Perfluorocycloparaphenylenes: Fully fluorinated carbon nanorings by Ni-mediated one-pot synthesis

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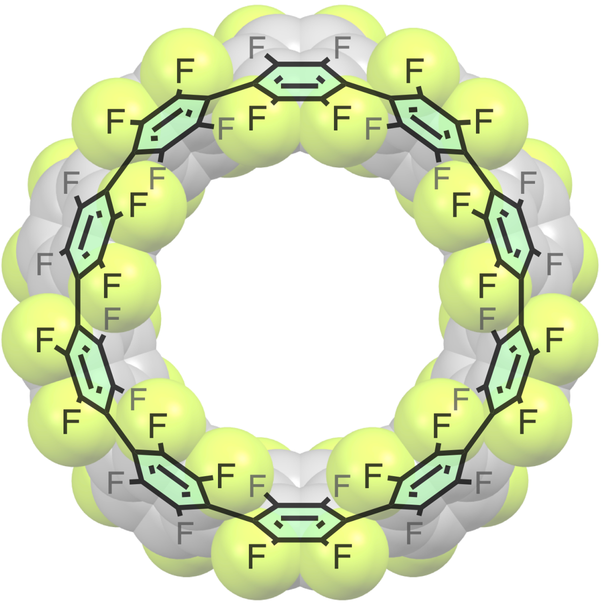
Graphical abstract:



Abstract:

Perfluorinated aromatic compounds, the so-called *perfluoroarenes*, are widely used in materials science owing to their high electron affinity and characteristic intermolecular interactions. However, methods to synthesize highly strained perfluoroarenes have remained elusive so far, which greatly limits their structural diversity. Herein, we report the synthesis and isolation of perfluorocycloparaphenylenes (PFCPPs) as a class of ring-shaped perfluoroarenes. Using macrocyclic nickel complexes, we succeeded in synthesizing PF[*n*]CPPs (*n* = 10, 12, 14, 16) in one-pot without noble metals. The molecular structures of PF[*n*]CPPs (*n* = 10, 12) were determined by X-ray crystallography to confirm their tubular alignment. Photophysical and electrochemical measurements revealed that PF[*n*]CPPs (*n* = 10, 12) exhibit wide HOMO–LUMO gaps, high electron affinity, and strong phosphorescence at low temperature. PFCPPs are not only useful as electron-accepting organic semiconductors but can also be used for accelerating the creation of topologically unique molecular nanocarbon materials.

Main text

Organic fluorine compounds have found widespread applications in pharmaceutical, agricultural, and materials science[1–5]. The introduction of fluorine into organic molecules often strongly affects their properties, including their polarity, solubility, and lipophilicity. Among many organic fluorine-containing compounds, fluorinated arenes are used as semiconductors, light-emitting materials, and liquid crystals[6]. Owing to its negative inductive effect, the incorporation of fluorine into materials leads to a decrease in orbital energy. As such, it is important to develop synthetic methods that provide access to aromatic molecules containing many C–F bonds[7–9], and the extreme targets of the research field are aromatic molecules wherein all hydrogen atoms are replaced with fluorine atoms, *i.e.*, perfluoroarenes[10–14]. However, methods to synthesize strained perfluoroarenes remain very limited. It is known that various fluorinated fullerenes (Fig. 1a, top left) can be obtained from the addition of fluorine to the unsaturated bonds of fullerenes, but these are virtually the only examples of highly strained perfluoroarenes[15]. Although Suzuki and co-workers have shown that perfluororubrene (Fig. 1a, top right) possesses a twisted structure with a slight strain[16], a method to apply more strain to perfluoroarenes has not yet been reported.

Here, we report the synthesis of perfluorocycloparaphenylenes (PFCPPs), a class of highly strained ring-shaped perfluoroarenes (Fig. 1a, bottom) in which all hydrogen atoms of the corresponding cycloparaphenylenes (CPPs)[17–19] are replaced with fluorine atoms. This replacement of hydrogen with fluorine can be expected to result in a significant change of the structural and electronic properties of the PFCPPs[20]. Two major methods for the synthesis of CPPs have been reported: (i) converting C6 units, such as cyclohexane and cyclohexadiene, of macrocyclic precursors into benzene rings[21,22], and (ii) reductive elimination from macrocyclic metal–arene complexes (metal = Pt, Ni, Au)[23–25]. However, even partially fluorinated CPPs (F_8[6]CPP, F_{12}[9]CPP, F_8[12]CPP, F_4[10]CPP, F_4[12]CPP) synthesized by the groups of Yamago and Jasti[26–28] require multiple steps (method (i), Fig. 1b), and there has no successful synthesis of CPP derivatives from *ortho*-functionalized aryl groups by the Pt method[17–19]. We hypothesized that PFCPPs can be obtained in one-pot based on method (ii). Considering that the reductive elimination of perfluorobiphenyl occurs from the stable (2,2'-bipyridyl)Ni(C_6F_5)$_2$ complex promoted by acids or oxidants[29,30], we assumed that

Ni might be a suitable metal for the construction of macrocyclic precursors for PFCPPs (Fig. 1c).

Our synthetic route to PFCPPs is outlined in Fig. 2. Starting from 2,3,5,6,2',3',5',6'-octafluorobiphenyl (**1**), deprotonation by lithium diisopropylamide (LDA) and subsequent transmetallation to Ni(dnbpy)Br_2 (dnbpy = 4,4'-di-*n*-nonyl-2,2'-bipyridyl) produced a mixture of macrocyclic complex **2**. After evaporation of the solvent and replacing it with *m*-xylene, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) was added and the resulting mixture was stirred at 130 °C for 5 hours to promote the reductive elimination of aryl–aryl bonds from Ni. As a result, PF[*n*]CPPs (n = 10, 12) were obtained in 9.2% and 7.6% yield, respectively, together with a trace amount (<1%) of PF[14]CPP and PF[16]CPP. These PF[*n*]CPPs are highly strained perfluoroarenes, as evident from their high strain energies of 60.2 (n = 10), 49.9 (n = 12), 42.6 (n = 14), and 37.2 kcal·mol^{-1} (n = 16) estimated by DFT calculations (for details, see the SI). Considering that PF[*n*]CPPs were not obtained when 2,2'-bipyridyl or 4,4'-di-*t*-butyl-2,2'-bipyridyl was used, the *n*-nonyl groups of the dnbpy ligand should be crucial for preventing the precipitation of intermediates. For each PF[*n*]CPP (n = 10, 12, 14, 16), one singlet signal was observed in the ^{19}F NMR spectra at –138.25 (n = 10), –138.50 (n = 12), –138.64 (n = 14), and –138.84 ppm (n = 16). The trend to shift resonances to lower magnetic field with increasing ring size is similar to the case of ^{1}H NMR chemical shifts of [*n*]CPPs[17]. The corresponding high-resolution mass spectra were recorded using the negative mode of the LDI-TOF MS (laser desorption/ionization time-of-flight mass spectrometry) technique. While ^{13}C NMR signals could not be collected due to the low solubility of PF[*n*]CPPs, these compounds were identified based on spectral measurements.

The structures of PF[*n*]CPPs (n = 10, 12) were successfully determined by X-ray crystallography. Single crystals of PF[10]CPP and PF[12]CPP were obtained from THF and hexafluorobenzene/*n*-hexane solutions, respectively. As shown in Fig. 3a,b, perfluoroarene structures with CPP skeletons (F_{40}[10]CPP and F_{48}[12]CPP) were unambiguously confirmed. For PF[10]CPP, THF used for recrystallization is contained within the ring, despite the fact that these molecules are strongly disordered, whereas PF[12]CPP contains 4 molecules of hexafluorobenzene inside and outside the rings. The crystal packing of these PFCPPs is shown in Fig. 3c,d. In both PFCPPs, the ring cavities are aligned along the *a*-axis. This result stands in contrast to the behavior of [*n*]CPPs of the same size (n = 10, 12), which show herringbone-like packing[31,32], indicating that the influence of fluorine atoms on the molecular alignment in crystal state is significant. Similar tubular packing was also found for partially fluorinated CPPs[26–28]. The torsion angles between pairs of benzene rings are summarized in Fig. 3e. The averaged dihedral angles observed in X-ray crystallography (PF[10]CPP: 54.7°; PF[12]CPP: 55.7°) and those obtained from DFT optimizations at the B3LYP/6-31G(d) level of theory (PF[10]CPP: 50.4°; PF[12]CPP: 51.3°) are higher than those of [10]- and [12]CPP (calculated: ~33°; observed: 23–27°)[31–33], which is most likely caused by the steric repulsion between fluorine atoms.

In order to investigate the effect of C–F bonds on the π-electrons in PFCPPs, optical and electrochemical measurements as well as DFT calculations were carried out. The PFCPPs showed absorption in the UV region with absorption peaks at 270 nm for both PFCPPs (Fig. 4a), which is hypsochromically shifted compared to those of the corresponding CPPs ([10]CPP: 340 nm; [12]CPP: 338 nm)[33,34]. While no obvious fluorescence was detected ($\Phi < 0.01$) at room temperature, bright phosphorescence was observed at low temperature (≤ 150 K). As shown in Fig. 4a, as dispersed solids in PMMA (poly(methyl methacrylate)), these PFCPPs exhibited phosphorescence with peak tops at 437 nm (PF[10]CPP) and 509 nm (PF[12]CPP) with long lifetimes (τ) of 2.0 s and 0.6 s, respectively. The phosphorescence quantum yields (Φ) in ethanol at 77 K were 0.21 (PF[10]CPP) and 0.62 (PF[12]CPP) (for details, see the SI). These photoluminescence properties clearly indicate that intersystem crossing occurs much more quickly compared to [10]- and [12]CPPs, which exhibit high fluorescence quantum yields at room temperature ([10]CPP: 0.46–0.65; [12]CPP: 0.66–0.89), presumably owing to the large dihedral angles of the PFCPPs (Fig. 3e)[33,34].

Next, cyclic voltammograms were recorded (Fig. 4b). In acetonitrile, both PFCPPs showed a reduction potential (–1.23 V vs ferrocene(II)/ferrocenium(III)) higher than those of previously reported CPPs and partially fluorinated CPPs, indicating that the perfluorination increases the electron affinity of CPPs[26–28]. Fig. 4c shows the HOMO and LUMO of PF[10]CPP with their energies calculated at B3LYP/6-31G(d) level of theory (for details on PF[12]CPP, see the SI). While the shape and distribution of each frontier molecular orbital of PF[10]CPP are almost identical to that of [10]CPP, the

HOMO–LUMO gap is wider (PF[10]CPP: 4.24 eV) than that of [10]CPP (3.54 eV)[33], which is in line with the hypsochromic shift of the absorption spectra.

In summary, we have synthesized and isolated PF[*n*]CPPs (n = 10, 12, 14), which represent highly strained perfluorocarbon molecules. The synthesis of these PFCPPs was accomplished in a one-pot fashion via deprotonation of octafluorobiphenyl, transmetallation to Ni(dnbpy)Br_2, and oxidant-promoted reductive elimination. The high solubility of intermediates enhanced by the *n*-nonyl groups of dnbpy might be the key to the success of this concise synthesis. PF[*n*]CPPs (*n* = 10, 12, and 14) were identified by spectroscopic analysis (^{19}F NMR and LDI-TOF MS), and the solid-state structures of PF[10]CPP and PF[12]CPP were unambiguously determined by X-ray crystallography. In the crystal structure, PF[10]CPP and PF[12]CPP exhibit a tubular shape, and the ring cavities are connected one-dimensionally. The dihedral angles between pairs of benzene rings in the PFCPPs are larger than those of the corresponding CPPs due to the steric repulsion between fluorine atoms. Optical and electrochemical measurements revealed wide HOMO–LUMO gaps and high electron affinity for PF[*n*]CPPs (*n* = 10 and 12), which also show strong phosphorescence at extremely low temperature. The large dihedral angles between pairs of benzene rings are presumably the reason why intersystem crossing takes place quickly in the case of PF[*n*]CPPs (*n* = 10 and 12). As this is the first efficient synthetic route to highly strained perfluoroarenes, this noble metal-free one-pot synthesis of PFCPPs represents a huge breakthrough in fluorocarbon chemistry. Apart from the obvious interesting electronic features of strained PFCPPs, it should also be possible to create highly strained molecular nanocarbon materials by further converting the reactive C–F bonds of PFCPPs. PFCPPs are not only attractive as electron-deficient aromatic materials but are also potentially applicable to further transformations for the creation of highly strained and topologically unique molecular nanocarbon materials[35].

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Author Contributions

K.I. and Y.S. conceived the concept and prepared the manuscript with feedback from the other authors. H.S., M.K., and T.K. performed the synthetic experiments. Y.S. performed the X-ray crystallographic measurements. M.S., T.N., and Y.T. performed the photophysical measurements. A.Y. provided critical comments.

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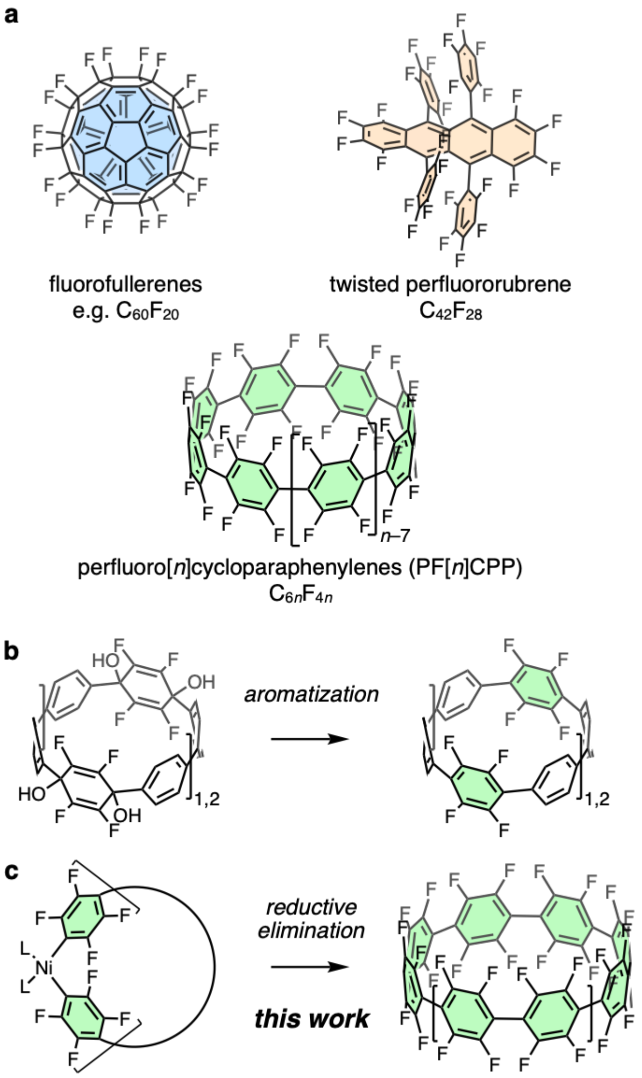
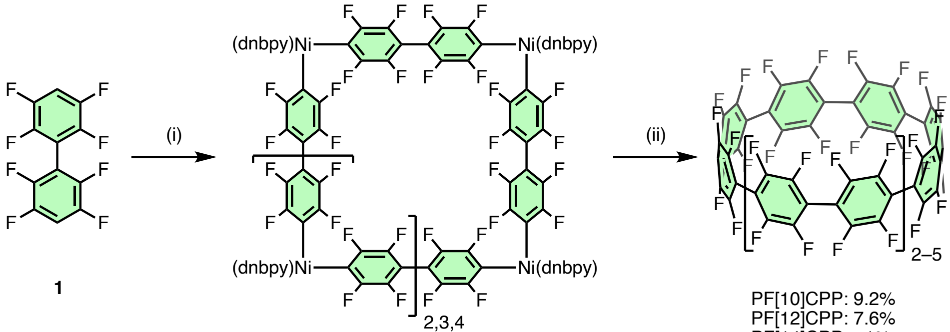


Fig. 1. Fluorocarbon molecules. (**a**) Structures of fluorofullerenes (top left), perfluororubrene (top right), and perfluorocycloparaphenylenes (PFCPPs) (bottom). (**b**) A synthetic scheme of previously reported partially fluorinated CPPs. (**c**) The synthetic strategy for PFCPPs (this work).

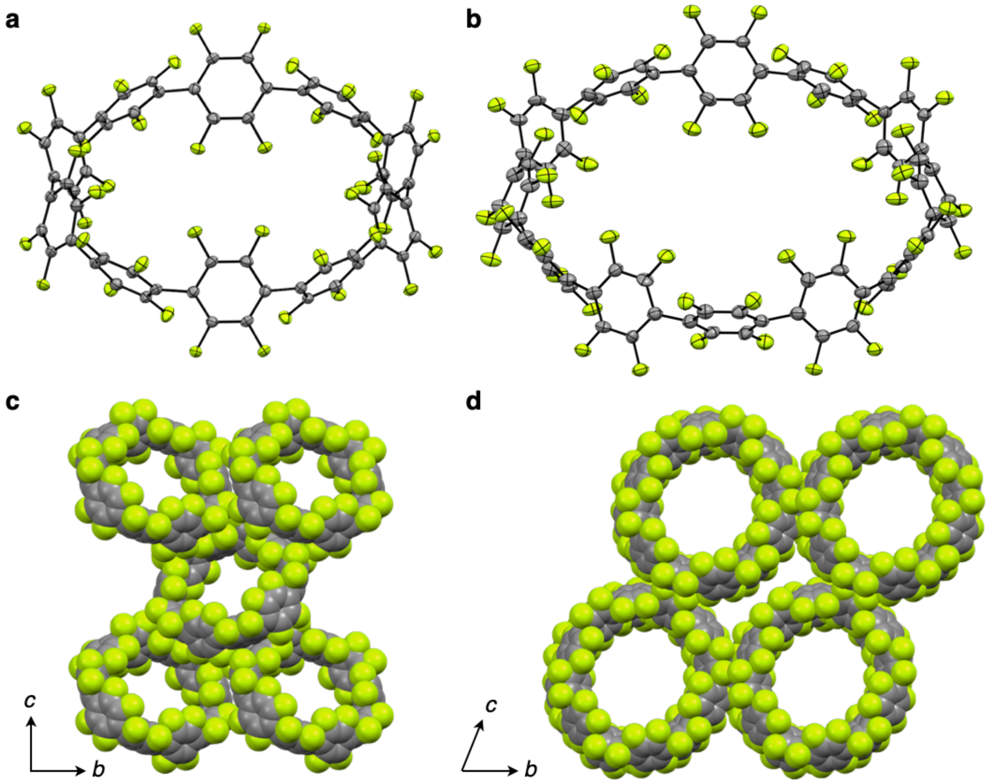


1

2
not isolated

PF[10]CPP: 9.2%
PF[12]CPP: 7.6%
PF[14]CPP: <1%
PF[16]CPP: <1%

Fig. 2. Synthesis of PFCPPs. Reaction conditions: (i) LDA, Ni(dnbpy)Br_2, THF, –78 °C, 30 min; (ii) DDQ, *m*-xylene, 130 °C, 5 h. Abbreviations: LDA = lithium diisopropylamide; dnbpy = 4,4'-di-*n*-nonyl-2,2'-bipyridyl; DDQ = 2,3-dichloro-5,6-dicyano-*p*-benzoquinone.



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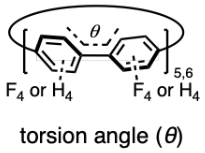

	PF[10]CPP	PF[12]CPP	[10]CPP	[12]CPP
calculated	50.4°	51.3°	32.7°	33.4°
observed	54.7°	55.7°	27.3°	23.3°

Fig. 3. X-ray crystal structures of PF[*n*]CPPs (n = 10, 12). (**a**,**b**) Structures of PF[10]CPP (**a**) and PF[12]CPP (**b**) with thermal ellipsoids at 50% probability. Solvent molecules are omitted for clarity. (**c**,**d**) Packing structures of PF[10]CPP (**c**) and PF[12]CPP (**d**); gray: carbon; green: fluorine. Solvent molecules are omitted for clarity. (**e**) The dihedral angles (*θ*) around the C–C single bonds of PFCPPs and corresponding CPPs. Calculations were performed at the B3LYP/6-31G(d) level of theory. Dihedral angles obtained from X-ray crystallography are averaged.

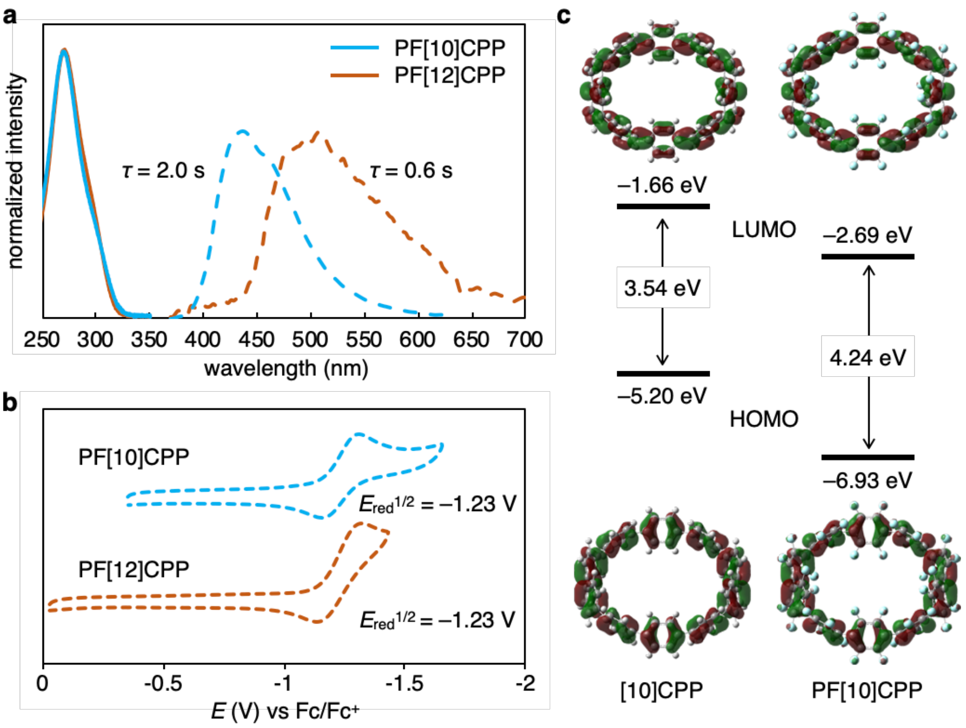

Fig. 4. Photophysical properties of PF[*n*]CPPs (*n* = 10, 12). (**a**) UV-vis absorption spectra of dichloromethane solutions of PF[10]CPP and PF[12]CPP at room temperature (solid lines), and phosphorescence spectra of PF[10]CPP and PF[12]CPP dispersed in PMMA at 16 K upon excitation at 254 nm (dashed lines). (**b**) Cyclic voltammograms of PF[10]CPP and PF[12]CPP in acetonitrile (supporting electrolyte: $[n\text{-Bu}_4\text{N}][\text{PF}_6]$; scan rate: 0.1 V s^{-1}). (**c**) Frontier molecular orbitals (isovalue: 0.02) and their energies (eV) of [10]CPP and PF[10]CPP calculated by B3LYP/6-31G(d) level of theory. PMMA = poly(methyl methacrylate); Fc = ferrocene.

Data availability

Materials and methods, experimental procedures, photophysical studies, and NMR spectra are available in the Supplementary Information. Crystallographic data for the structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre under deposition numbers CCDC 2057897 (PF[10]CPP) and 2057898 (PF[12]CPP). Copies of the data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/.

Additional Information

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Competing interests

The authors declare no competing interests.

[Manuscript Information]

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