

Modulation of [8]CPP properties by bridging two phenylene units

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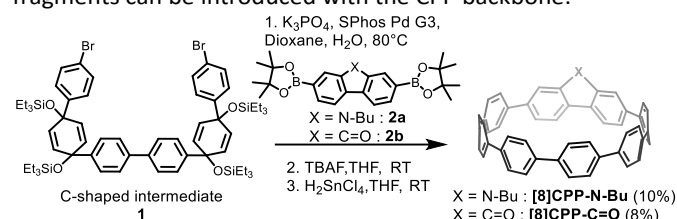
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We report the synthesis and characterization of two new fluorophores, consisting of a [8]cyclo-*para*-phenylene core in which two phenylenes are bridged by either a nitrogen atom or a carbonyl group. The nitrogen bridge increases the HOMO-LUMO gap, whereas the carbonyl bridge decreases it. These results provide guidelines to control the electronic properties of nano hoops.

The [n]cyclo-*para*-phenylenes (CPPs), cyclic oligophenylenes in which n phenylenes are linked by their *para* positions, belong to a family of π -conjugated cyclic and radial systems known as nano hoops. Thanks to their unique conjugation, nano hoops have original properties compared with their linear analogues.¹ For example, our group recently showed that a phosphorescent organic light emitting diode based on a cyclic tetracarbazole ([8]CPP-4N-Bu) performed better than the one using a linear tetracarbazole.² In particular, their specific shape gives them complexation properties³ which, together with unique fluorescence properties, can be used for sensing applications.⁴ In addition, thanks to their photostability, solubility, high Stokes displacement and low toxicity, they have been used as fluorescent markers.⁵ In this context, it is important to define general design rules to control the fluorescence properties of CPP-based fluorophores. Some publications report the tuning of CPPs fluorescence by modifying their size,⁶ incorporating a donor and/or acceptor moiety^{3b, 7} or breaking their symmetry.⁸ In the present work, the structural modification is minimal since we study the impact of a single bridge between two phenylenes of [8]cyclo-*para*-phenylene [8]CPP, such as a nitrogen atom in [8]CPP-N-Bu and a carbonyl unit in [8]CPP-C=O, on its structural, electrochemical and photophysical properties. This simple structural modification changes some properties (eg HOMO-LUMO gap) while leaving some others unchanged (eg fluorescence for the nitrogen bridge) providing an interesting way to control the CPP electronic properties. These bridges were chosen because the modifications compared to [8]CPP are minimal, allowing interesting comparisons from a fundamental point of view, fluorenone being well-known known to have a detrimental effect on the emission, prevented their use as light emitters.⁹ Note that a [9]CPP displaying six carbonyl bridges has already been reported,¹⁰ but its structure is too different from that of [8]CPP-C=O to allow judicious comparisons, while [8]CPP-N-Bu will be compared to [8]CPP-4N-Bu displaying four nitrogen bridges.^{2, 11}

The targeted nano hoops were synthesized by a modular synthetic method (Scheme 1). The synthesis of the three

precursors **1**, **2a** or **2b** is described in the SI. **1** was obtained in 44% yield in four steps, an improvement compared to the reported synthesis (yield: 31%).¹² After Suzuki-Miyaura coupling between **1** and dipinacol-boron precursors **2a** and **2b**, deprotection of the silyl groups and reductive aromatization, the targeted nano hoops [8]CPP-N-Bu and [8]CPP-C=O were obtained with a global yield of 10 and 8% respectively over the three steps. This approach is versatile as various molecular fragments can be introduced with the CPP backbone.



Scheme 1. Synthesis of the nano hoops [8]CPP-N-Bu and [8]CPP-C=O

Having synthesized [8]CPP-N-Bu and [8]CPP-C=O, we turned to their structural characterization by X-ray diffraction of crystals (Fig.1). [8]CPP-N-Bu crystallizes in the orthorhombic Pca21 space group, with one molecule in general position in the asymmetric unit, and [8]CPP-C=O in the monoclinic P21/c space group, with one disordered molecule on an inversion center in the asymmetric unit. [8]CPP, which also displays 8 phenylenes, will be used here as a model compound to unravel the structural specificities induced by the bridge.¹³ As the main factors behind the specific electronic properties of nano hoops are the deformation of the building units and their relative arrangement, three structural parameters were considered: the mean diameter \emptyset , the mean torsion angle θ , and the mean displacement angle ω (Table 1 and SI). As expected, bridging two phenylenes in [8]CPP has no impact on \emptyset (11.0-11.1 Å for the three nano hoops), which is more related to the number of phenylenes. However, it can be noted that [8]CPP-N-Bu is closer to a perfect circle (min/max axis of 10.6/11.4 Å) than [8]CPP-C=O (10.4/11.6 Å) than [8]CPP (10.3/11.7 Å). Furthermore, bridging two phenylenes reduces ω : 8.7° for the two bridged nano hoops vs 9.6° for [8]CPP. Remarkably, incorporating a nitrogen atom has no impact on θ (24.3-24.4° for [8]CPP and [8]CPP-N-Bu), whereas θ is reduced by the carbonyl group (16.6° for [8]CPP-C=O). In conclusion, bridging two phenylenes of [8]CPP leads to more circular nano hoops, with less bent phenylenes and, depending on the nature of the bridge, has no

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impact (nitrogen atom) or decreases the torsion between

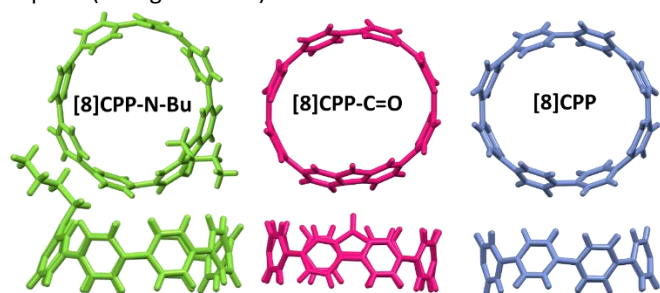


Figure 1. Single-crystal structures of the three nano hoops; disorder omitted for clarity.

phenylenes (carbonyl unit). Note that the four nitrogen bridges in **[8]CPP-4N-Bu** induce a decrease of θ (19.0°) and ω (7.1°).^{11b} All these geometrical changes will impact the π -conjugation, in turn modifying the electronic properties. **[8]CPP-N-Bu** and **[8]CPP-C=O** organize in a herringbones pattern with different tilt angles and displacement parameters (Fig.S69-70), which are at the origin of the open pore structure of **[8]CPP-N-Bu** and the closed pore structure of **[8]CPP-C=O** (Fig.S67-68). This difference in packing could induce some difference in the charge transport properties, which are of key importance for organic semiconductors. When using the sodium or lithium ionic radius to probe the intra-nano hoops voids, both nano hoops lead to an open pore structure (Fig.S67-68), showing their potential as organic battery electrode materials, an emerging field of applications of nano hoops.^{1h, 14} DFT optimization of the structure of the three nano hoops gave a similar geometry for **[8]CPP-N-Bu** and **[8]CPP**, while **[8]CPP-C=O** has a θ of 24.4° , higher than in the X-Ray structure and similar to the other nano hoops. From these optimized structures and using a homodesmotic reaction (Fig.S35), we estimated the strain energy at 73 and 72 kcal.mol⁻¹ for **[8]CPP-N-Bu** and **[8]CPP-C=O** identical to **[8]CPP**.¹⁵ Thus, the bridge, which plans two phenylenes, has no impact on the strain energy. Actually, even four nitrogen bridges do not increase the strain energy (72 kcal.mol⁻¹ for **[8]CPP-4N-Bu**).^{11b} Electrochemical analyses of **[8]CPP-N-Bu** and **[8]CPP-C=O** were carried out by cyclic voltammetry (CV) in DCM both for oxidation and reduction and compared with **[8]CPP**^{11b} (Fig.S23-27). CVs show several successive oxidation processes, with maxima at 1.00 and 1.60 V for **[8]CPP-N-Bu**, 1.07 and 1.21 V for **[8]CPP** and 1.14, 1.45, 1.69 and 2.08 V for **[8]CPP-C=O**.

Table 1 Structural, optical and electrochemical properties of **[8]CPP-N-Bu**, **[8]CPP-C=O** and **[8]CPP**

	[8]CPP-N-Bu	[8]CPP-C=O	[8]CPP ^{11b}
ϕ (Å)	11.0	11.0	11.1
[min-max]	[10.6-11.4]	[10.4-11.6]	[10.3-11.7]
ω ($^\circ$)	8.7	8.7	9.6
θ ($^\circ$)	24.4	16.6	24.3
λ_{abs}^a (nm)	338	307, 336	333
λ_{em}^a (nm)	529	582	529
QY ^a (nm)	0.20	0.02	0.25
τ_r^a (ns)	9.2	5.6	10.6
k_r^a (10^7 s ⁻¹)	2.2	0.36	2.4
k_{nr}^a (10^7 s ⁻¹)	8.7	17.5	7.0
$\lambda_{\text{abs-film}}^b$	366	355	346
$\lambda_{\text{em-film}}^b$	550	—	570
QY ^b	0.11	—	0.08
LUMO (eV) ^c	-2.49	-3.18	-2.60
HOMO (eV) ^c	-5.29	-5.42	-5.28
ΔE (eV) ^c	2.80	2.24	2.68

^aIn cyclohexane. ^bFrom a spin-coated film. ^cFrom electrochemical data (DCM)

The three nano hoops display a quasi-reversible first oxidation process. When recurrent CVs are performed reaching high potential values, electrodeposition processes are observed for **[8]CPP-N-Bu** and **[8]CPP-C=O** by the modification of the successive CVs and by the formation of an insoluble deposit showing also the different electrochemical behaviour induced by the bridges. In reduction, there are one or two reduction waves with maxima at -2.02 and -2.23 V for **[8]CPP-N-Bu**, at -1.93 V for **[8]CPP** and at -1.36 V for **[8]CPP-C=O**, showing the impact of the bridge on the reduction processes. While the waves are irreversible for **[8]CPP-N-Bu** and **[8]CPP**, it is indeed reversible for **[8]CPP-C=O**. The HOMO and LUMO energies evaluated from the onset potentials of the first oxidation and reduction waves are -5.29, -5.28, -5.42 eV on the one hand and -2.49, -2.60, -3.18 eV on the other for **[8]CPP-N-Bu**, **[8]CPP** and **[8]CPP-C=O** respectively. This feature reflects the electron-rich and -poor character induced by the nitrogen atom and the carbonyl group, respectively. The HOMO of the three

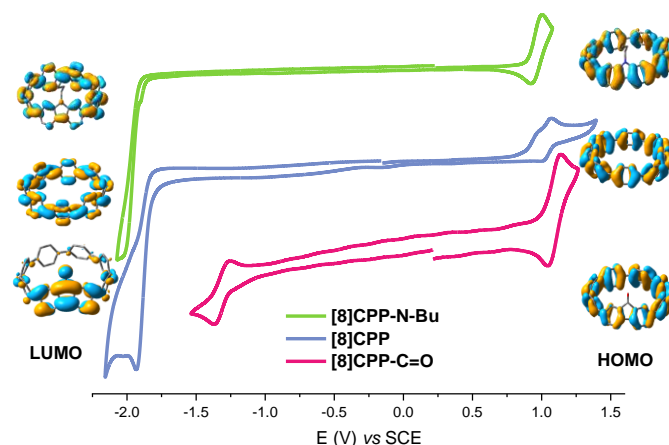


Figure 2. Cyclic voltammograms of **[8]CPP-C=O**, **[8]CPP-N-Bu** and **[8]CPP** measured in DCM (middle) and the representation of the LUMO (left) and HOMO (right)

nano hoops are delocalized throughout the molecule without any involvement of the bridge (Fig.2). Electron density is highest on carbazole in **[8]CPP-N-Bu** and on phenylenes in **[8]CPP-C=O**. Conversely, the LUMO of **[8]CPP-C=O** is fully localized on the fluorenone, while those of **[8]CPP** and **[8]CPP-N-Bu** are

delocalized on all the nano hoop cores. Except for the HOMO energy of **[8]CPP-N-Bu**, the trend observed for the frontier orbitals is that followed for the corresponding fragments, *i.e.* *N*-butyl carbazole (-5.47 and -1.73 eV), biphenyl (-6.18 and -1.79 eV) and fluorenone (-6.33 and -3.11 eV), see Fig.S21,22. These similar trends show that bridging a biphenyl incorporated in a CPP has the same impact as bridging a biphenyl. For **[8]CPP-N-Bu**, the HOMO is not as high as might be expected considering the electronic parameters since it is at the same level as that of **[8]CPP**. The effect of geometrical parameters, and in particular of ω , cannot be neglected since they are well known for playing a key role in the evolution of the HOMO and LUMO energies.¹⁶ Decreasing ω of **[8]CPP-N-Bu** (8.7°) compared to **[8]CPP** (9.6°) decreases the HOMO level, as already observed in nano hoops.^{11a, 16-17} Although the three nano hoops are built on the cyclic association of eight phenylenes, the different first oxidation/reduction potentials show the role played by the bridge on electrochemical properties. Thus, incorporating a nitrogen bridge into **[8]CPP** to give **[8]CPP-N-Bu** increases the LUMO energy without impacting the HOMO energy, which in turn increases the HOMO-LUMO gap. Note that the gap of **[8]CPP-4N-Bu** is at 2.78 eV^{11b} showing that increasing the number of nitrogen bridges does not induce a further increase of the gap. The carbonyl bridge of **[8]CPP-C=O** provides the opposite result with a drop of the gap. As the energy levels of the frontier orbitals are key parameters for the use of organic materials as semiconductors, this discovery is important for future applications in electronics.

The optical properties of the three nano hoops were characterized by UV-visible absorption spectroscopy as well as by stationary and time-resolved emission spectroscopy in cyclohexane (Fig.3) and in thin film (Fig.S18). **[8]CPP-N-Bu** and **[8]CPP** show similar absorption spectra. TD-DFT study indicates that the shoulder at around 400 nm and the main band (at 338 and 333 nm) of both nano hoops are due to similar transitions. The shoulder is classically attributed to a HOMO→LUMO transition with forbidden symmetry in **[8]CPP** (oscillation strength $f=0.00$, in black Fig.S31). Symmetry breaking due to the nitrogen bridge in **[8]CPP-N-Bu** makes this transition less forbidden ($f=0.03$), but not enough to impact the experimental

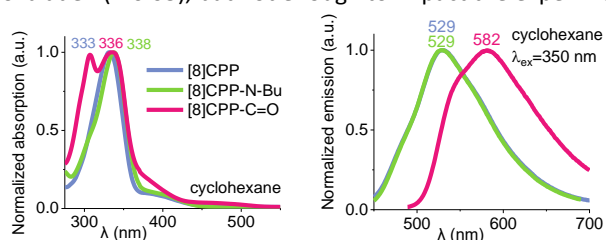


Figure 3. Absorption (left) and emission (right) spectra of the three nano hoops

absorption spectrum. The main band is due to two transitions (in blue and green Fig.S31). **[8]CPP-N-Bu** shows another transition exhibiting a charge-transfer character from the H-1 orbital localized only on carbazole to LUMO (in pink). But the oscillation strength of this transition is too weak ($f=0.2$) and, above all, its position is too close ($\lambda_{th}=323$ nm) to the others for the corresponding band to be visible on the spectrum. Similarly, **[8]CPP-C=O** also features a main band at 336 nm due to similar transitions than **[8]CPP** and **[8]CPP-N-Bu**. Unlike the other two

nano hoops, **[8]CPP-C=O** exhibits a red-shifted shoulder at around 475 nm due to a partially allowed HOMO→LUMO transition ($f=0.04$). In addition, its shoulder at around 400 nm is larger than those of **[8]CPP-N-Bu** and **[8]CPP** in agreement with the higher oscillator strength of the corresponding HOMO→L+1 transition ($f=0.16$ for **[8]CPP-C=O** vs 0.00 and 0.03 for **[8]CPP** and **[8]CPP-N-Bu**, respectively).

The emission spectra of the three nano hoops are broad and unstructured, as often observed for **[8]CPP**-based nano hoops.^{1a, 11b, 17-18} Remarkably, the emission spectra of **[8]CPP-N-Bu** and **[8]CPP** are almost superimposable, with a maximum at 529 nm. In addition, they have similar fluorescence quantum yields QY of around 0.2 and singlet lifetimes τ_s of around 10 ns, resulting in similar radiative and non-radiative k_r and k_{nr} rates. Thus, both nano hoops display similar deactivation pathways for photoexcited states and it can be concluded that incorporating a nitrogen bridge has no impact on the optical properties (both absorption and emission) of a **[8]CPP**. Optical properties are then determined more by the CPP core than by the ability of the nitrogen bridge to donate electrons. **[8]CPP-4N-Bu** displays a similar QY (0.20) but lower τ_s (6.2 ns) and maximal emission wavelength (483 nm),^{11b} showing that the nitrogen bridges impact the emissive state if they are numerous. A different behavior is observed for **[8]CPP-C=O**. Indeed, its emission spectrum in cyclohexane is red-shifted compared to those of **[8]CPP-N-Bu** and **[8]CPP**, with a maximum at 582 nm. In addition, **[8]CPP-C=O** has a low QY of 0.02 and a small τ_s of 5.6 ns. Thus, the k_r is lowered by one order of magnitude and this feature is assigned to the intramolecular charge transfer (ICT) occurring in **[8]CPP-C=O**. Solvatochromic experiments were finally carried out to confirm this feature and assess the role played by the bridge in the ICT (Fig.S13-15). Firstly, the absorption maxima of the three nano hoops are almost unaffected by solvent polarity (shifts of 5, 2, 8 nm for **[8]CPP-N-Bu**, **[8]CPP-C=O** and **[8]CPP** respectively). As often observed, emission spectra are more influenced by solvent polarity. Thus, for **[8]CPP-C=O**, there is a bathochromic shift of 68 nm from the less polar cyclohexane to the more polar acetonitrile, whereas the emission of **[8]CPP** and **[8]CPP-N-Bu** are both only slightly sensitive to solvent polarity (shift of 14-15 nm). **[8]CPP-C=O** displays a donor-acceptor character consistent with its LUMO localized on the fluorenone moiety. A dipole moment in the excited state μ^* of 14 D was therefore evaluated for **[8]CPP-C=O** using the Lippert-Mataga formalism (Fig.S16), indicating a significant ICT. This value is close to the highest value of 15 D reported for a CPP incorporating an acenaphthylene.^{3b} Therefore, incorporating a carbonyl bridge in **[8]CPP** induces a significant ICT in **[8]CPP-C=O**, while the nitrogen bridge leaves the solvatochromic properties of **[8]CPP** unchanged.

In thin film, the absorption spectra of **[8]CPP-N-Bu**, **[8]CPP-C=O** and **[8]CPP** show a maximum at 366, 355 and 346 nm respectively (Fig.S18). Thus, the evolution of the position of the main absorption band as a function of the presence and nature of the bridge remains unchanged from the study in cyclohexane. In emission, **[8]CPP-N-Bu** and **[8]CPP** show broad, unstructured spectra with maxima at 550 and 570 nm (QY_f=0.11 and 0.08), while **[8]CPP-C=O** is non-emissive. Thus, bridging two

phenylenes in [8]CCP with a carbonyl group induces fluorescence annihilation in the solid state, while a nitrogen atom maintains the quantum yield. From solution to solid state, the quantum yields of [8]CCP and [8]CPP-N-Bu are divided by about 3 and 2 respectively, showing that the classical aggregation induced quenching, very often observed in linear materials, is absent. Thus, the three nano hoops appear to exhibit weak intermolecular interactions, which can be tuned by the bridge. This is important for optical applications.

In summary, we have reported the synthesis, and the structural, electrochemical and photophysical properties and molecular modelling of two nano hoops consisting of a [8]CPP possessing a bridge between two phenylenes: [8]CPP-N-Bu (nitrogen atom as bridge) and [8]CPP-C=O (carbonyl group as bridge). By comparison with unbridged parent analogue [8]CPP, we have demonstrated that the presence of the bridge has a different impact on structural, electrochemical and photophysical properties, depending on its nature. For example, incorporating a nitrogen bridge in [8]CPP to give [8]CPP-N-Bu has no impact on the mean torsion angle θ , nor on the HOMO energy, nor on the photophysical properties in cyclohexane (absorption and emission spectra, QY, τ_s), whereas a carbonyl bridge in [8]CPP-C=O strongly modifies all these parameters (lower θ and HOMO, new low-energy band in the absorption spectrum, red-shifted fluorescence, lower QY and τ_s). Defining the evolution of the electronic properties of nano hoops as a function of their design is a crucial step in understanding these new π -conjugated systems. As nano hoops now enter the era of applications,^{2, 11, 19} these results can be used to design organic materials with specific properties.

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Conflicts of interest

There are no conflicts to declare.

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