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[n]-Cyclo-9,9-dibutyl-2,7-fluorene (n=4,5): Nanoring size influence in carbon bridged cyclo-*para*-phenylenes

Lambert Sicard, Fabien Lucas, Olivier Jeannin, Pierre-Antoine Bouit, Joëlle Rault-Berthelot, Cassandre Quinton, Cyril Poriel*

Abstract: For the last ten years, ring-shaped π -conjugated macrocycles possessing radially directed π -orbitals have been subject to intense research. The electronic properties of these rings are deeply dependent on their size. However, most studies involve the flagship family of nanorings: the cyclo-*para*-phenylenes. We report herein the synthesis and study of the first examples of cyclofluorenes possessing five constituting fluorene units. The structural, optical and electrochemical properties were elucidated by X-ray crystallography, UV-vis absorption and fluorescence spectroscopy, and cyclic voltammetry. By comparison with a shorter analogue, [4]-cyclofluorene, we show how the electronic properties of [5]-cyclofluorenes are drastically different from those of [4]-cyclofluorenes, highlighting the key role played by the ring size in the cyclofluorene family.

Cyclofluorenes, cyclic association of fluorene units *via para* linkages,^[1-4] constitute one family of the new generation of nanorings, macrocycles that possess radially directed π -orbitals. Since the first reported synthesis of nanorings (some cyclo-*para*-phenylenes, CPPs, Chart 1, Top) in 2008,^[5] such ring-shaped π -conjugated macrocycles have been subject to intense research worldwide.^[6-10] Cyclofluorenes (Chart 1, Bottom) belong to the family of bridged CPPs^[1-3, 11-14] and the first examples were reported in 2015 and 2016 by the groups of Yamago^[1] and Huang.^[2] In these examples, three or four fluorene units were connected together at their C2 and C7 positions to form highly strained structures. In 2018, our group showed that the family of [4]-cyclofluorenes displays an unusual tunability of its structural and electronic characteristics.^[3] Indeed, a simple modification of the chain length (methyl, ethyl or propyl) borne by the fluorene bridge induces a shift of the fluorescence emission, which was correlated to the specific arrangement of the fluorene units. In addition, photophysical investigations of cyclofluorenes have allowed to shed light on a possible origin of the instability of linear oligofluorenes in Organic Light-Emitting Diodes.^[15] Thus, despite only four examples of cyclofluorenes having been reported to date,^[1-3] this family of nanorings has already led to intriguing electronic and structural characteristics which generates a growing interest. Also, considering the key role played by the fluorene in the construction of high performance linear organic semi-conductors,^[16, 17] investigating the cyclic association of this building block appears particularly appealing.

Considering the field of nanorings, the influence of the ring size on the electronic properties is probably the most fascinating feature.^[7, 18-20] However, if this has been deeply studied in the case of CPPs, it is far to be the case for the other nanoring families. For cyclofluorenes, very few data are available but the first results seem to show that the impact of the ring size in this family is as important as in CPPs. Regarding for example the emission properties, it has been shown that [3]-cyclofluorenes are not fluorescent whereas [4]-cyclofluorenes possess a green to green/blue fluorescence with a quantum yield of ca 0.2/0.3.^[1] The HOMO

energy levels of the former have also been reported to be higher than those of the latter. However, the structural/electronic

properties of cyclofluorenes possessing more than four constituting units are still unknown and hence the study of the impact of the ring size expansion on the properties is very limited.

In the present work, we report the first examples of two bridged [10]CPP nanorings possessing five fluorene units, namely [5]-cyclo-9,9-dibutyl-2,7-fluorene [5]C-diBu-F and [5]-cyclo-9,9-dihexyl-2,7-fluorene [5]C-diHex-F. Thanks to a structure-properties relationship study, we show that the different electronic characteristics between [5]C-diBu-F and its shorter analogue with four fluorene units, [4]C-diBu-F, can be linked to the torsion and the bending of the phenylene units. Thus, it was found that the electronic properties of [5]-cyclofluorenes are closer to those of their linear analogues (resolved emission in the blue region, high quantum yield...), keeping nevertheless some characteristics of nanorings (*i.e.* forbidden HOMO→LUMO transition).

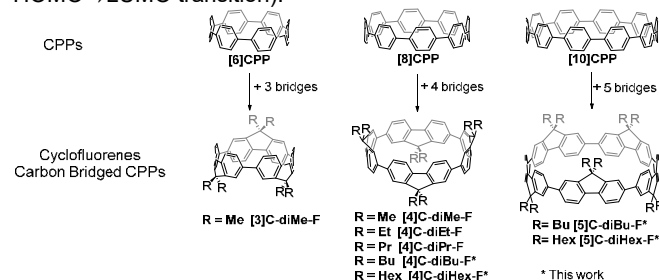
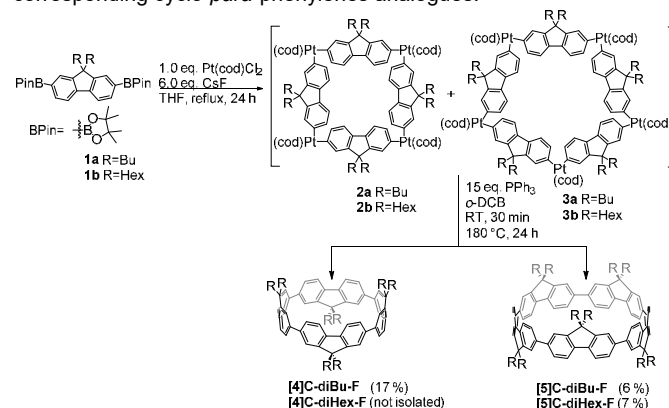


Chart 1. Cyclofluorenes reported to date^[1-3] and their corresponding cyclo-*para*-phenylenes analogues.



Scheme 1. Synthesis of cyclofluorenes

The synthetic pathway reported in Scheme 1 is inspired by the Pt-mediated macrocyclization of Yamago and coworkers^[21] and the boryl-route modification of Isobe and coworkers.^[22] The intermediates **2a** and **3a**, based on four and five square-shaped platinum complexes, were formed (not isolated) by stirring the dipinacol fluorene **1a** with Pt(cod)Cl₂ and cesium fluoride in a refluxing THF solution for 24 h. Then, the dried crude mixture containing **2a** and **3a** was treated with triphenylphosphine in *o*-dichlorobenzene, 0.5 h at room temperature (rt) and 24 h at 180 °C to provide [4]C-diBu-F and [5]C-diBu-F with 17% and

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6% yield respectively. Note that in the case of other [4]-cyclofluorenes synthesized through a similar route and bearing smaller alkyl chains on the bridge (Chart 1), no five membered nanoring was reported.^[1-3] As Yamago's group reported the isolation of a [3]-cyclofluorene with short methyl chains, **[3]C-diMe-F** (Chart 1),⁷ it is reasonable to assume that the chain length influences the relative stabilities of the trimer, tetramer and pentamer Pt complexes. Indeed, if the triangle complex is stable with the methyl chains, the longer alkyl chains (ethyl, propyl, butyl) could destabilize the triangle in favour of the square. We can hypothesize that a longer chain length (*i.e.* hexyl) is correlated to the formation of larger nanorings. In order to confirm this hypothesis, another dipinacol fluorene bearing hexyl chain **1b** was used to get **[4]C-diHex-F** (not isolated) and **[5]C-diHex-F**. Analysis of the crude products by ¹H NMR has shown that in the case of the butyl chain, the ratio of 4-cyclofluorene vs 5-cyclofluorene is 7:3 whereas a 6:4 ratio is found for the hexyl chain (see Figures S57-58). This shows that longer alkyl chains borne by the fluorene bridge enable the formation of 5-cyclofluorene, confirming the influence of the alkyl chain length on the nanoring's size. As the relationship between the nanoring's size and its electronic and structural properties is a central point in the field, reaching two nanoring sizes in a two-step sequence appears as an interesting synthetic feature.^[18, 23-25]

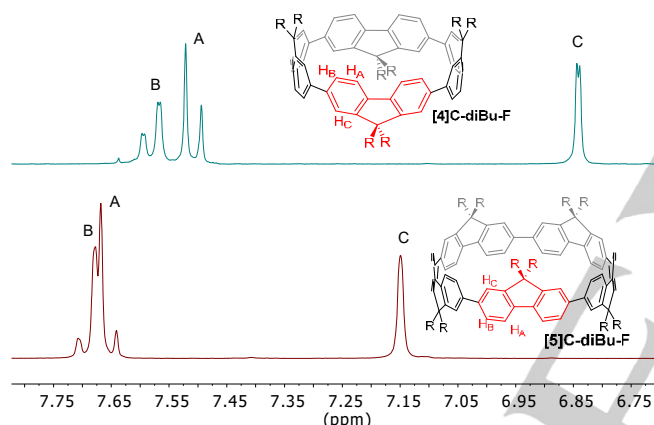


Figure 1. Parts of the ¹H NMR spectrum of **[4]C-diBu-F** (Top) and **[5]C-diBu-F** (Bottom) in CD₂Cl₂ (full spectra in Figures S47, S51).

The ¹H NMR spectra (Figure 1) of **[4]C-diBu-F** (even number of fluorenes) and **[5]C-diBu-F** (odd number of fluorenes) are surprisingly similar in the aromatic region with the presence of 3 signals. When increasing the size of the nanoring, all signals are deshielded. Thus, H_c of **[5]C-diBu-F** ($\delta=7.15$ ppm) is shifted by 0.3 ppm compared to its analogue in **[4]C-diBu-F** ($\delta=6.84$ ppm), most likely due to the fact that a smaller ring size increases the ring current^[12, 26] and the magnetic shielding effect. Despite being less intense, this effect was also described for CPPs (**[8]CPP**: $\delta=7.48$ ppm, and **[10]CPP**: $\delta=7.56$ ppm in CDCl₃)^[7, 27] and for other nanorings such as paraphenylene-2,6-naphthylenes.^[28] On the other hand, a significant difference between the two cyclofluorenes was detected in the alkyl chain resonances, which provides key information about the dynamic in solution. Indeed, all the aliphatic signals corresponding to the butyl units of **[4]C-diBu-F** are split compared to those of **[5]C-diBu-F** (see Figure S47, 51). In **[4]C-diBu-F**, it appears that one of the two butyl chains of each fluorene unit is positioned towards the centre of the ring. This leads to a shielding of all the signals corresponding to the hydrogen atoms of the inner chains. For example, the inner methyl group is found at a very low chemical shift of -0.58 ppm whereas its outer homologue is found at 0.78 ppm. This characteristic is not observed for the larger **[5]C-diBu-F** for which only one set of signals is detected for the two butyl chains borne by a fluorene unit. This means

that **[5]C-diBu-F** displays a time-averaged dynamic structure at room temperature due to the expansion of the macrocycle size whereas **[4]C-diBu-F** displays a single isomer with an $\alpha\beta\alpha\beta$ topology as shown by a NOESY experiment (see Figure S50). Thus, the number of building units in cyclofluorenes has a key influence on the structural properties in solution.

Molecular structures of **[4]C-diBu-F** (CCDC 1957018) and **[5]C-diBu-F** (CCDC 1957017) were fully revealed by X-ray diffraction on single crystals (Figure 2). We note that **[5]C-diBu-F** crystallises with a molecule of chloroform, localized outside of the nanoring, with which there doesn't seem to be any interaction. Both **[5]C-diBu-F** and **[4]C-diBu-F** crystallize in a P-1 space group. For **[4]C-diBu-F**, an $\alpha\beta\alpha\beta$ conformation is observed (in accordance with the conclusion drawn by NMR) whereas for **[5]C-diBu-F** an $\alpha\alpha\beta\alpha\beta$ conformation is observed.

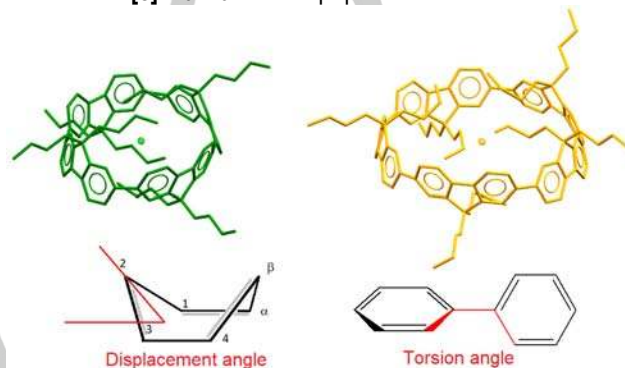


Figure 2. Top. ORTEP drawing of **[4]C-diBu-F** (Left) and **[5]C-diBu-F** (Right), barycentres (not considering the alkyl chains) are shown. Bottom. Sketch of the displacement (Left) and torsion angles (Right).

[4]C-diBu-F forms a distorted ellipsoidal nanoring with axes of 12.0 and 9.8 Å (Figure S1). This is similar to the cyclofluorene analogue bearing propyl chains, **[4]C-diPr-F** (11.9 and 10.0 Å, CCDC 1031896^[2]) but different from its analogue bearing ethyl chains, **[4]C-diEt-F**, which forms a perfect circle (11.0 Å, CCDC 1580867^[3]). This shows the importance of the length of the alkyl chain borne by the fluorene bridge on the structural characteristics of the ring (and hence on the electronic properties as previously discussed in literature). **[5]C-diBu-F** also displays an ellipsoidal deformation (13.3 and 13.6 Å) but much less pronounced than **[4]C-diBu-F**.

The deformations of the constituted units and their relative arrangement^[19] are at the origin of the specific properties of nanorings. Three structural parameters are usually considered to characterize a nanoring: the out-of-plane distortion, the displacement angle and the torsion angle (see Figure 2, definitions and detailed calculations in SI, Figures S2-4, Tables S3-5). First, the out-of-plane distortion can be measured by the distance C2-C7 of a fluorene unit. These distances are longer in **[5]C-diBu-F** than in **[4]C-diBu-F** (average values of 6.75 Å and 6.66 Å respectively; d_{C2-C7} in fluorene= 6.85 Å). Furthermore, the mean displacement angle^[7] decreases: 7.9° for **[4]C-diBu-F** vs 6.2° for **[5]C-diBu-F**. Thus, both the out of plane distortion, and the mean displacement angles are in favour of a more strained structure and more bent fluorenes and phenylenes in **[4]C-diBu-F** compared to **[5]C-diBu-F**. This is confirmed by the calculation of the strain energy, which is higher for **[4]C-diBu-F** than for **[5]C-diBu-F** (89 and 70 kcal/mol respectively, see calculation details in Figures S45-46). These values are higher than those found for non-bridged **[8]CPP** and **[10]CPP** (72 and 58 kcal/mol respectively), showing that the bridge and its substituents create a certain degree of hindrance to the nanoring, which increases the strain energy.

The torsion angle between two adjacent units of an oligomer (cyclic^[19] or linear^[29, 30]) is also one of the most important parameter involved in the delocalization of π -electrons. The external torsion angle between the fluorene units of **[5]C-diBu-F**,

averaged at 27.9° with a large distribution comprised between 3.7 and 42.0° (Table S5), is lower than that of **[4]C-diBu-F**, averaged at 30.8° with a low distribution (between 26.4 and 34.2°). The same observations between even-numbered and odd-numbered CPPs have been described.^[31] One can nevertheless note that this trend is different from that of CPPs, strictly considering the number of phenyl units (8 in **[4]C-diBu-F** and 10 in **[5]C-diBu-F**). From **[8]CPP** to **[10]CPP** as the number of phenyl units increases, the average torsion angle also increases (24.3 and 27.3° resp., see Table 1), whereas from **[4]C-diBu-F** to **[5]C-diBu-F**, despite a same phenyl number evolution, the torsion angle decreases. The number of phenyl rings and the parity of the number of constitutive units are key parameters in the understanding of the evolution of nanorings' properties. Herein, **[5]C-diBu-F**, possessing 10 phenyl units, is a bridged **[10]CPP** but with torsion angles specific to odd-numbered nanorings.

Table 1. Selected electronic and structural data of cyclofluorenes and corresponding CPPs

	[4]C-diBu-F	[5]C-diBu-F	[5]C-diHex-F	[8]CPP	[10]CPP
λ_{ABS}^a [nm]	349	355	355	331	335
λ_{EM}^a [nm]	515	440 466	443 466	528	464
Φ^a	0.21	0.61	0.61	0.25	0.59
τ_f^a [ns]	3.0; 8.4	1.4; 4.3	1.8; 4.4	3.0; 10.6	3.9
E_{ox}^b [V]	0.88 (sh) 0.98 >1.5	1.03 1.21 1.43 >1.5	1.00 1.40 1.63 1.78 2.03	1.07 1.22	1.23 1.43
HOMO ^{b,c} [eV]	-5.1	-5.3	-5.3	-5.3	-5.5
LUMO ^{b,c} [eV]	-2.2	-2.8	-2.1	-2.6	-2.5
Mean torsion angle ^d	16.9°	14.7°	-	24.3°	27.3°
Mean displacement angle ^d	7.9°	6.2°	-	9.6°	8.0°

a. in cyclohexane, b. from CVs recorded in CH₂Cl₂, c. calculated from the onset oxidation/reduction potentials, d. from X-Ray.

Electrochemical analyses of **[4]C-diBu-F** and **[5]C-diBu-F** were performed by cyclic voltammetry (CV) in CH₂Cl₂ (see oxidation in Figure 3 and reduction in Figure S38-39, all potentials are given vs SCE). In oxidation, **[4]C-diBu-F** presents a first reversible wave with a maximum at 0.98 V and a shoulder at 0.88 V (Figure 3, blue line). CV of **[5]C-diBu-F** is drastically different with three successive oxidation waves at 1.03, 1.21 and 1.43 V (Figure 3, black line). Interestingly, these three waves are found to be reversible showing the high stability of the species involved in these processes. From the onset of the first wave, the HOMO energy levels are evaluated at -5.1 eV for **[4]C-diBu-F** and at -5.3 eV for **[5]C-diBu-F**. Regarding the LUMO energies, **[5]C-diBu-F** displays a significantly decreased LUMO (-2.8 eV) compared to that of **[4]C-diBu-F** (-2.2 eV). In the following section will be discussed the evolution of the HOMO/LUMO levels: a) upon size change (for both CPPs and cyclofluorene families), b) when bridging a CPP to give a cyclofluorene, c) upon the chain length change.

a) *Effect of the size.* As the size of the cyclofluorene increases from 4 to 5 units, there is a decrease of both HOMO and LUMO energies. As the LUMO decrease (0.6 eV) is more intense than the HOMO decrease (0.2 eV), there is a gap contraction of 0.4 eV when the number of fluorene units increases (from 2.9 eV for **[4]C-diBu-F** to 2.5 eV for **[5]C-diBu-F**). This gap contraction is also observed for linear oligophenylenes (but with different HOMO/LUMO evolutions) whereas a gap expansion is observed for the CPPs family. This feature is indeed different from that observed between the two non-bridged model compounds belonging to the CPPs family, i.e. **[8]CPP** and **[10]CPP**. In identical experimental conditions, these two molecules display a different electrochemical behaviour with

two quasi-reversible oxidation waves observed for **[8]CPP** (1.07 V and 1.22 V) and a combination of a reversible (1.23 V) and an irreversible wave (1.43 V) for **[10]CPP** (Figure S42). The HOMO of **[8]CPP** and **[10]CPP** are respectively evaluated at -5.3 and -5.5 eV, indicating a decrease of the HOMO energy when increasing the ring size.

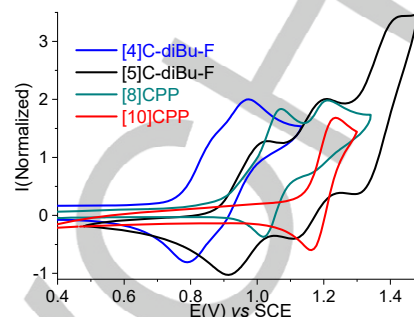


Figure 3. Normalized cyclic voltammograms of **[4]C-diBu-F** and **[5]C-diBu-F** and corresponding CPPs **[8]CPP** and **[10]CPP**, CH₂Cl₂+Bu₄NPF₆ 0.2 M, 100 mV.s⁻¹, Pt disk working electrode. The CVs are normalized (2 electrons) at the 2nd oxidation.

Reduction of **[8]CPP** and **[10]CPP** occurs in a similar range providing LUMO energy of ca -2.6 and -2.5 eV respectively. As predicted by theoretical calculations,^[6] the increase of the CPP size leads to an increase of the LUMO and a decrease of the HOMO and therefore to a gap expansion from 2.7 to 3.0 eV. As the CPP becomes smaller, the higher strain induces (i) a decrease of the mean torsion angle and (ii) an increase of the phenyl bending (measured by the mean displacement angle). The change of these geometrical parameters leads to a shift of the molecular orbital (MO) energies: the smaller the nanoring, the lower the LUMO energy and the higher the HOMO energy. In 2012, Itami and coworkers defined general rules, which explain the LUMO/HOMO evolution for CPPs (Figure S5).^[19] They have shown that the LUMO energy is mainly governed by the torsion effect (the less twisted, the lower the LUMO) and only slightly by the bending effect (the more bent, the lower the LUMO) whereas the HOMO energy is mainly affected by the bending effect (the more bent, the higher the HOMO) and, to a lesser extent, by the torsion effect (the less twisted, the higher the HOMO). These rules explain that the less twisted and more bent **[8]CPP** (mean torsion angle: 24.3°, mean displacement angle: 9.6°) has a lower LUMO (-2.6 eV) and a higher HOMO (-5.3 eV) than the more twisted and less bent **[10]CPP** (mean torsion angle: 27.3°, mean displacement angle: 8.0°, LUMO: -2.5 eV and HOMO: -5.5 eV). It seems that these rules can also be applied to the present cyclofluorenes. Indeed, **[4]C-diBu-F** displays a higher HOMO level (-5.1 eV) than that of **[5]C-diBu-F** (-5.3 eV) assigned to the more bent phenyl units found in the smaller ring (displacement angles of **[4]C-diBu-F**: 7.9° and of **[5]C-diBu-F**: 6.2°). This trend for the HOMO energy towards size is also found for CPPs. However, and unlike CPPs, when the size of the cyclofluorene increases, the LUMO decreases (-2.2 eV for **[4]C-diBu-F** and -2.8 eV for **[5]C-diBu-F**) due to the decrease of the mean torsion angle (16.9° for **[4]C-diBu-F** and 14.7° for **[5]C-diBu-F**). The size expansion provides a cyclofluorene slightly more difficult to oxidize but easier to reduce. The evolution of the frontier MO energies of cyclofluorenes in relation to size is hence different from that of CPPs but can be rationalized with the same rules.

b) *Effect of the bridges.* The presence of bridges in both **[4]C-diBu-F** and **[5]C-diBu-F** also has an impact on the oxidation/reduction potentials and resulting HOMO/LUMO energy levels revealed by the comparison with their non-bridged counterparts, **[8]CPP** and **[10]CPP** respectively. From **[8]CPP** to **[4]C-diBu-F** both HOMO and LUMO energies are increased leading to a 0.2 eV gap expansion whereas from **[10]CPP** to

[5]C-diBu-F, HOMO energy increases and LUMO energy decreases leading to a 0.5 eV gap contraction. The increase of the HOMO levels when bridging the CPPs to give the cyclofluorenes with 4 units (-5.3 eV for **[8]CPP** and -5.1 eV for **[4]C-diBu-F**) and 5 units (-5.5 eV for **[10]CPP** and -5.3 eV for **[5]C-diBu-F**) is due to the lowering of the torsion angles observed for cyclofluorenes (16.9° for **[4]C-diBu-F** and 14.7° for **[5]C-diBu-F**) compared to the non-bridged CPPs (24.3° for **[8]CPP** and 27.3° for **[10]CPP**). The difference, induced by the bridges, between the torsion angles of CPPs and cyclofluorenes is so important that it seems to become the main parameter which drives the HOMO level (instead of the bending). The evolution of the LUMO levels when bridging a CPP is more difficult to rationalize since from **[8]CPP** (-2.6 eV) to **[4]C-diBu-F** (-2.2 eV) the LUMO energy increases whereas from **[10]CPP** (-2.5 eV) to **[5]C-diBu-F** (-2.8 eV) the LUMO energy decreases. In fact, it seems that the LUMO energy of the small rings (more bent) are governed by the bending effect whereas the one of the large rings (less bent) are governed by the torsion effect. Thus, when bridging **[8]CPP** (displacement angle: 9.6°) to give **[4]C-diBu-F** (displacement angle: 7.9°), the phenylene units are less bent and hence according to the rules established by Itami (Figure S5),^[19] the LUMO energy increases. When bridging **[10]CPP** (torsion angle: 27.3°) to give **[5]C-diBu-F** (torsion angle: 14.7°), the phenylene units are less twisted and hence the LUMO energy decreases.

c) *Effect of the chain length.* It should be noted that the other [5]-cyclofluorene analogue synthesized in this work, **[5]C-diHex-F**, displays an electrochemical behaviour different from **[5]C-diBu-F**. The two first waves are reversible with maxima at 1.0 V and 1.4 V (see CVs in Figure S40). Three other oxidation waves are then observed at higher potentials (1.63, 1.78 and 2.03 V). The HOMO and LUMO levels of **[5]C-diHex-F** are evaluated at -5.3 and -2.1 eV respectively, identical to and higher than the ones of **[5]C-diBu-F** (-5.3 and -2.8 eV). Since no crystal structure could be obtained for **[5]C-diHex-F**, we cannot precisely rationalize these observations as done above. It is however reasonable to hypothesize that the longer chains will induce slightly higher torsion angles between the fluorenes (due to an increase of the steric hindrance in the nanoring cavity) but without changing their displacement angles. Since the HOMO levels are governed by the bending effect (torsion angles being in the same range) and the LUMO levels by the torsion effect, it would explain why the HOMO level remains unchanged whereas the LUMO level increases with the length of the chains. Changing the fluorene substituents from butyl to hexyl has therefore a significant influence on the electrochemical properties of the cyclofluorenes with 5 units. This result shows the singularity of this family of nanorings and the importance of the bridge substitution on their properties.

The optical properties of both **[4]C-diBu-F** and **[5]C-diBu-F** (Figure 4) and their corresponding CPPs (**[8]CPP** and **[10]CPP**) were characterized by UV/visible absorption spectroscopy as well as stationary and time-resolved fluorescence in cyclohexane. The absorption spectrum of **[4]C-diBu-F** displays a main band at 349 nm with two shoulders, one at 334 nm and the other, very large above 400 nm. In the light of Time Dependent-DFT (Figure S44), the band above 400 nm is assigned to a symmetry forbidden HOMO→LUMO transition as typically observed for nanorings. The band at 349 nm is assigned to two transitions. The first (modelized at 382 nm) implies two contributions HOMO-1→LUMO and HOMO→LUMO+1. The second (modelized at 372 nm) also involves two contributions: HOMO-2→LUMO and HOMO→LUMO+2. This kind of MO diagram is typical of CPPs^[19] and bridged CPPs with four units.^[11] The absorption properties of **[5]C-diBu-F** appear very similar to those of its shorter analogue with two main bands: a thin and intense band at 355 nm and a large and weak one above 400 nm (Figure 4, Middle). TD-DFT analyses indicate that these bands involve the

same transitions (and orbitals) as **[4]C-diBu-F**. The weak band above 400 nm is assigned to the classic HOMO→LUMO transition (due to the odd number of units and the symmetry breaking, the oscillator strength is weak but not null, $f=0.014$). The band at 355 nm is due to two transitions, each having two contributions: HOMO-1→LUMO and HOMO→LUMO+1 on one hand and HOMO-2→LUMO and HOMO→LUMO+2 on the other hand. We can note for this band, an experimental bathochromic shift between **[5]C-diBu-F** and **[4]C-diBu-F** ($\Delta\lambda_{\text{exp}} = 6$ nm), which is in accordance with theoretical calculations ($\Delta\lambda_{\text{th}} = 10$ nm). This shift observed for **[5]C-diBu-F** is assigned to the more important decrease/increase of LUMO+2, LUMO+1/HOMO-1, HOMO-2 energy levels than that of HOMO/LUMOS. This size dependence red shift is not observed for the non-bridged analogues^[20] and emphasizes the singularity of the optical properties of cyclofluorenes. Finally, it should be noted that the optical gap of **[5]C-diBu-F** is expanded compare to that of **[4]C-diBu-F** ($\Delta E_{\text{opt}} = 2.86$ eV vs 2.76 eV) following the same trend than that detected by electrochemistry.

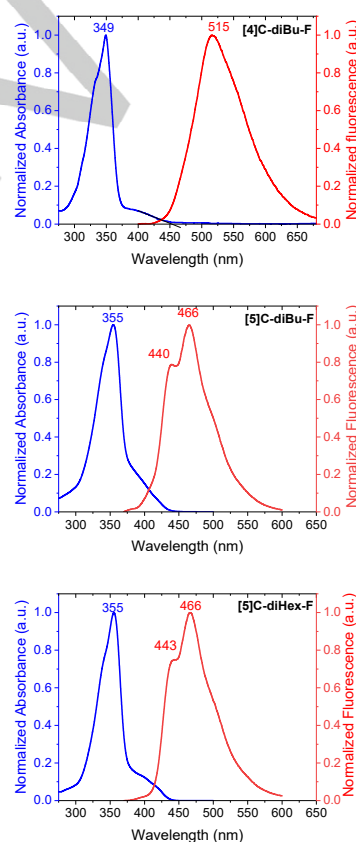


Figure 4. Absorption/emission spectra in cyclohexane of **[4]C-diBu-F** (Top, $\lambda_{\text{exc}} = 340$ nm), **[5]C-diBu-F** (Middle, $\lambda_{\text{exc}}=310$ nm) and **[5]C-diHex-F** (Bottom, $\lambda_{\text{exc}}=310$ nm)

In emission spectroscopy, **[5]C-diBu-F** (Figure 4, Middle) surprisingly displays a slightly resolved spectrum with two bands at 440 and 466 nm. This is a very different behaviour from that of its shorter analogue **[4]C-diBu-F** (which displays an unresolved spectrum centred at 515 nm, Figure 4, Top) and all the cyclofluorenes^[1-3] and the CPPs (until ten units) reported to date.^[7] There is therefore an asymmetry between the absorption and emission spectra of **[5]C-diBu-F**. Similar features are observed for linear oligo(*para*-phenylenes): a broad and featureless band in absorption and a well resolved thin emission due to the planarization of the molecule in the excited state.^[32] Therefore, one can conclude that the emission properties of **[5]C-diBu-F** resembles to those of its linear counterpart, such as 9,9-dihexyl-2,7-pentafluorene: $\lambda_{\text{em}} = 412$ and 440 nm (in

CHCl₃).^[33] In addition, there is a 50 nm bathochromic shift between the two fluorescence maxima of [4]C-diBu-F (515 nm) and [5]C-diBu-F (466 nm), similar to that observed between [8]CPP and [10]CPP (64 nm). If in the case of CPPs, some explanations have been provided,^[20] the origin of this feature remains to be elucidated in the case of cyclofluorenes. The fluorescence quantum yields of [5]C-diBu-F and [4]C-diBu-F were respectively measured to be 0.61 and 0.21, very similar to those of [10]CPP and [8]CPP (0.59 and 0.25, measured in identical conditions), showing the small influence of the bridges on the emission efficiency. The fluorescence decay curves of [5]C-diBu-F provide two lifetimes, $\tau=1.4$ and 4.3 ns, which are around half those of [4]C-diBu-F, $\tau=3.0$ and 8.4 ns (Table 1). One can note that the longer lifetime (4.3 ns) of [5]C-diBu-F is very similar to that measured for non-bridged analogue [10]CPP (3.9 ns). Thus, the time-resolved emission properties seem to be driven more by the number of constituting phenyl units than by the presence of the bridges.

The specificity of the optical characteristics of [5]-cyclofluorenes is confirmed by the study of [5]C-diHex-F. Indeed, the electronic properties of [5]C-diHex-F appear very similar to those of [5]C-diBu-F, Table 1. Of particular interest, a similar resolved fluorescence spectrum with the same two bands (443, 466 nm, Figure 4, Bottom-right) and a high quantum yield (0.61) was obtained for [5]C-diHex-F. The lifetimes measured, 1.8 and 4.4 ns, are also almost identical to that of [5]C-diBu-F, indicating that a similar molecular fragment is involved in these deactivation processes.

To summarize, we have synthesized the first examples of [5]-cyclofluorenes and have shown their singular structural and electronic behaviour. In the cyclofluorenes family, as the size of the nanoring increases from 8 to 10 constitutive phenyl units: (i) the phenyl units are less bent (as for CPPs) and less twisted (oppositely to CPPs), (ii) the HOMO and the LUMO are decreased (as and oppositely to CPPs respectively) and (iii) the fluorescence emission is improved and blue shifted (as in CPPs) and resolved (oppositely to CPPs). Thus, the ring enlargement confers [5]-cyclofluorenes specific electronic properties compared to [4]-cyclofluorenes. Furthermore, the cyclofluorenes display specific properties compared to CPPs due to the rigidity induced by the bridges. If the properties of CPPs are well known as of now, other families of nanorings such as cyclofluorenes remain barely explored. For all nanorings, defining the evolution of their structural and electronic properties as a function of the ring size is a crucial step in the understanding of these new generations of π -conjugated systems and their possible applications.^[34, 35] For example, it has been recently reported that the size does not influence the emission characteristics of CPPs geodesic phenine frameworks,^[23] which is different from that highlighted for CPPs^[20, 36] or the present cyclofluorenes. This shows the significant specificities of each family of nanorings and the richness of this research field.

Experimental Section

Experimental Details can be found in Supplementary Information.

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Keywords: cyclofluorene • nanorings • ring bridging • ring size effect

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