N-doped cycloparaphenylenes: Tuning electronic properties for applications in thermally activated delayed fluorescence

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Abstract

We theoretically characterize a series of substituted cycloparaphylene nanohoops to study the effect of incorporating an electron-withdrawing group into their cyclic structure. We systematically vary the nature, position, and number of nitrogen-containing acceptor groups in both neutral (pyridine) and charged forms (pyridinium and methylpyridinium) to provide insights into how this functionalization affects the structural, electronic, and optical properties of these systems. We focus also on the singlet-triplet energy difference, with low values found, which might pave the way to further applications in the field of devices for light-emitting applications providing a potential class of TADF-based emitters.

KEYWORDS
density functional theory, donor–acceptor cycloparaphenylenes, optoelectronic properties, TD-DFT, thermally activated delayed fluorescence

1 INTRODUCTION

Organic Electronics is a field of rapid growth attracting interest from interdisciplinary domains including electronics & engineering, chemistry, physics, and materials science, not to mention the great commercial interest toward its applications.[1,2] The facile tunability of organic molecules has paved the way for a wealth of organic-based materials to be synthesized with novel key properties. Already, small organic molecules find their place in photovoltaic cells,[3,4] light-emitting transistors,[5–9] and diodes,[10–12] to name just a few of these applications. The flexibility of organic materials over inorganic has enabled the birth of the “soft electronics” market, including devices that can twist, bend or mould to any surface or textile. With so many possibilities arising from unique properties of organic molecules, the future of organics appears bright: not only do organic materials promise more innovative technologies but also are far more sustainable (organic molecules are abundant, easily synthesized and potentially...
Therefore, the motivations for development of organic-based devices are still valid: (i) to surpass the applicability of silicon-based devices by expanding the functionality of electronics; and (ii) to be more sustainable in terms of energy efficiency while manufactured using low resource usage methods.

In particular this study consists in the deployment of a family of not yet fully explored organic nanorings, an emerging subclass of macrocycles\(^{[13–18]}\) with great possibilities for their application as active materials in optoelectronic devices. The cyclic topology of these systems already presents intriguing properties due to its unique combination of strain and bending, and the radial arrangement of \(\pi\)-orbitals; contrarily to the case of linear oligomers most studied up to date. Actually, some nanorings have recently been studied, displaying competitive charge-transport and photophysical properties, at least from the theoretical point of view.\(^{[19]}\) Complementarily, there have been recent advances toward other related \(\pi\)-extended systems\(^{[20–22]}\) which may afford a fine-tuned and fully controlled synthesis of short carbon nanotubes from these molecular building blocks, to possibly contribute to a new realm of technology with light weight, low cost, flexible electronics. To realise this potential, the often conflicting design protocols for efficient charge injection and transport, light emission on charge recombination, and exciton diffusion, need to be overcome. Significant efforts in this direction have been reported in last years, but to our knowledge these processes has not been systematically explored in the context of small nanorings. In this regard, we theoretically investigate here Donor–Acceptor (D-A) cycloparaphenylene (CPP) derivatives,\(^{[23–30]}\) whose molecular design strategy is presented in Figure 1, and specifically a large set of Nitrogen-doped (N-doped) CPPs. Note that the choice of the systems is motivated by recent experimental achievements\(^{[31]}\) but extended to other substitution patterns for which the D-A moieties might be of key importance in steering new mechanisms for light emission (vide infra). Figure 2 shows the chemical structure of all the compounds studied.

The manuscript is organized into the following sections. We will outline first (section 2) the set of theoretical models selected for studying accurately these systems, in both their ground- and excited-states, and in gas- or solution-phase. Next we address in detail (subsections 3.1 and 3.2) the structural and optoelectronic properties of a set of N-doped CPPs, derived from the pristine \([8\text{CPP}](\text{where square brackets indicate the number of benzene rings of the CPP system})\) by varying the position, type and number of the acceptor groups. In doing so, we hope to shed light on the structure–property relationships that govern these challenging systems once functionalized. Then, we also conduct (subsection 3.3) a size-dependent study of N-doped CPPs, including other members such as \([6\text{CPP}](\text{and}[10\text{CPP}],\text{analyzing if the structural and optoelectronic effects of N-doping change with the diameter of the nanorings. Next, we study their optical properties (subsection 3.4), and then consider (subsection 3.5) the suitability of these nanorings to exhibit light emission via a novel thermally activated delayed fluorescence (TADF) mechanism. Note that the design of organic semiconductors with TADF properties, which are primarily based on D-A moieties,\(^{[32,33]}\) has seen enormous progress in recent years.\(^{[34–37]}\) In this regard, we evaluate the impact of the acceptor groups on reducing the singlet-triplet energy gap, and we concomitantly employ some metrics for rationalizing the nature of these excited-states, aiming at evaluating their potential as emitters in OLED applications.

## 2 | THEORETICAL FRAMEWORK

### 2.1 | General issues

All the calculations reported here were done with the G09 package,\(^{[38]}\) using Gabedit,[\(^{39}\) Multiwfn,\(^{[40]}\) and the NANCY_EX package\(^{[41,42]}\) for post-processing of the results. To model the electrostatic effects arising in solution, and, thus, to truly compare whenever possible with the set of experimental results mostly performed in acetonitrile or in dichloromethane (DCM), for charged nanohoops we employ the conductor-like polarization...
continuum model (CPCM)\textsuperscript{[43,44]} according to recent recommendations,\textsuperscript{[45]} while the neutral compounds are treated by the standard PCM model.\textsuperscript{[46]} The cost-effective basis set 6-31G* was fixed for most of the calculations reported here. The larger def2-TZVP basis set\textsuperscript{[47,48]} was also used, as a sanity check in some cases, to verify the completeness of the 6-31G* basis set, for instance, for the TD-DFT calculations.

2.2 | Ground-state calculations

Due to the expected interplay between large size and concurring stereoelectronic effects arising from CPP strained cyclic topology, density functional theory (DFT) is the most appropriate theoretical method (vide infra) for studying accurately their properties at a reasonable computational cost. We preliminarily selected some hybrid exchange-correlation flavors, ordered for their increasing weight (in %) of Hartree–Fock (HF) like exchange, to address the possible impact of this technicality on the ground-state properties: M06-L (0\%),\textsuperscript{[49]} B3LYP (20\%),\textsuperscript{[50,51]} M06-2X (54\%),\textsuperscript{[49]} and M06-HF (100\%),\textsuperscript{[49]} as well as the range-separated \(\omega\)B97XD.\textsuperscript{[52]} After the initial benchmarking done, we also applied the -D3(BJ) dispersion correction\textsuperscript{[53,54]} to take into account possible missing intramolecular (long-range) interactions. We have always verified that all real frequencies are obtained in all cases for the optimized ground-state geometries.

2.3 | Excited-state calculations

Figure 3 sketches all the processes involved, using a simplified representation of the relevant potential energy surfaces as a function of a generalized coordinate \(Q\). Note that we are basically interested in disclosing the underlying structure–property guidelines for these materials, and not in pursuing the benchmark of theoretical methods against large datasets; nonetheless, based on recent key studies of excited-state properties,\textsuperscript{[55,56]} we have also selected the PBE0 functional\textsuperscript{[57]} for the TDA-DFT part in addition to the functionals employed for the ground-state part. The main difference between this and a previous study, which also included some calculations for a subset of the N-doped CPPs,\textsuperscript{[31]} relies not only on benchmarking of theoretical methods but also on unexplored excited-state light-emitting properties (vide infra).
Vertical excitation energies, from the ground-state optimized geometries to the first lowest singlet $E_v(S_1)$ or triplet $E_v(T_1)$ excited-states, were calculated within the time-dependent (TD)-DFT approximation using the Tamm–Dancoff (TDA)-DFT linear-response approach,[58,59] which provides improved accuracy specially for triplet state energies[60–62] and keeps also other advantages (e.g., lower cost) for further applications to large systems.[63] The difference between the vertical singlet and triplet absorption energies gives the corresponding (vertical) singlet-triplet splitting, $\Delta E_{ST^v}$.

We also compute in some cases the adiabatic excitation energies, $E_a(S_1)$ and $E_a(T_1)$, which accounts for the reorganization energy ($\lambda$) on relaxation of the excited-state geometries, through the corresponding TDA-DFT gradients. The energy difference between these two states is denoted as $\Delta E_{ST^a}$. The optimized lowest triplet excited-state was also accessed (in some cases) by spin-unrestricted calculations and yielded the same result as the TDA-DFT (within $\pm 0.05$ eV) for the $E_a(T_1)$ values.

3 | RESULTS AND DISCUSSION

3.1 | Study of the structural effects of acceptor substituents into [8]CPP

We evaluate first the structural effects of substituting a CH by a N atom or a N-containing (NH$_2$ or NCH$_3$) group by calculating: (i) the dihedral angle between adjacent phenyl units; and (ii) the bond length alternation (BLA) for all phenyl units, measuring the degree of $\pi$-conjugation along the backbone of the selected N-doped CPPs, also compared with the pristine [8]CPP case.

**Table 1** Bond Length Alternation (BLA, in Å), calculated as $\text{BLA} = \frac{1}{2} [ (r_1 + r_3) - (r_2 + r_4) ]$, and dihedral angles ($\theta$, in degrees) along the backbone of the selected N-doped CPPs, also compared with the pristine [8]CPP case.

<table>
<thead>
<tr>
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<tbody>
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<td>BLA</td>
<td>BLA</td>
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<td>0.030</td>
<td>0.031</td>
<td>18.5</td>
<td>0.002</td>
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</tbody>
</table>

A positive (negative) sign for the angles implies a (anti-)clockwise orientation. All values obtained from the optimized geometries at the B3LYP-D3(BJ)/6–31G* level. The phenyl rings 1 and 3 carry the nitrogen functionality in all cases.
rings of the backbone. Note that we refer in the following to the doping of the molecule when this substitution is done, even when replacing a CH by a N atom creates an isoelectronic (and closed-shell) compound. We discuss as a matter of illustration only a subset (see Figure 2) of the systems tackled: 1,15-diaza-[8]CPP$^2$, H,H-1,15-diaza-[8]CPP$^2$ and $N\_N$-dimethyl-1,15-diaza-[8]CPP$^2$, with the corresponding results presented in Table 1 and compared with the [8]CPP molecule.

The architecture of CPPs confers to the systems a unique cyclic structure of strained, sp$^2$ hybridized, and para-linked phenyl rings. Generally speaking, the most energetically favored conformation found in real samples$^{[64]}$ is that which reduces ortho, ortho' steric interactions between adjacent phenyl rings while maximizing $\pi$-conjugation. Regarding the dihedral angles, and independently of the exchange-correlation functional applied, the unsubstituted [8]CPP assumes a staggered orientation with adjacent phenyl rings cantering alternately by about $\pm 30^\circ$, with a dihedral angle slightly reduced (i.e., by up to $5^\circ$) with respect to that of the corresponding linear oligomer.$^{[65,66]}$ The same configuration is also retained by N-doped CPPs, although more planar angles are predicted due to a reduced steric hindrance between the nitrogen lone pair and the adjacent aryl C—H group (Table 1).

The evolution of the BLA calculated by all the assessed DFT methods is shown in Figure 4. All functionals give qualitatively consistent results and, as expected from the absence (full presence) of HF-like exchange, the M06-L (M06-HF) predicts the lowest (highest) values according to the overdelocalization error (full localization) of this functional. Since the BLA and optical excitations are properties intimately connected.$^{[67,68]}$ these methods are expected to underestimate (overestimate) exciton energies.$^{[69]}$ The M06-2X and $\omega$B97XD methods behave similarly, especially for the 1,15-diaza-[8]CPP$^2$ and $N\_N$-dimethyl-1,15-diaza-[8]CPP$^2$ cases, while B3LYP-D3(BJ) lies between M06-L and M06-2X, following the increasing weight of the HF-like exchange introduced into the method.$^{[70]}$ We also note that the $\omega$B97XD method had been shown previously to overestimate systematically the experimental absorption maxima for the set of increasingly longer (6–12)CPPs$^{[71]}$ and we will, thus, rely in the following in the B3LYP-D3(BJ) optimized geometries as a compromise. We calculate with this method a diameter of 11.0±0.5 Å for molecule 1, to be compared with an experimental (X-ray) value of 10.9±0.2 Å.$^{[31]}$ and that the precise location of the N atom could not be experimentally resolved, which precludes a more detailed comparison between experimental and theoretical results for individual bond lengths.

**FIGURE 4** Bond Length Alternation (BLA, in Å), calculated as $\text{BLA} = \frac{1}{2} \sum_i \left( r_i - \langle r_i \rangle \right)$, along the phenyl rings of (top) 1,15-diaza-[8]CPP$^2$, (middle) H,H-1,15-diaza-[8]CPP$^2$, and (bottom) $N\_N$-dimethyl-1,15-diaza-[8]CPP$^2$, calculated at various levels of theory and with the 6–31G* basis set. The phenyl rings 1 and 3 carry the nitrogen functionality in all cases.
3.2 | Electronic properties of N-doped [8]CPPs

We inspect in detail the energy and shape of the frontier molecular orbitals of cyclic compounds, at the B3LYP/6-31G* level, and compare with those of the pristine [8]CPP molecule and of their corresponding N-doped linear oligomers. Figure 5 shows the trend in the energy difference between the highest occupied (HO) and the lowest unoccupied (LU) molecular orbital (MO), and how it is reduced in all cases with respect to that of the undoped [8]CPP, with a more pronounced impact for the protonated or alkylated nanohoops. Actually, we can see that further increasing the content of N in molecules 1-3 has small effects on the HOMO (up to 0.1 eV) or LUMO (up to 0.3 eV) energies, which are found delocalized over the whole backbone, and thus on the corresponding gap. Interestingly, the energy of the HOMO is only weakly altered for the whole set of molecules studied, ranging between 5.1 and 5.6 eV for most of the cases unless for the multiply charged compounds 6 and 9, but the LUMO energy is dramatically stabilized by up to 1 eV in some cases when going from the neutral to any of the charged N-doped CPPs. This trend fully agrees with the experimental decrease in the cathodic peak potential for the reduction of compounds 1-3 and 7-8, according to a recent study. [31]

We now compare cyclic vs. linear N-doped paraphenylenes, CPPs and LPPs, respectively, using the same computational protocol for both. The increased conjugation of the former (evidenced for instance by lower BLA values in a fewer rings) is consistent with a lower HOMO-LUMO gap (e.g., 3.33 eV and 3.76 eV calculated here, respectively, for aza-[8]CPP 1 and aza-[8]LPP). The narrowing of the HOMO-LUMO gap (2.5-2.7 eV) for the charged cyclic compounds was also observed for a subset of the parent N-doped LPPs, being for instance now of 2.55 and 2.80 eV for aza-[8]CPP 1 and aza-[8]LPP 1, respectively.

Actually, for molecules 4-9, the HOMO is evenly distributed over the electron-rich phenylene backbone, the moiety acting as a donor, whereas the LUMO is located mainly on the N-(methyl)pyridinium core, acting thus as the acceptor, resulting in a pronounced intramolecular donor-acceptor orbital separation. Only in the triply-alkylated nanohoop 9, where the acceptor groups are evenly positioned around the nanohoop, they result in a more extended distribution of the LUMO orbital compared to other cases. Summarizing, the incorporation of a neutral pyridine moiety has a negligible effect compared to insertion of pyridinium and methylpyridinium units, both on the LUMO energies and on the intramolecular HOMO-LUMO separation, a fact that could be further explored (vide infra) for promoting new light emission mechanisms.

3.3 | Increasingly longer N-doped [n]CPPs

We subsequently look at the effect of decreasing/increasing the number (n) of aromatic rings of the N-doped nanohoop on the HOMO-LUMO orbitals for a subset of representative geometries, that is, aza-[n]CPP, H-aza-[n]CPP+, and N-methylaza-[n]CPP+ compounds, with n=6, 8, and 10, and their corresponding linear oligomers (see Figure 6). Note that if n=8, these compounds correspond to numbers 1, 4, and 7 in Figure 2 before, and that again the B3LYP/6-31G* level of theory is used. As is known from literature, the CPPs have decreasing HOMO energies and increasing LUMO energies (increasing band gap) with increasing molecular size, opposite to linear oligomers. For example, the N-methylaza-[n]CPP+ series, with increasing molecular size, exhibit an increase in the HOMO-LUMO gap from 2.57 to 2.74 eV for the N-methylaza-[6]CPP+ to N-methylaza-[10] CPP+ cases, respectively, reaching rapidly the saturation values. However, the opposite trend is observed in the linear oligomers, with a decreasing HOMO-LUMO gap from 3.18 to 2.92 eV, respectively.

Furthermore, it seems that the aforementioned size-scaling electronic properties for CPPs are less prominent with increasing acceptor strength (pyridine < methylpyridinium < pyridinium). Whereas for the aza-[n]CPP series of compounds, the HOMO-LUMO gap increases monotonically from...
2.87 to 3.37 eV when going from the aza-[6]CPP to the aza-[10]CPP system, as it also happens for the unsubstituted [n]CPPs, the gap does not significantly alters (up to 0.1-0.2 eV) in the other two cases, reflecting the strong localization of both frontier molecular orbitals in spatially separated fragments of the molecule. Thus, the conclusions drawn before about the impact of inserting pyridinium and methylpyridinium units are expected to also approximately hold, independently of the nanoring size, as it was also recently inferred experimentally after comparing aza-[6]CPP with aza-[8]CPP and N-methylaza-[6]CPP with N-methylaza-[8]CPP. The same trend regarding the evolution of the HOMO-LUMO gap is also found for the N-doped linear paraphenylenes, although to a lesser extent due to edge effects: the gap decreases monotonically from 3.98 to 3.81 eV for the aza-[6]LPP and aza-[10]LPP cases, and changes up to 0.1-0.3 eV in the other cases, again reflecting some localization of both frontier molecular orbitals in spatially separated fragments of the charged molecules.

**FIGURE 6** From left to right: Increasingly longer cyclic (top) and linear (bottom) N-substituted nanohoops aza-[n]CPP, H-aza-[n]CPP⁺, and N-methylaza-[n]CPP⁺.

**FIGURE 7** Simulated UV-vis absorption spectra (in dichloromethane and at the TDA-B3LYP/6–31G* level) of N-doped nanohoops: (top) aza-[8]CPP 1; 1,15-diaza-[8]CPP 2; 1,15,31-triaza-[8]CPP 3; (middle) H-aza-[8]CPP⁺ 4; H,1,15-diaza-[8]CPP⁺ 5; H,H,1,15-diaza-[8]CPP²⁺ 6; (bottom) N-methylaza-[8]CPP⁺ 7; N,N-dimethyl-1,15-diaza-[8]CPP²⁺ 8; N,N,N-trimethyl-1,15,31-triaza-[8]CPP³⁺ 9; also compared with the pristine [8]CPP case.
3.4 Optical properties of N-doped [8]CPPs

The TDA-DFT approach was used to provide results and insights into the photophysical properties of the set of N-doped [8]CPPs. We remind first that all unsubstituted [n]CPPs experimentally share a common absorption maximum at 340 nm, independently of solvents, which is perfectly reproduced here with the TDA-B3LYP/6-31G* // B3LYP-D3(BJ)/6-31G* protocol for the [8]CPP case (see Figure 7) although care with this functional must be considered for much longer oligomer sizes. Nonetheless, this level of theory has been also used before for pristine [n]CPPs and can thus help to compare with previously published results. Thus, we tackle next the simulated UV-vis absorption spectra of all the D-A nanohoops 1–9, presented in Figure 7.

It can be immediately seen how for the neutral N-doped nanohoops 1–3 a major absorbance peak is also observed around 340–350 nm, slightly red-shifted on increasing the content of N in perfect agreement with experimental results. Note that contrarily to what was found before for the unsubstituted [8]CPP, for these N-doped [8]CPPs, the HOMO-LUMO transition is not forbidden due to partial symmetry breaking induced by the presence of nitrogen, although the oscillator strength values are very low. Actually, for both [8]CPP and neutral N-doped nanohoops 1–3, the transition ($\pi \rightarrow \pi^*$) giving rise to the absorption maximum is composed of approximately equal combinations of one-electron excitations from HOMO−1 to LUMO and HOMO to LUMO, and from HOMO−2 to LUMO and HOMO to LUMO1,2. The spectra drastically change for the charged compounds 4–9, see also Figure 7, displaying a larger number of peaks and shoulders and, thus, reflecting a more complicated manifold of one-electron transitions giving rise to the corresponding excitations. Since experimental results are available for compounds N-methylaza-[8]CPP+ 7 and N,N-dimethyl-1,15-diaza-[8]CPP2+ 8, we include in Figure 8 the energy and shape of a subset of the molecular orbitals involved into the lowest-energy excitations for these systems, as well as the corresponding (non-negligible) oscillator strengths. Actually, the introduction of the electroactive groups breaks the degeneracy of the HOMO−1/HOMO−2 and LUMO−1/LUMO−2 orbitals found in undoped [n]CPPs, which helps explaining the shape of the spectra involving multiple allowed absorption bands. Note that a broad absorption spectrum is advantageous for photovoltaic applications, to harvest the largest possible number of photons.

We also investigate if the choice of the functional would have any influence on the results obtained so far by comparing the HOMO-LUMO energy absorptions of 7 and 8, situated experimentally at 460 and 554 nm, respectively, with the theoretical results (M06-L, B3LYP, PBE0, M06-HF, and ωB97XD functionals). We also investigate the effect (if any) of enlarging substantially the basis set going from the 6-31G* to the def2-TZVP one, choosing for that the PBE0 model as a test case. Table 2 shows how the values are largely underestimated (overestimated) by the M06-L (M06-HF and ωB97XD) methods, following the conclusions about the performance of these methods also achieved in previous sections on
We have found a \( \Delta E_{ST} \) value of around 0.5 eV for compounds 1-3, in perfect agreement with the similar behavior of these systems with respect to [8]CPP. This gap is instead approximately halved for the set of compounds 4-8. This reduction is related (vide infra) to the spatial separation, and thus poor overlap, of the HOMO and LUMO corresponding orbitals, as it was qualitatively evidenced in Figure 5. However, for compound 9, which registers a larger overlap between these orbitals (see also Figure 5) the value increases again showing the marked relationship between these two quantities in agreement with other recent studies.\(^{86,87}\)

### Table 2: Calculated vertical (lowest) singlet excitation energies (in eV) of compounds N-methylaza-[8]CPP\(^\ast\) and N,N-dimethyl-1,15-diaza-[8]CPP\(^2\ast\), with different functionals and basis sets

<table>
<thead>
<tr>
<th>Method(^a)</th>
<th>N-methylaza-[8]CPP(^\ast) 7</th>
<th>N,N-dimethyl-1,15-diaza-[8]CPP(^2\ast) 8</th>
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<tr>
<td>TDA-M06-L/6-31G*</td>
<td>1.54</td>
<td>1.52</td>
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<tr>
<td>TDA-B3LYP/6-31G*</td>
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<td>TDA-PBE0/6-31G*</td>
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<td>2.23</td>
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<td>TDA-PBE0/def2-TZVP</td>
<td>2.41</td>
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</tr>
<tr>
<td>TDA-(\text{mB}97XD)/6-31G*</td>
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<td>3.54</td>
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<tr>
<td>TDA-M06-HF/6-31G*</td>
<td>4.46</td>
<td>4.18</td>
</tr>
<tr>
<td>Experimental values(^b)</td>
<td>2.69</td>
<td>2.24</td>
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</table>

\(^a\)At the B3LYP-D3(BJ)/6-31G* optimized geometries and with DCM as solvent. 
\(^b\)From Ref. [31].
To determine more quantitatively the nature of the excited-states calculated so far, we resort to a set of descriptors mostly employed within the context of charge-transfer (CT) excitations, that is, the extent of the electron-hole distance ($D_r$, in Å) as measured by the weighted distance between the corresponding centroids of the orbitals:

$$D_r = \frac{\sum_i n_i^o \langle \phi_i | r | \phi_j \rangle - \langle \phi_j | r | \phi_i \rangle}{\sum_i n_i^o}$$

with $\phi_i^o$ referred again to the set of occupied (virtual) orbitals, and $n_i^o$ the corresponding coefficients, for the involved TDA-based excitation. We also rely on the overlap between the detachment and attachment densities, $\phi_3^2$, based on the rearrangement of the electronic density removed on electronic excitations (i.e., the detachment density matrix) and housed in the excited state of interest (i.e., the attachment density matrix), using the NANCY_EX package for both $S_1$ and $T_1$ states. Note that these two metrics consider by definition all the orbitals involved in the electronic excitation, gathering the results in Table 3.

We remind that some of us$^{[33,82]}$ and others$^{[86]}$ have found before a direct correlation between low $\Delta E_{ST}$ values and high (low) values of $D_r$ ($\phi_3$), an issue that we would like to further corroborate here. Actually, Figure 9 displays the existing interplay (or correlation) between some of the variables monitored ($\Delta E_{ST}$, $\phi_3(S_1)$, and $\Delta r(S_1)$) and indicates how this is indeed the case. Similar correlation is obtained when plotting $\phi_3(S_1)$ and $\Delta r(S_1)$ as a function of $\Delta E_{ST}$. Since $\phi_3$ has normalized limiting values, 0 (1) when the electronic transition is of charge-transfer (locally excited) character by nature, we can corroborate that: (i) $\phi_3$ values close to 0.5, like those found for the $S_1$ excited-state of molecules 4-8, indicate a mixed character although being predominantly 1CT; and (ii) the $T_1$ excited-state of all molecules displays values of $\phi_3 > 0.5$, and, thus, with a more pronounced locally-excited (LE) character ($^2$LE). The $\Delta r$ metrics involves the manifold of one-electron transitions contributing to the excited-state, with some

TABLE 3  Calculated vertical (lowest) singlet and triplet excitation energies (in eV), and their energy difference, for the set of N-doped CPPs 1 to 9

<table>
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<tr>
<th>Compound</th>
<th>$E_v(S_1)$</th>
<th>$\Delta r(S_1)$</th>
<th>$\phi_3(S_1)$</th>
<th>$E_v(T_1)$</th>
<th>$\Delta r(T_1)$</th>
<th>$\phi_3(T_1)$</th>
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<tr>
<td>1</td>
<td>2.85 (0.006)</td>
<td>1.03</td>
<td>0.80</td>
<td>2.36</td>
<td>0.28</td>
<td>0.86</td>
<td>0.49</td>
</tr>
<tr>
<td>2</td>
<td>2.76 (0.006)</td>
<td>1.04</td>
<td>0.79</td>
<td>2.29</td>
<td>0.26</td>
<td>0.85</td>
<td>0.47</td>
</tr>
<tr>
<td>3</td>
<td>2.68 (0.005)</td>
<td>0.23</td>
<td>0.80</td>
<td>2.22</td>
<td>0.07</td>
<td>0.85</td>
<td>0.46</td>
</tr>
<tr>
<td>4</td>
<td>2.25 (0.088)</td>
<td>5.92</td>
<td>0.46</td>
<td>2.00</td>
<td>3.22</td>
<td>0.68</td>
<td>0.25</td>
</tr>
<tr>
<td>5</td>
<td>2.23 (0.065)</td>
<td>5.60</td>
<td>0.49</td>
<td>1.98</td>
<td>3.10</td>
<td>0.69</td>
<td>0.25</td>
</tr>
<tr>
<td>6</td>
<td>2.21 (0.018)</td>
<td>4.32</td>
<td>0.56</td>
<td>1.94</td>
<td>2.75</td>
<td>0.70</td>
<td>0.27</td>
</tr>
<tr>
<td>7</td>
<td>2.41 (0.040)</td>
<td>5.96</td>
<td>0.46</td>
<td>2.18</td>
<td>3.37</td>
<td>0.70</td>
<td>0.23</td>
</tr>
<tr>
<td>8</td>
<td>2.21 (0.006)</td>
<td>4.77</td>
<td>0.53</td>
<td>1.98</td>
<td>3.06</td>
<td>0.69</td>
<td>0.23</td>
</tr>
<tr>
<td>9</td>
<td>2.64 (0.031)</td>
<td>1.57</td>
<td>0.70</td>
<td>2.24</td>
<td>0.65</td>
<td>0.80</td>
<td>0.40</td>
</tr>
</tbody>
</table>

The oscillator strengths are given in parentheses. The values of $\Delta r$ (in Å) and $\phi_3$ for each excited-state are also given. All values obtained at the TDA-PBE0/def2-TZVP level, unless for $\phi_3$ in which the basis set used was the 6-31G* one.

$^a$At the B3LYP-D3(BJ)/6-31G* optimized geometries and with DCM as solvent.

Figure 9 displays the existing interplay (or correlation) between some of the variables monitored ($\Delta E_{ST}$, $\phi_3(S_1)$, and $\Delta r(S_1)$) and indicates how this is indeed the case. Similar correlation is obtained when plotting $\phi_3(S_1)$ and $\Delta r(S_1)$ as a function of $\Delta E_{ST}$. Since $\phi_3$ has normalized limiting values, 0 (1) when the electronic transition is of charge-transfer (locally excited) character by nature, we can corroborate that: (i) $\phi_3$ values close to 0.5, like those found for the $S_1$ excited-state of molecules 4-8, indicate a mixed character although being predominantly 1CT; and (ii) the $T_1$ excited-state of all molecules displays values of $\phi_3 > 0.5$, and, thus, with a more pronounced locally-excited (LE) character ($^2$LE). The $\Delta r$ metrics involves the manifold of one-electron transitions contributing to the excited-state, with some

![Interplay between the calculated $\Delta r$ (in Å) and $\phi_3$ values, and the $\Delta E_{ST}$ (in eV) energy difference, at the TDA-PBE0/def2-TZVP level. The solid lines are a guide to the eye](image-url)
cutoff ($\Delta r > 1.5 - 2.0 \text{ Å}$) proposed before to distinguish a charge-transfer excitation from a localized one. This quantity is thus expected to give a better indication of the spatial confinement of the orbitals. Table 3 also includes the numerical values of $\Delta r$, indicating a much more marked CT character for compounds 4-8 than for 1-3. Note also how the values of $\Delta r(T_1)$ are normally lower than $\Delta r(S_1)$ owing to the more confined character of triplet excitons. Overall, according to these results, we can reduce the set of potential TADF candidates to molecules 4-8 ideally.

We remind that, in addition to the exploration of these materials as emitters, the development of host materials acting as matrix is also relevant. Generally speaking, and besides other factors as chemical and thermal robustness, the host molecules must possess a high triplet energy level to minimize back energy transfer from the emitter to the host. Actually, comparing the $E_T(T_1)$ values provided in Table 3 for compounds 4-8, ranging between 1.9 and 2.2 eV, with the experimental triplet energy levels$^{[81]}$ of some traditional hosts as CBP (2.6 eV), TPBI (2.65 eV), mCBP (2.8 eV), or DPEPO (3.0 eV), we can see how this condition would also match. Another energy alignment should arise between emitters and hosts: the former should have a higher HOMO (lower Ionization Potential) and a lower LUMO (higher Electron Affinity) than the latter. A general compilation of experimental IP and EA values for host materials, as is given in Ref. [81], provides roughly speaking the following limits: $5.5 < \text{IP} < 6.5$ and $2.0 < \text{EA} < 3.5$ eV, which would approximately translate into the conditions $3.8 < -\epsilon_{\text{HOMO}} < 4.6$ and $4.1 < -\epsilon_{\text{LUMO}} < 6.5$ eV, thanks to the linear relationship existing between calculated (B3LYP) HOMO/LUMO energies and experimental IPs/EAs.$^{[93]}$ Recovering now the HOMO and LUMO values of emitters 4-8 displayed in Figure 5, we can see how this is always the case, with HOMO (LUMO) energies being higher (lower) than the thresholds derived above.

4 | CONCLUSIONS

The impact of chemical functionalizations of the CPP backbone was established although a thorough theoretical study, carefully analyzing the effect of forcing an intramolecular D-A structure on substitution of phenylene rings by an acceptor moiety. First of all, the results quantitatively reproduced the available (but scarce) experimental data, and, thus, enabled suitable bracketing of the accuracy of the computational tools employed. Substantial electronic changes were observed on substitution with strong N-doped acceptor groups, such as pyridinium and methylpyridinium, affecting also the lowest singlet and triplet excited states and their nature. We also studied how the optoelectronic properties evolve with the size of the nanohoop, and how they hold for other acceptor moieties as far as the molecular design principle is no longer altered.

The state-of-the-art quantum-chemical methods and tools employed for modelling these nanorings allowed us to predict remarkably low singlet-triplet energy gap, and wholly characterize the nature of the excited-state involved. Thus, this study also opens up new ways to exploit systems with cyclic topology as TADF molecular emitters for OLEDs applications, considering that the singlet-triplet energy difference is at least halved with respect to the pristine (undoped) parent compound, approaching values lower than the 0.3 eV energy threshold, as well as other key energy alignments are matched. We hope this finding will stimulate further theoretical and experimental work within this cutting-edge domain.

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