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Electronic and Charge Transport Properties in Bridged versus Unbridged Nanohoos: Role of the Nanohoop Size

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Abstract: In the field of π -conjugated nanohoos, the size of the macrocycle has a strong impact on its structural characteristics, which in turn affect its electronic properties. In this work, we report the first experimental investigations linking the size of a nanohoop to its charge transport properties, a key property in organic electronics. We describe the synthesis and study of the first example of a cyclo-carbazole possessing five constituting building units, namely [5]-cyclo-*N*-butyl-2,7-carbazole, [5]C-Bu-Cbz. By comparison with a shorter analogue, [4]-cyclo-*N*-butyl-2,7-carbazole, [4]C-Bu-Cbz, we detail the photophysical, electrochemical, morphological and charge transport properties, highlighting the

key role played by the hoop size. In particular, we show that the saturated field effect mobility of [5]C-Bu-Cbz is four times higher than that of its smaller analogue [4]C-Bu-Cbz (4.22×10^{-5} vs $1.04 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). However, the study of the other organic field-effect transistor characteristics (threshold voltage V_{TH} and subthreshold slope SS) suggest that a small nanohoop is beneficial for good organization of the molecules in thin films, whereas a large one increases the density of structural defects, and hence of traps for the charge carriers. The present findings are of interest for the further development of nanohoos in electronics.

Introduction

π -Conjugated materials are at the heart of organic electronic devices such as organic light-emitting diodes (OLED), organic field-effect transistors (OFET) and organic photovoltaics (OPV).^[1,2] The fantastic development of this technology undoubtedly arises from the development of precise molecular design tactics, which have allowed a perfect fit between a molecular/material property and a specific characteristic of an electronic device. The development of new molecular fragments and of new families of organic semiconductors is undoubtedly the strategy, which has allowed for the most important breakthroughs. The development of fullerenes is surely one of the nicest example to illustrate this feature.^[3–6] In

2008, a new generation of π -conjugated systems, namely molecular nanohoos, has appeared in the literature.^[7] Nanohoos belong to the family of curved π -systems, and have attracted a considerable attention worldwide due to their uncommon electronic properties arising from the radially distributed π -conjugation.^[8–13] However, their incorporations in organic electronic devices remain poorly developed,^[14–16] surely due to the difficulty to reach decent amount of materials for device fabrication. However, in recent years, the first experimental data on the charge transport of nanohoos have been reported^[16–19] and have revealed, coupled to theoretical insights,^[18,20–22] the potential of nanohoos. Used as host in red emitting phosphorescent OLED, nanohoos have also recently shown very promising results, being more efficient than their linear counterparts (external quantum efficiency of 17 vs 11 %).^[23]

Charge transport in organic semi-conductors is a central notion in organic electronics,^[24] which drives the performance of the three principal devices, OLED, OFET and OPV. Investigating the charge transport of nanohoos is therefore an important step in their development.

The first measurement of nanohoop mobility was reported in 2017 by Yamago and co-workers.^[16] A low electron mobility value of $5 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was measured in an electron-only device using the space-charge-limited current (SCLC) technique. In 2021, the first detailed structure-properties-device performances relationship study of functional materials based on nanohoos has shown how the nanohoop supramolecular arrangement can affect the corresponding OFET characteristics.^[18] FE mobility values of approximately $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ were measured with interesting OFET character-

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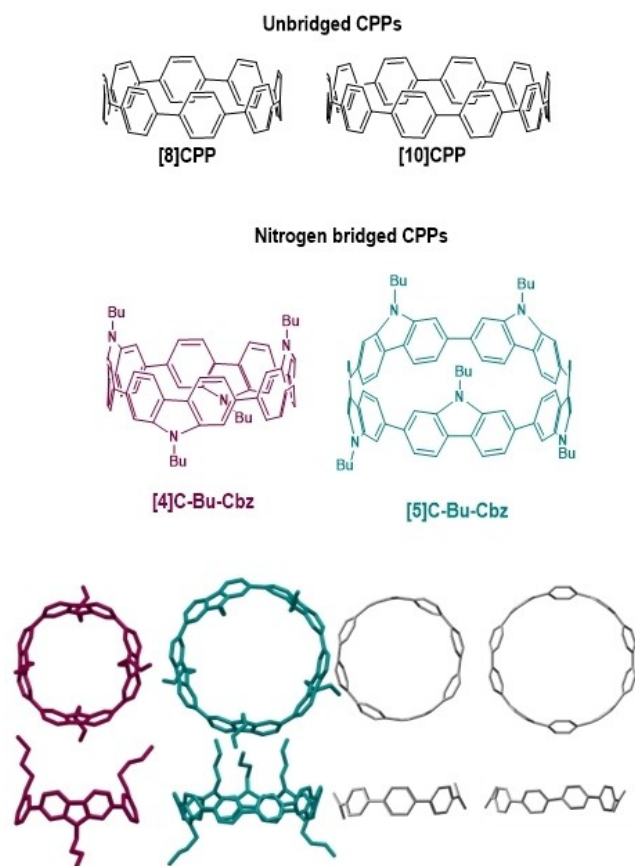
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istics (low V_{Th} , low SS, high stability under electrical stress). The recent molecular design works performed by Du and co-workers have allowed to reach an electron mobility (SCLC) of $2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is the highest value reported so far in the field.^[19] These first data have shown that functional nano-hoops can be used as semi-conductors. However, defining the link between molecular structure and charge transport properties is one of the next barriers to lift in the field. In nano-hoop chemistry, the electronic properties are driven by both the nature of the building units and by the hoop size; in the last five years, an increasing number of reports has been published on the subject.^[25–32] However, as far as we know, there is no report on the experimental assessment of the influence on charge transport of the nano-hoop size. In 2019, it has been shown that theoretical mobility of CPPs correlates with its hoop size and was mainly controlled by the reorganization energy.^[33] This theoretical study has undoubtedly inspired the present work. Through two examples of size expansion (Scheme 1), we report herein the first experimental evidence on the link between the size and the charge transport in nano-hoops.

The two couples studied in the purpose of this work are: [10]-cyclo-*para*-phenylene [10]CPP versus [8]-cyclo-*para*-phenylene [8]CPP and [5]-cyclo-*N*-butyl-2,7-carbazole [5]C-Bu-Cbz versus [4]-cyclo-*N*-butyl-2,7-carbazole [4]C-Bu-Cbz.



Scheme 1. Cyclo-carbazoles with four ([4]C-Bu-Cbz) or five ([5]C-Bu-Cbz) carbazole units and their corresponding cyclo-*para*-phenylene analogues ([8]CPP and [10]CPP). Molecular structures obtained from DFT (B3LYP/6-31 g(d,p)).

They possess either 10 ([10]CPP and [5]C-Bu-Cbz) or 8 ([8]CPP and [4]C-Bu-Cbz) phenyl units, bridged, two by two, by a nitrogen atom in the case of cyclo-carbazoles and unbridged in the case of CPPs. Bridges effects are an important concept in organic electronics, widely described for linear π -conjugated systems.^[34–38] For nano-hoops, the impact of the bridges on the electronic properties has also started to be investigated.^[18,39] Note that this work also reports the first example of a [5]-cyclo-carbazole nano-hoop possessing five units, [5]C-Bu-Cbz. The whole study includes electrochemical, photophysical (in solution and in thin film), morphological and charge transport investigations and is coupled to theoretical calculations. We notably show that the saturated FE mobility of [5]C-Bu-Cbz is four times higher than that of its smaller analogue [4]C-Bu-Cbz (4.22×10^{-5} vs $1.04 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). However, study of the other OFET parameters (threshold voltage V_{Th} , subthreshold slope SS) suggests that a small nano-hoop is beneficial for a good organization of the molecules in thin films whereas a large one increases the density of structural defects, and hence of traps for the charge carriers. In addition, we show for both nano-hoop families that when the size decreases, the charge carrier mobility (SCLC) increases ($2.78 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for [4]C-Bu-Cbz vs $7.75 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for [5]C-Bu-Cbz and $1.21 \times 10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for [8]CPP vs $1.1 \times 10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for [10]CPP).

Results and Discussion

Both [4]C-Bu-Cbz and [5]C-Bu-Cbz were synthesized by following the Pt approach initially developed by Yamago and co-workers in 2010^[40] (Figure 1, top). First, the nitrogen atom of 2,7-dibromocarbazole was alkylated with a butyl chain and then functionalized with pinacolato boron units to give **1** (Chart S1 in the Supporting Information). The cyclization step follows an optimized procedure previously reported.^[17] The intermediates **2** and **3**, based on four and five square-shaped platinum complexes, were formed (not isolated) by stirring the bispinacolato diboron carbazole **1** with Pt(COD)Cl₂ and cesium fluoride at 70 °C in 1,2-dichloroethane (DCE) for 24 h. Then, the carefully dried crude mixture containing both **2** and **3** was treated with triphenylphosphine in *ortho*-dichlorobenzene, 1 h at room temperature (RT) and 48 h at 180 °C to provide [4]C-Bu-Cbz and [5]C-Bu-Cbz with 58 and 2% yield, respectively. Despite [5]C-Bu-Cbz has been obtained with a low yield, the formation of a nano-hoop with five constituting units appears very interesting to increase the molecular diversity of nano-hoops. Indeed, this synthetic approach allows the formation of two nano-hoop sizes, which is undoubtedly an interesting synthetic feature in the field, especially if an electronic application is targeted.^[41–44]

In ¹H NMR, when increasing the size of the nano-hoop (from [4]C-Bu-Cbz to [5]C-Bu-Cbz) and hence its number of building units, all signals are deshielded, especially H_c (Figure 1 bottom-left). This is assigned to the ring current^[45,46] and the magnetic shielding effect, which is increased when the size of the nano-hoop decreases.^[9,47] The most shifted signal is observed for H_c, which is detected at 6.98 ppm for [5]C-Bu-Cbz and at

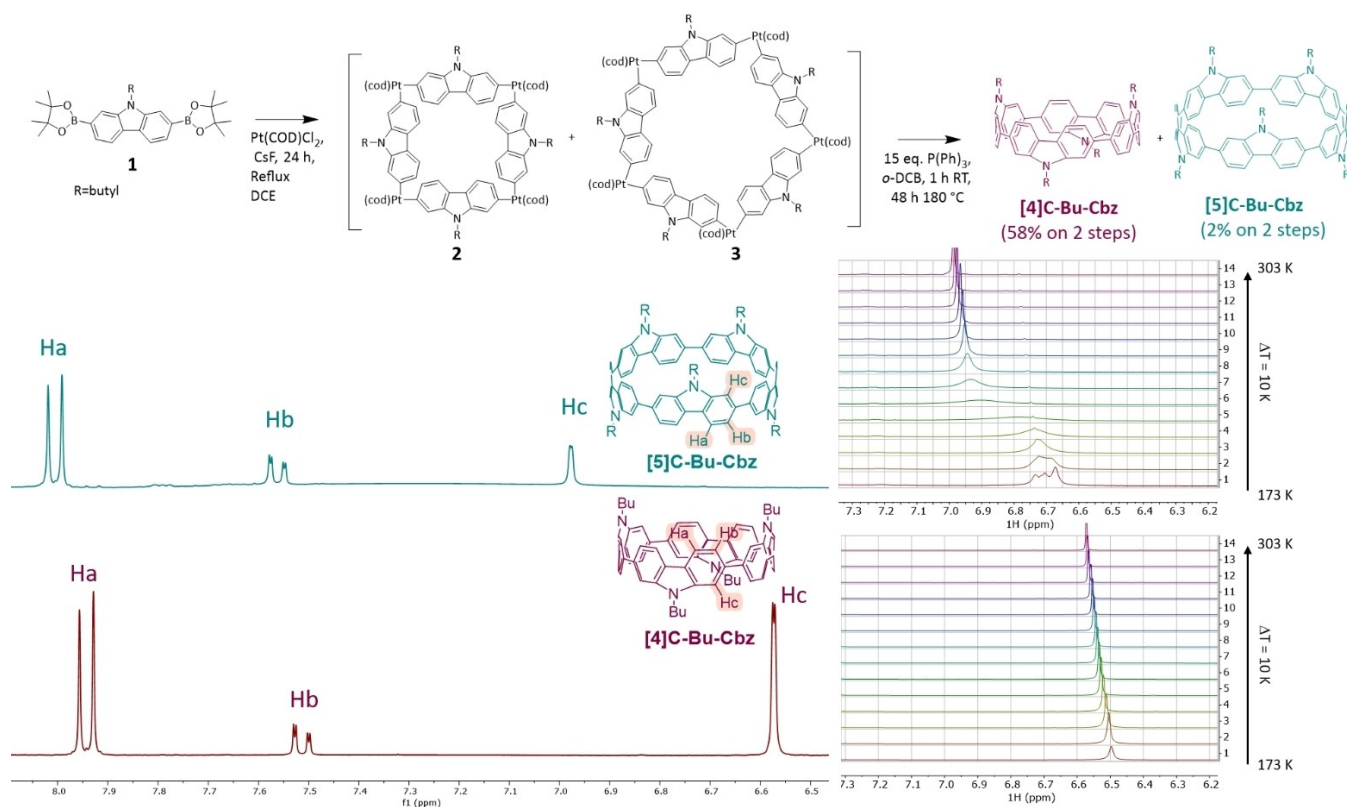


Figure 1. Top: Synthesis of [4]C-Bu-Cbz and [5]C-Bu-Cbz. Bottom: left: parts of the ^1H NMR spectra of [5]C-Bu-Cbz and [4]C-Bu-Cbz in CD_2Cl_2 (full spectra in Figures S1 and S2); right: zoom in on the Hc signal of the ^1H NMR spectrum as a function of the temperature of [5]C-Bu-Cbz (upper) and [4]C-Bu-Cbz (lower) in CD_2Cl_2 (full spectra in Figures S8–S11).

6.57 ppm for [4]C-Bu-Cbz. The main difference between [5]C-Bu-Cbz and [4]C-Bu-Cbz is their dynamics in solution. It has been previously shown in the case of nitrogen or carbon bridged cycloparaphenylenes with four building units (such as [4]C-Bu-Cbz) that a single conformer with an $\alpha\beta\alpha\beta$ orientation (i.e., with the bridges alternatively pointing up and down) is obtained.^[17,48] In the case of [5]C-Bu-Cbz, variable temperature NMR studies indicate that a time-averaged dynamic structure is detected at room temperature, Figure 1 bottom-right. Indeed, if increasing the temperature up to 373 K does not modify the ^1H NMR spectrum (Figure S10), decreasing the temperature yields a very different behaviour. Hc illustrates well this behaviour. Indeed, from 303 to 173 K, the Hc signals become broader before splitting, after coalescence, in several signals at 173 K, which correspond to the different conformers of [5]C-Bu-Cbz (Figure 1, bottom right, and Figure S8). The same experiment performed with [4]C-Bu-Cbz does not show any modification, thus indicating that a single conformer exists at room temperature (Figure 1, bottom right, and Figure S11). This shows the importance of the number of constituting units, that is, the size of the nano hoop, and the resulting strain on the dynamics of nano hoops in solution.^[49] This is confirmed by the theoretical estimation of the strain energy, which is higher for [4]C-Bu-Cbz than for [5]C-Bu-Cbz (72 and 56 kcal mol⁻¹, respectively), see the Supporting Information for details of the calculation.

Electrochemical analyses of [5]C-Bu-Cbz were performed by cyclic voltammetry (CV) in CH_2Cl_2 for the oxidation and in DMF for the reduction (Figures S12–S15) and compared with [10]CPP and with [4]C-Bu-Cbz in order to respectively shed light on the impact of the bridging and of the nano hoop size. In oxidation, [5]C-Bu-Cbz displays an electrochemical behaviour reflecting an electrodeposition process occurring at the first oxidation wave, around 1.14 V vs SCE. The deposit growth is evidenced by the reduction detected at the reverse scan and by the regular increase of its redox wave when recording recurrent cycles (for a detailed study of the electrodeposition processes, see Figure S13). The deposit is oxidized at a lower anodic value than [5]C-Bu-Cbz. From the onset of the first wave, the HOMO energy level is evaluated at -5.22 eV for [5]C-Bu-Cbz, slightly below that of [4]C-Bu-Cbz (HOMO: -5.18 eV). Similarly, the LUMO energy of [5]C-Bu-Cbz, evaluated at -2.51 eV, is deeper than that of [4]C-Bu-Cbz (-2.40 eV). Thus, as the size of the cycloparaphenylene increases from 4 to 5 units, there is a decrease of both HOMO and LUMO energies. Because the LUMO decrease (0.11 eV) is larger than the HOMO decrease (0.04 eV), there is a gap contraction of 0.07 eV when the number of carbazole units increases (from 2.78 eV in [4]C-Bu-Cbz to 2.71 eV in [5]C-Bu-Cbz). This feature is in accordance with the trend obtained by theoretical calculations ($-5.18/-1.76$ eV for [4]C-Bu-Cbz vs $-5.19/-1.83$ eV for [5]C-Bu-Cbz).

This HOMO/LUMO evolution with size is significantly less intense than that previously reported for cyclofluorenes (gap: 2.9/2.5 eV for cyclofluorenes with four and five units, respectively^[25]), showing the key role played by the building unit on the molecular orbital energies in nanohoop chemistry. The influence of the bridge is also an interesting feature to determine. Bridging leads to an increase of the HOMO energy of 0.28 from -5.50 eV for [10]CPP to -5.22 eV for [5]C-Bu-Cbz but keeps the LUMO energies unaffected (-2.51 eV for both [10]CPP and [5]C-Bu-Cbz) giving a gap contraction of 0.29 eV. In the series with 8 phenyl units, [8]CPP and [4]C-Bu-Cbz, the opposite effect is observed: the LUMO is more affected by the bridge (-2.60 eV for [8]CPP vs -2.40 eV for [4]C-Bu-Cbz) than the HOMO (-5.28 eV for [8]CPP vs -5.18 eV for [4]C-Bu-Cbz) leading to decrease of the HOMO–LUMO gap (2.68 eV for [8]CPP vs 2.78 eV for [4]C-Bu-Cbz). At a first glance, it can be hypothesized that the presence of an electron rich atom such as nitrogen in cyclocarbazoles logically increases the HOMO energy level compared to their CPP analogues. However, in nanohoops, the distortion of the hoop induced by steric effects can also have an important impact on these energy levels.^[48] The presence of one nitrogen bridge thus induces two effects: a steric effect (rigidification of two phenylene units) and an electronic effect (arising from the electron donating behaviour of the nitrogen) shifting both the HOMO/LUMO energy levels. In order to discriminate the electronic versus geometric impact of the bridges, we computed the HOMO and LUMO levels of [8]CPP and [10]CPP both in their optimized geometry and in the optimized geometry of [4]C-Bu-Cbz and [5]C-Bu-Cbz, in which the bridges have been removed and replaced by hydrogen atoms. For both sizes, we observed the same trend: the HOMO is more affected by the geometry (for [10]CPP, -5.45 and -5.23 eV in the optimized geometry and in the geometry of its bridged analogue respectively and for [8]CPP, -5.37 and -5.23 eV) than the LUMO (for [10]CPP, -2.20 and -2.26 eV in the optimized geometry and in the geometry of its bridged analogue respectively and for [8]CPP, -2.27 eV for both geometries). Thus, the increase of the HOMO upon bridging is predominantly due to the modification of the geometry of the nanohoop and the increase of the LUMO is due to the electron-donating nature of the nitrogen atom.

The optical properties of both [4]C-Bu-Cbz and [5]C-Bu-Cbz (Figure 2) and their corresponding CPP homologues ([8]CPP and [10]CPP) were characterized by UV/visible absorption spectroscopy as well as stationary and time-resolved emission spectroscopy in cyclohexane (Figures S17–S28). Both [4]C-Bu-Cbz and [5]C-Bu-Cbz display similar absorption spectra with the main bands and shoulders at 257/292/337/410 nm for [4]C-Bu-Cbz and at 265/292/342/410 nm for [5]C-Bu-Cbz, (Figure 2). One can note that the shoulder at 410 nm in [5]C-Bu-Cbz is more intense than that in [4]C-Bu-Cbz. TD-DFT analyses indicate that these shoulders and the lowest energy bands of both nanohoops are due to similar transitions involving similar orbitals (Figure 3). The shoulder above 400 nm is classically assigned, in the case of [4]C-Bu-Cbz, to a symmetry forbidden HOMO→LUMO transition (oscillator strength equal to 0.000). However, in [5]C-Bu-Cbz, due to the odd number of carbazole

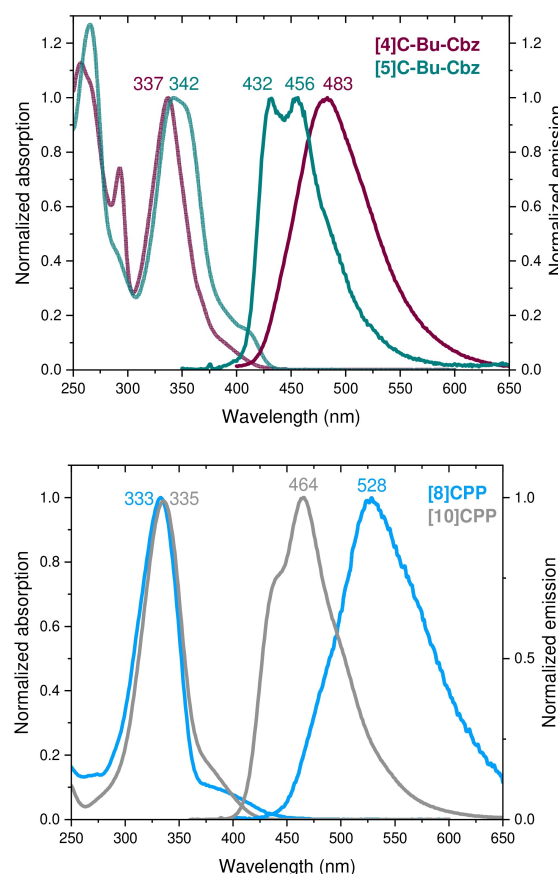


Figure 2. Absorption/emission spectra in cyclohexane of [4]C-Bu-Cbz and [5]C-Bu-Cbz (top: $\lambda_{\text{ex}} = 337$ and 340 nm for [4]C-Bu-Cbz and [5]C-Bu-Cbz, respectively) and [8]CPP and [10]CPP (bottom: $\lambda_{\text{ex}} = 350$ nm).

units and the resulting symmetry breaking, the oscillator strength is weak but not null ($f = 0.08$). This is the reason why the shoulder detected at around 400 nm is more intense for [5]C-Bu-Cbz compared to [4]C-Bu-Cbz.

One can also note that the main band of [5]C-Bu-Cbz centred at 342 nm is broader than that of [4]C-Bu-Cbz centred at 337 nm. This is also due to the lower symmetry of the nanohoop based on an odd number of carbazole units. While the orbitals of [4]C-Bu-Cbz are degenerate and optical transitions simulated at the same energy, the lower symmetry of [5]C-Bu-Cbz induces a larger number of transitions at different energies. This size dependence broadening is not observed for CPP analogues (Figures S27–S28), which are both based on an even number of phenylene units and are thus highly symmetrical. This shows the singularity of the optical properties of cyclocarbazoles versus those of CPP parents.

The emission spectrum of [5]C-Bu-Cbz in cyclohexane shows two maxima at 432 and 456 nm. This spectrum is structured in comparison with its smaller analogue [4]C-Bu-Cbz (only one band at 483 nm) and its unbridged analogue [10]CPP (which displays nevertheless a shoulder around 440 nm in addition to the band at 464 nm), Figure 2. This property is different from all cyclocarbazoles and CPPs (until 10 units) reported to date but similar to what is observed for cyclo-

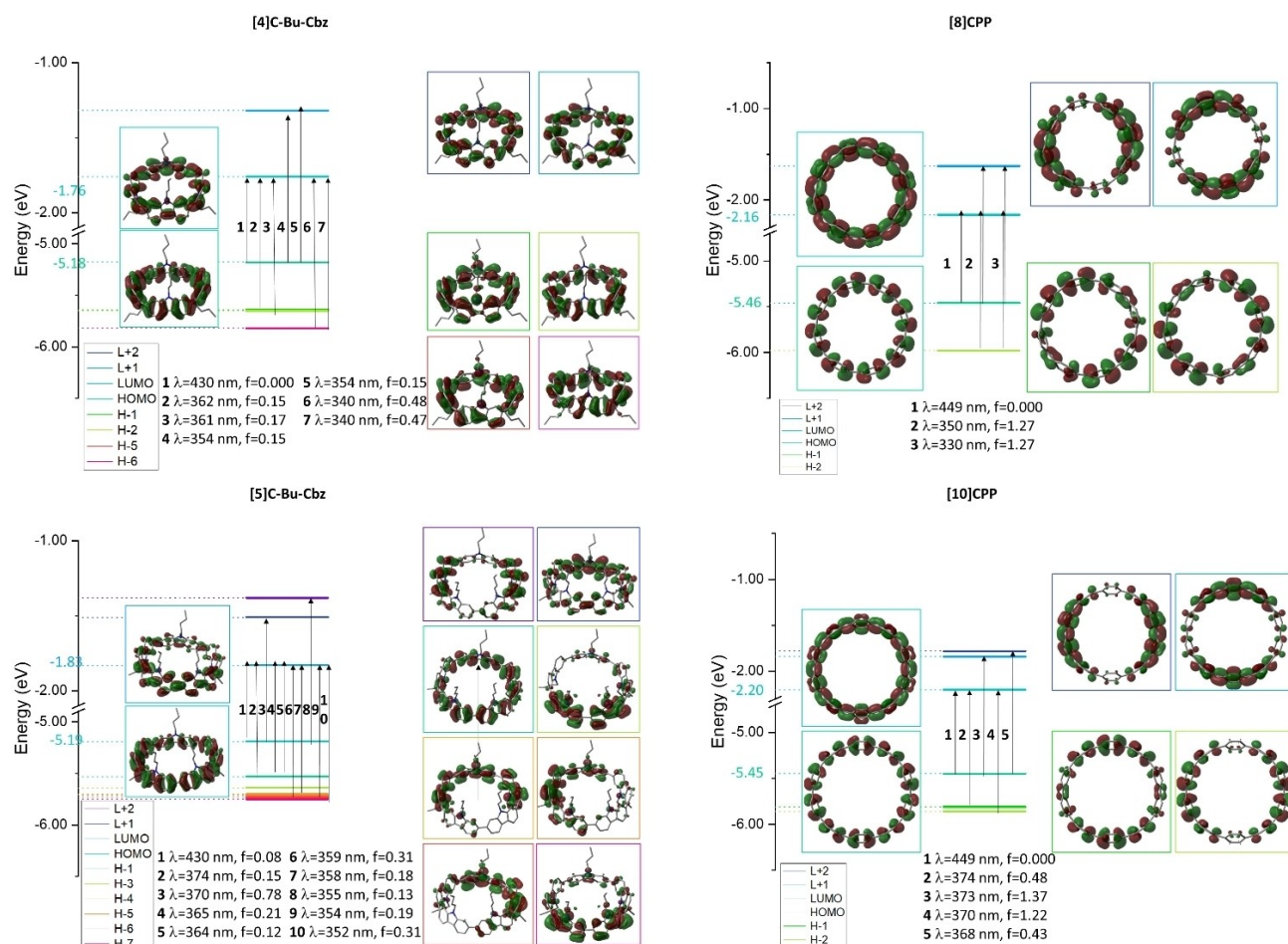


Figure 3. Representation of the energy levels and the main molecular orbitals involved in the electronic transitions of [4]C-Bu-Cbz and [5]C-Bu-Cbz (left) and [8]CPP and [10]CPP (right) obtained from TD-DFT, B3LYP/6-311 + G(d,p), shown with an isovalue of 0.02 [ebohr^{-3}]^{1/2}. For clarity, only the major contribution of each transition is shown (see the Supporting Information for details).

fluorenes with five units, analogues of [5]C-Bu-Cbz displaying also 10 phenylenes and five bridges (Figure S26).^[25] Thus, the structured emission spectrum could be due to the planarization of a part of [5]C-Bu-Cbz in its excited state, facilitated by its larger size (compared to [4]C-Bu-Cbz) and the bridges (compared to [10]CPP). Furthermore, the fluorescence maximum of [5]C-Bu-Cbz is blue-shifted by 51 nm compared to [4]C-Bu-Cbz similarly to the trend observed for [10]CPP and [8]CPP (blue shift of 64 nm when the size increases). The fluorescence quantum yields of [5]C-Bu-Cbz and [4]C-Bu-Cbz are 0.56 and 0.20, respectively, close to those of [10]CPP and [8]CPP, 0.59 and 0.25, respectively. Thus, the bridges have an influence on the shape and width of the emission spectra but not on the fluorescence efficiency. This is an interesting consideration, which should be considered for the further design of high-efficiency emitters based on nanostructures. In addition, [5]C-Bu-Cbz displays a lifetime which is half the one of [4]C-Bu-Cbz (respectively 3.1 and 6.2 ns), similarly to what is observed for the CPP analogues (3.9 and 10.6 ns respectively for [10]CPP and [8]CPP). Thus, as for quantum yield, the lifetime of these nanostructures appears to be more affected by their size

than by the presence of the bridges. The high quantum yields of the large nanostructures (ca. 0.6 for [5]C-Bu-Cbz and [10]CPP) is linked to the fact that their radiative constant k_r (181 and $151 \mu\text{s}^{-1}$, respectively) are superior to their non-radiative constant k_{nr} (respectively 142 and $105 \mu\text{s}^{-1}$) whereas the small nanostructures ([4]C-Bu-Cbz and [8]CPP) display a k_r (respectively 32.2 and $23.6 \mu\text{s}^{-1}$) much lower than their k_{nr} (respectively 129 and $70.8 \mu\text{s}^{-1}$). Therefore, as the strain energy increases, the quantum yield decreases. Note also that the k_{nr} of the bridged nanostructures are higher than those of the CPPs. This could be assigned to the dynamic of the alkyl chains, increasing non-radiative pathways.

In thin film, both absorption and emission spectra of [4]C-Bu-Cbz and [5]C-Bu-Cbz are similar to those in solution except that they are slightly red-shifted, indicating the absence of strong aggregation in the solid state (Figures S18 and S22). It should be noted that the quantum yields of [4]C-Bu-Cbz and [5]C-Bu-Cbz are almost equivalent in thin film (0.13 and 0.14%, respectively) whereas in solution the largest nanostructure displays the highest quantum yield (0.2 for [4]C-Bu-Cbz and 0.56 for

	[4]C-Bu-Cbz	[5]C-Bu-Cbz	[8]CPP	[10]CPP
Photophysics				
$\lambda_{\text{ABS}}^{[\text{a}]}$ [nm] sol	337	342	333	335
$\lambda_{\text{ABS}}^{[\text{a}]}$ [nm] film	347	359	346	351
$\lambda_{\text{EM}}^{[\text{a}]}$ [nm] sol	483	432, 456	528	464
$\lambda_{\text{EM}}^{[\text{a}]}$ [nm] film	495, 518	458	570	475
$\phi^{[\text{a}]}$ sol	0.20	0.56	0.25	0.59
$\phi^{[\text{a}]}$ film	0.13	0.14	0.08	0.34
$\tau_f^{[\text{a}]}$ [ns]	6.2	3.1	10.6	3.9
k_r [μs^{-1}]	32.2	181	23.6	151
k_{nr} [μs^{-1}]	129	142	70.8	105
Electrochemistry				
HOMO ^[b] [eV]	-5.18	-5.22	-5.28	-5.50
LUMO ^[b] [eV]	-2.40	-2.51	-2.60	-2.51
ΔE_{EL} [eV]	2.78	2.71	2.68	2.99
Theoretical calculations				
HOMO ^[c] [eV]	-5.18	-5.19	-5.37	-5.45
LUMO ^[c] [eV]	-1.76	-1.83	-2.27	-2.20
ΔE_{TH} [eV]	3.42	3.36	3.10	3.25
Charge transport				
μ_{FElin} [$\times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$]	1.03	0.93	d	d
μ_{FEsat} [$\times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$]	1.04	4.22	d	d
V_{TH} [V]	-12.8	-28.8	d	d
SS [V/Dec]	0.89	4.4	d	d
μ_{SCLC} [$\times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$] ^[e]	2.78	0.78	0.00121	0.00011

[a] in cyclohexane, [b] from CVs recorded in CH_2Cl_2 for oxidation and in DMF for reduction, [c] from B3LYP/6-311+G(d,p), [d] non measurable, [e] from SCLC.

[5]C-Bu-Cbz). Thus, the size of the cyclocarbazole does not impact its emission efficiency in the solid state.

Finally, OFET electrical characterizations and I–V measurements in two-terminal devices were performed to investigate the charge transport properties of the different nano hoops (Table 1, Figure 5, below). The mobilities of [10]CPP and [5]C-Bu-Cbz are measured for the first time, whereas that of [8]CPP and [4]C-Bu-Cbz have been previously reported.^[18] First, the nano hoops have been incorporated as active layer in OFETs possessing a bottom-gate bottom-contact (BG-BC) architecture (Figure S29^[50,51]).

The first striking result is obtained with [10]CPP as no field effect mobility (μ_{FE}) is measured for this molecule. The same behaviour was observed for [8]CPP.^[18] Theoretical calculations yield electronic couplings for holes between adjacent molecules (Figure 4) in the bulk crystal structure of [10]CPP (2 and 9 meV) slightly lower than in [8]CPP (10 and 18 meV); in contrast, the reorganization energy of [10]CPP is significantly lower than in [8]CPP (251 vs 313 meV). The fact that the transfer integrals are much smaller than the reorganization energies indicate that charge transport operates in the hopping regime. Based on the Marcus expression of the hopping rate, see Equation (1) below, this further suggests that [10]CPP and [8]CPP should exhibit comparable hole mobilities. Taking the largest value of the transfer integrals and the corresponding reorganization energies, the ratio of $k_{\text{ET}}^{-}[\text{8]CPP}/k_{\text{ET}}^{-}[\text{10]CPP}$ obtained from Equation (1) is indeed only on the order of 1.9.

$$k_{\text{ET}} = \frac{2\pi |J_{\text{AB}}|^2}{\hbar \sqrt{4\pi\lambda k_{\text{B}}T}} e^{-\frac{(\Delta G^0 + \lambda)^2}{4\lambda k_{\text{B}}T}} \quad (1)$$

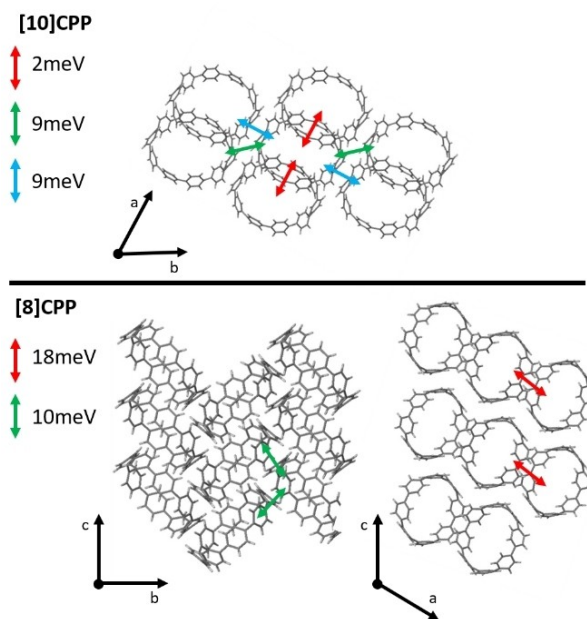


Figure 4. Computed electronic couplings for holes in the experimental crystal structure of [10]CPP (Top) and [8]CPP (bottom).

where k_{ET} is the hopping probability, J the electronic coupling, ΔG^0 the site energy difference between the two molecules (due here to the application of an external electric field) and λ the reorganization energy.

Cyclocarbazoles [4]C-Bu-Cbz and [5]C-Bu-Cbz display FE mobilities (Figure 5). As their HOMOs are higher than those of their CPP analogues, charge injection is favoured. The first

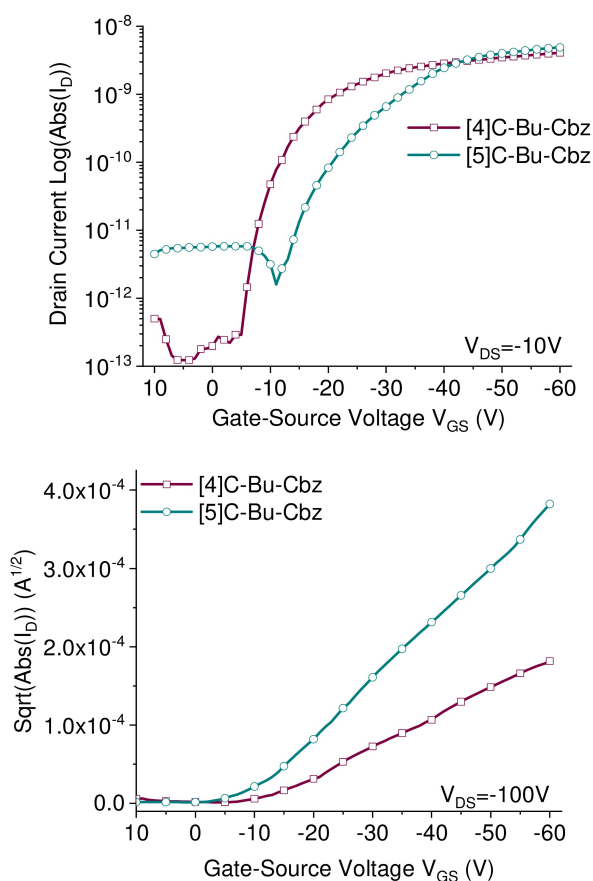


Figure 5. Transfer characteristics in linear (top) and saturated (bottom) regimes of [4]C-Bu-Cbz and [5]C-Bu-Cbz.

observation concerns the mobility in the saturated regime μ_{FEsat} ($V_{DS} = 100$ V). Remarkably, [5]C-Bu-Cbz displays an μ_{FEsat} four times larger than that of its smaller analogue [4]C-Bu-Cbz (4.22×10^{-5} vs $1.04 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively). Thus, when the size of the hoop increases, μ_{FEsat} increases as well. As no μ_{FE} can be measured for both [8]CPP and [10]CPP, this finding also shows the importance of the nature of the building unit in the charge injection and/or transport properties. However, the saturated μ_{FEsat} are measured at high electric field, $V_{DS} = 100$ V; in these conditions, traps into the semiconductor are filled and do not impact the carrier mobility. To compare the effect of the size, the capability of the nano-hoop to accumulate charges at the interface with the insulator should also be considered, as reflected by the threshold voltage (V_{TH}) and subthreshold slope (SS). V_{TH} is the gate-source voltage needed for the channel to be populated while SS is the voltage required to increase the current at the semiconductor/insulator interface by one order of magnitude. SS is particularly important in that purpose as it depends on both the defect density at the insulator/semiconductor interface and on the chemical structure of the semiconductor itself. Indeed, if the density of traps is high, most of the carriers initially injected do not participate in the electrical conduction within the channel. SS reflects hence the organization of the layer. The lowest and thus the best SS is

measured for [4]C-Bu-Cbz, 0.89 V/dec, whereas [5]C-Bu-Cbz displays a SS of 4.4 V/dec. The extraction of V_{TH} also confirms this trend since the lowest V_{TH} is estimated for the small nano-hoop [4]C-Bu-Cbz ($V_{TH} = -12.8$ V) compared to the large one [5]C-Bu-Cbz ($V_{TH} = -28.8$ V). These data suggest that a small nano-hoop is beneficial for a good organization of the molecules in thin films whereas a large one increases the density of structural defects, and hence of traps for the charge carriers, increasing in turn the V_{TH} .

To confirm this feature, AFM studies have been performed on the OFET layers (Figure 6). The film surface of both cyclo-carbazoles [4]C-Bu-Cbz and [5]C-Bu-Cbz, deposited on SU-8 insulating layers, remarkably presents a regular and smooth morphology with low surface roughness (root mean roughness R_q respectively of 0.42 and 0.75 nm). One can nevertheless note that the R_q of [4]C-Bu-Cbz is lower than that of [5]C-Bu-Cbz in accordance with the SS and V_{TH} values presented above. These data are also in accordance with the differences observed between linear and saturated FE mobilities. For [4]C-Bu-Cbz, the linear FE mobility ($\mu_{FElin} = 1.03 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) is almost identical to the saturated FE mobility ($\mu_{FEsat} = 1.04 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$); this indicates that the linear FE mobility is almost unaffected by traps. For [5]C-Bu-Cbz, we note a significant increase from $0.933 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for μ_{FElin} to $4.22 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for μ_{FEsat} , highlighting a higher trap density in [5]C-Bu-Cbz vs [4]C-Bu-Cbz. These data reflect the different degrees of molecular arrangements of the two cyclo-carbazoles.

In order to further confirm this analysis, electrical stress, using the gate bias stress protocol, has been performed. A stretched exponential model has been applied to evaluate the structural trap effect on the electrical stability of OFETs (Figure 7).

From these measurements, three parameters have been extracted. The first, ΔV_{THmax} is the maximum threshold voltage shift under unlimited stress, the second, β , is linked to the average deepness of level energy of traps and the third, t_0 , corresponds to the time for a carrier to be trapped. Figure 7 shows clearly the difference of electrical stability between OFETs made with either [4]C-Bu-Cbz or [5]C-Bu-Cbz. Interestingly, the carriers are quickly trapped in the case of [5]C-Bu-Cbz ($t_0 = 1.4 \times 10^3$ s) in comparison with [4]C-Bu-Cbz ($t_0 = 3.9 \times 10^4$ s). The maximum threshold voltage shift is also higher for [5]C-Bu-Cbz ($\Delta V_{THmax} = 30.3$ V) than for [4]C-Bu-Cbz ($\Delta V_{THmax} = 23.3$ V). The energy level of traps into the [5]C-Bu-Cbz layer ($\beta = 0.69$) is also deeper than for [4]C-Bu-Cbz ($\beta = 0.38$). These parameters extracted from electrical stress thus confirm the effect of nano-hoop size on the layer organization.

The case of CPP analogues is somewhat different as both display a high surface roughness, $R_q = 3.67$ nm for [8]CPP and $R_q = 1.22$ nm for [10]CPP (Figure 6, bottom). These differences between the two families of nano-hoops might be at the origin, at least partially, of the very different performance observed when incorporated in OFET devices.

The carrier mobilities were also extracted in a two-terminal device by applying the Mott–Gurney model to the I–V measurements (space-charge-limited current SCLC transport; Fig-

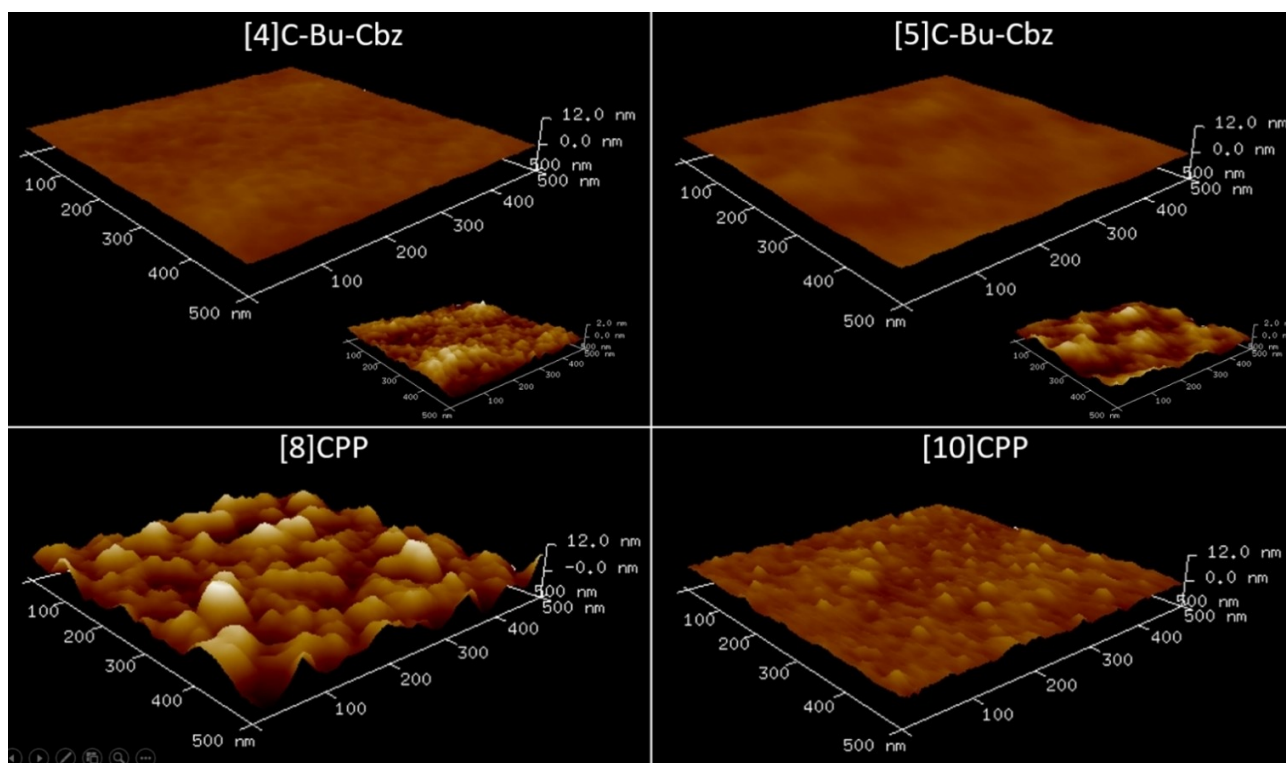


Figure 6. Two-dimensional ($500 \times 500 \text{ nm}^2$) AFM images of the semiconducting layer deposited under vacuum on an SU8 insulating layer.

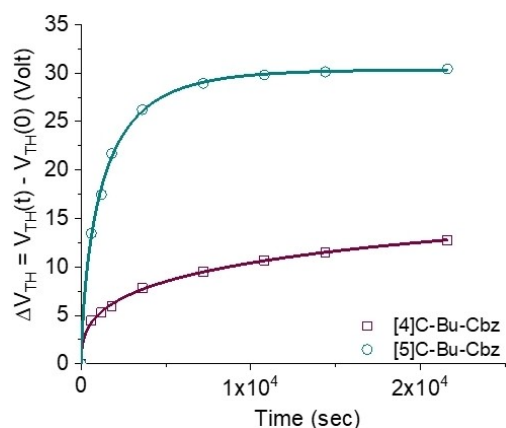


Figure 7. Threshold voltage behaviour under gate bias stress ($V_{G\text{Stress}} = -40 \text{ V}$, $V_{D\text{Stress}} = -10 \text{ V}$) for 6 h for [4]C-Bu-Cbz and [5]C-Bu-Cbz.

ure S30). The SCLC mobilities measured for the two cyclo-carbazoles are about three orders of magnitude higher than those of their CPP analogues, showing the significant impact of the bridging on the charge transport properties ($0.78/2.78 \times 10^{-4}$ for the cyclocarbazoles vs $1.21/0.11 \times 10^{-7} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for the CPPs). This can be related to the significant differences observed in the AFM images between the two families of compounds (Figure 6). Note that for [5]C-Bu-Cbz, the electric field to be applied to fill the defects is higher than that of [4]C-Bu-Cbz, in accordance with the difference observed for μ_{FEsat} .

Thus, for both nanohoop families, when the size decreases, the charge carrier mobility increases ($2.78 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for [4]C-Bu-Cbz vs $7.75 \times 10^{-5} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for [5]C-Bu-Cbz and $1.21 \times 10^{-7} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for [8]CPP vs $1.1 \times 10^{-8} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for [10]CPP), showing how the nanohoop size can have important implications on the charge transport.

Unfortunately, the electronic couplings among the carbazole-based nanohoops cannot be computed in absence of crystalline structures. On the other hand, we can compute the second key parameter, that is, the internal reorganization energy (λ_{reorg}), in [8]CPP, [10]CPP, [4]C-Bu-Cbz and [5]C-Bu-Cbz, to understand how the nature of the building block and hoop size modify the geometric distortions in singly charged nanohoop. We considered the most stable isomer of [5]C-Bu-Cbz where carbazoles are in the order up/down/up/down/up. We have used a displaced harmonic oscillator model where we project each intramolecular normal mode of vibration on the vector describing the geometric changes between the neutral and charged state to partition the reorganization energies into mode contributions. The normal modes of vibration and their frequency were computed with the Gaussian package at the DFT level using the M062X functional curing for self-interaction issues^[52] and a 6–31G(d,p) basis set (Figure 8). As the alkyl chains have no impact on the reorganization energies, they were replaced by hydrogen atoms. The normal mode contributions to relaxation energies were computed with the MOMAP package^[53] that follows a previously reported methodology.^[54] The DFT calculations yield the following total reorganization energies: [8]CPP (313 meV), [10]CPP (251 meV), [4]C-Bu-Cbz

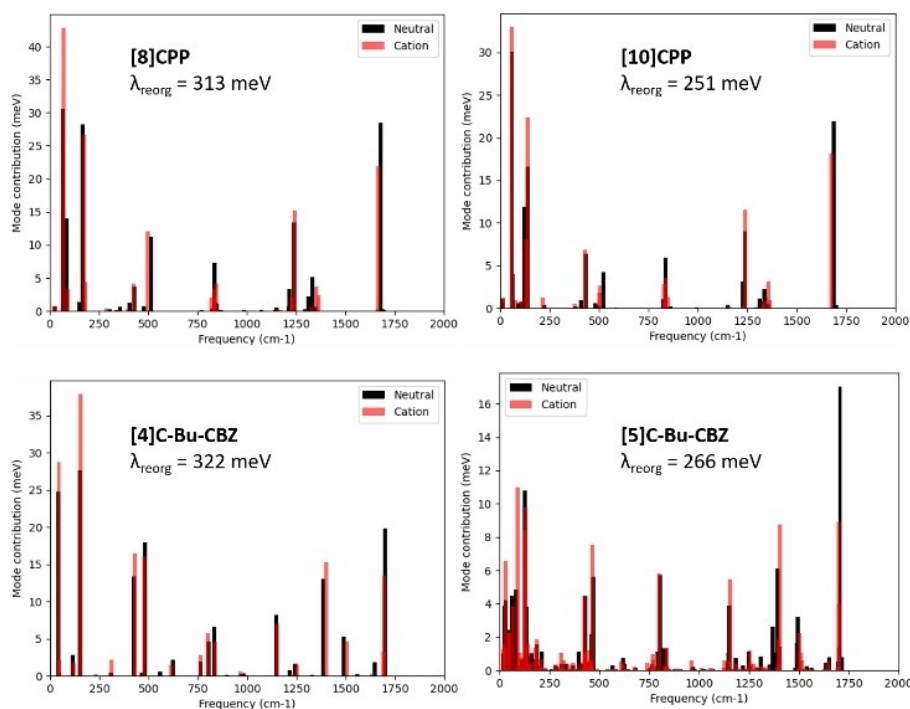


Figure 8. Relaxation energies on going from the neutral to oxidized geometry (red) and vice versa (black), partitioned into each mode contribution of a) [8]CPP, b) [10]CPP, c) [4]C-Bu-Cbz and d) [5]C-Bu-Cbz (the butyl chains have been removed for calculations). The total reorganization energy involved in the Marcus expression is the sum of the two contributions.

(322 meV) and [5]C-Bu-Cbz (266 meV). The results globally show that the number of carbazole units slightly increase the reorganization energy and conserve the dependency on the nanohoop size compared to the corresponding CPP analogues. Thus, as the size of the nanohoop increases, the reorganization energy decreases, as previously shown for CPPs by Houk, Yavuz and co-workers.^[20] The significant decrease in the reorganization energy going from [4]C-Bu-Cbz to [5]C-Bu-Cbz is fully consistent with the larger FE mobilities measured in the staured regime; hopping rates estimated with Equation (1) for the same transfer integrals and the reorganization energies computed for [4]C-Bu-Cbz and [5]C-Bu-Cbz point to an increase by a factor of 2 with nanohoop size, in deep consistency with the factor of 4 measured experimentally in the OFET devices.

Looking into details in the contributors to the reorganization energies, we find a mode involving the dihedral torsions around 60 cm^{-1} , a second mode assigned to “nanohoop breathing” around 140 and 170 cm^{-1} for [10]CPP and [8]CPP respectively while the third mode is the notable C=C stretching of the benzene rings around 1670 cm^{-1} . Increasing the size of the nanohoop has lowered down the contributions of these modes by $\sim 10\text{ meV}$ in [10]CPP. In the carbazole nanohoos, we do not recover such three dominating modes but more low to medium contributions to the reorganization energy with regard to the CPP molecules. In [4]C-Bu-Cbz, we observe the decrease in magnitude of the C=C contribution at 1670 cm^{-1} . A mode involving bending and torsion in the carbazole unit is also present at 40 cm^{-1} , and is comparable to the torsion modes present for the CPPs mentioned above. In the case of [5]C-Bu-

Cbz compared to [4]C-Bu-Cbz, a higher number of low contributions to the relaxation energies arises when adding an extra carbazole unit. We do conserve a high contribution from the bending/torsion modes around 150 cm^{-1} and observe that the mode involving the benzene stretching has regained a sizeable contribution. These results demonstrate that geometry relaxation processes upon charging involve both changes in the geometry of the individual rings together with variations in the torsion angles between adjacent rings, thus promoting rather large internal reorganization energies. For the sake of comparison, the corresponding value is about 100 meV for a pentacene molecule made of five fused benzene rings.^[55]

Conclusion

In the field of nanohoos, defining the evolution of the electronic properties as a function of the nanohoop size is a crucial step in the understanding of these new-generation π -conjugated systems and their applications, notably in organic electronics.^[14,17,18,20,23] Thanks to the synthesis of the first cyclo-carbazole with five building units, [5]C-Bu-Cbz, this work details the impact of the hoop size on the electronic and charge transport properties for two families of nanohoos, CPPs and cyclo-carbazoles. The size expansion from four to five carbazole units leads to a decrease in both HOMO and LUMO energy levels providing a slight gap contraction of 0.08 eV . This gap contraction is less marked than that observed in cyclofluorenes series (0.4 eV), thereby showing the important role played by

the nature of the bridge in the tuning of molecular orbital energies. Regarding the optical properties, we show that the bridges have an influence on the shape, position and width of the emission spectra but not on the fluorescence efficiency.

The charge transport studies are the most important data reported herein considering the possible future of nano hoops in organic electronics. These studies correlate the nano hoop size to the mobility. We notably show that the saturated FE mobility of [5]C-Bu-Cbz is four times higher than that of its smaller analogue [4]C-Bu-Cbz (4.22×10^{-5} vs $1.04 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). However, the study of V_{TH} and SS coupled to AFM studies suggests that a small nano hoop is more beneficial for a good organization of the molecules in thin films, whereas a larger nano hoop increases the density of structural defects, and hence of traps for the charge carriers. It is evident that other families of nano hoops and other nano hoop sizes should be investigated to go deeper into the establishment of design rules. Such studies are mandatory to reach high-performance devices based on nano hoops. In the light of recent works that have shown their potential in phosphorescent OLEDs,^[23] nano hoops can become a new class of promising organic semiconductors.

Deposition Numbers 871414 (for [8]CPP) and 871415 (for [10]CPP) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

Data available in article supplementary material.

Keywords: charge transport · cyclocarbazoles · hoop size effect · nano hoops

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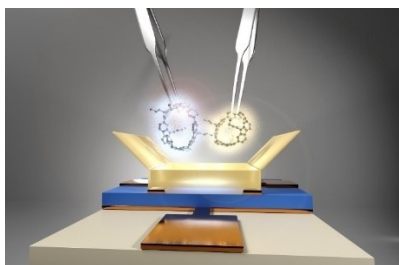
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RESEARCH ARTICLE

Experimental/theoretical investigations link the size of a nanohoop to its charge transport properties, which are key in organic electronics. The first cyclocarbazole possessing five constituting building units was synthesized and studied. Comparison of the photophysical, electrochemical, morphological and charge transport properties with those of a shorter analogue highlights the key role played by the hoop size. Corresponding cycloparaphenylenes with eight and ten phenyl units were also compared. Notably the saturated field effect mobility of the five-unit cyclocarbazole is four times higher than that of its smaller analogue.



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Electronic and Charge Transport Properties in Bridged versus Unbridged Nanohoops: Role of the Nanohoop Size

