cz CT, the contribution of the longer DF (24µs) is higher compared to the decay collected at 560 nm (emission maximum of PhOx CT). Conversely, at this latter wavelength, the shorter DF component presents a higher contribution. This behavior indicates that Cz CT is the one that lives longer and can be related to the higher increase of the Cz CT emission band in degassed cyclohexane compared to the PhOx CT one. The different decay behaviour of the Cz and PhOx emission bands is consistent with their different magnitudes of TADF contributions (**Figure 8**). These facts suggests that the Cz and PhOx CT states (singlet and triplet) are independent from each other without communicating trough ISC and FRET.

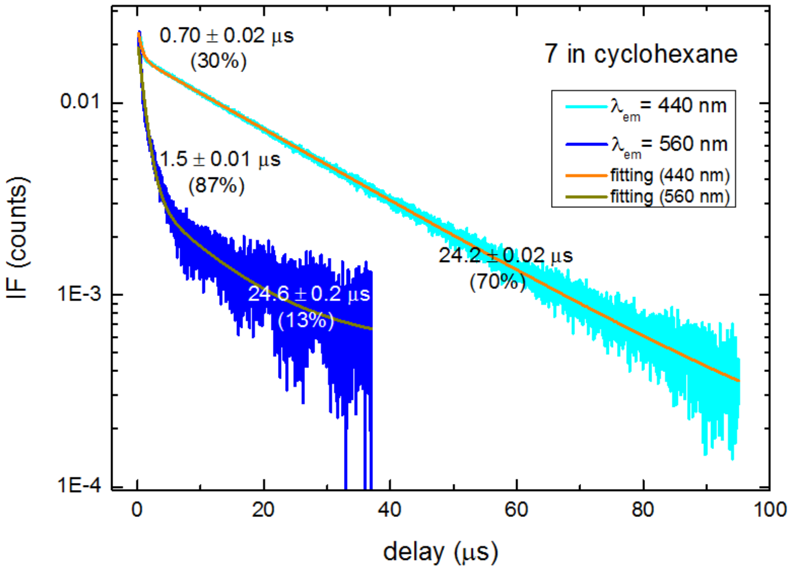
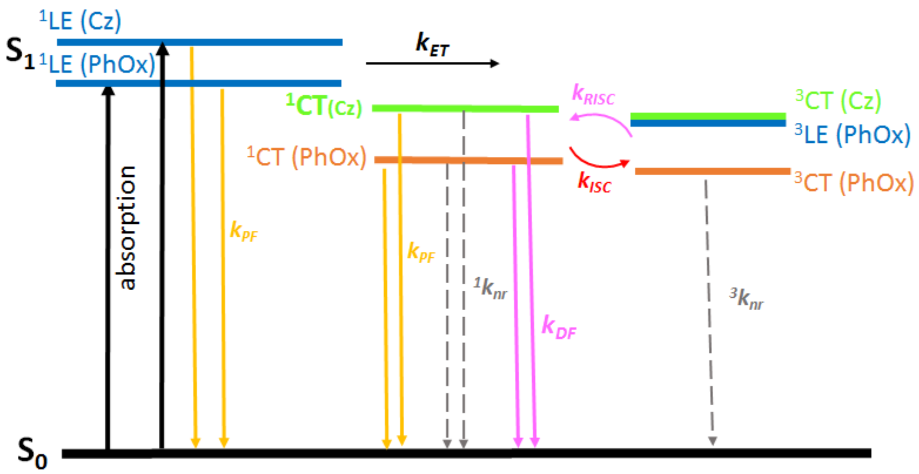


Figure 8: Fluorescence decays (μs regime) of **7** in cyclohexane, collected on the emission maximum of CT Cz (light blue) or CT PhOx (dark blue). Decays were recorded in the absence of oxygen. Excitation wavelength: λ_{exc}=355 nm.

To summarize, a general kinetic scheme showing all the photophysical processes involved was built with the help of the fluorescence and TDDFT results (**Scheme 5**). We can see that after the absorption, the PF (k_{PF}) emission could arise from LE (PhOx) and/or both CT states (involving Cz or PhOx). On the other hand, the DF (k_{DF}) only arises from the CT states. The non-radiative decay (k_{nr}) is quite important for this class of materials especially for the ones showing low PLQY.



Scheme 5: Proposed general energy diagram showing the relative position of the energy levels (singlet and triplet), involved in the emission properties of compound **4 -7**.

CONCLUSION

We have synthesized a whole family of new compounds presenting dual emission from two charge transfer states as well as TADF emission properties. The DFT calculations show that electronic excited CT states of different energies can be formed when molecules contain both carbazole and phenoxazine donors. Beyond the typical local emission of donor and acceptor moieties, these molecules are characterized by the presence of a double CT emission involving respectively Cz and PhOx mainly in solution. Moreover, especially for the first series, it seems that the Cz and PhOx CT states are independent from each other. The CT emission involving carbazole is more intense in the 1st series, particularly for molecules containing a larger number of carbazoles. The double emission, especially observed in the 1st series leads to chromaticity coordinate values that vary from warm-white to cold-white, thus demonstrating that this class of molecules can be considered potentially highly suitable for white-light display applications. Moreover, a gradual bathochromic shift with the increasing number of substituents was observed in all three series, both in absorption and in solid state emission, leading to a fine tuning of the color emission. Increasing the number of carbazole units improves the solid-state photoluminescence quantum yield, up to 18% in PMMA films. Conversely, fluorescence yields remain rather low in solution. Moreover, it was demonstrated that increasing the number of phenoxazine units helps to improve the TADF properties in this class of materials, in line with the stronger donor properties of phenoxazine compared to carbazole.

Besides the photophysical properties, we have also observed intriguing electrochemical behaviors for these compounds. We have demonstrated the sequential oxidation of phenoxazine and carbazole units in agreement with their relative donor strength. More importantly, we propose a mechanism explaining the (polyfluoro)benzonitrile irreversible reduction. We believe that the fluoride anion acts as a leaving group in the anion radical formed upon electron uptake, but the fluorine expulsion only occurs after dimerization, provided that the number of substituents remains small. In the other cases, a reversible reduction is observed showing that the anion radical formed remains stable.

In conclusion, the dual emission developed by using two different donors can be considered as a promising strategy: i) to tune the emission color by properly selecting the parent molecules, and ii) to achieve white luminescence for lighting applications. In fact, we hope that this work should help single white-light-emitting organic TADF molecules becoming prominent in future display and lighting applications.

SUPPORTING INFORMATION

- SYNTHESIS PROTOCOLES
- NMR AND MASS SPECTRA
- XRD Analysis
- DFT Calculations
- Electrochemistry
- UV-Vis Absorption spectra
- Emission spectra

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KEYWORDS: benzonitrile; phenoxazine; carbazole; TADF; photophysics.

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