ORGANIC LETTERS

XXXX
Vol. XX, No. XX
000–000

Donor–Acceptor Segregated Paracyclophanes Composed of Naphthobipyrrole and Stacked Fluoroarenes

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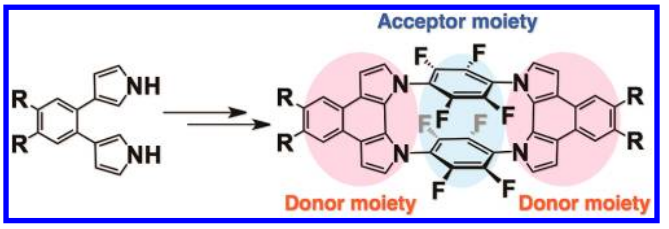
Received March 31, 2013

ABSTRACT



The expeditious synthesis of donor–acceptor segregated paracyclophanes has been achieved by a selective S_NAr reaction of hexafluorobenzene with *o*-dipyrrolylbenzenes and subsequent cyclodehydrogenation. An orthogonally arranged D–A segregated structure was confirmed by X-ray crystallography. The combined results of DFT calculations and absorption spectra revealed the charge transfer (CT) nature from the naphthobipyrrole (donor) to the stacked fluoroarene moiety (acceptor).

Cyclophanes possessing a rigid and stacked structure such as [2,2]paracyclophane have attracted a great deal of attention due to the interest in strongly stacked π-systems.[1,2] Such stacked/strained π-systems are regarded as excellent models for studying not only molecular design and synthesis[3] but also optical and electrical properties.[4] Recently, π-stacked structures have been used in the fields of molecular electronics as (super)conductors and field effect transistors (FET) and molecular photonics as organic light emitting diodes (OLED).[5] Considering electrical conductors and superconductors as well as photovoltaic cells, donor–acceptor segregated structures are a key issue. Such structures have typically been achieved in the solid state as cocrystals or mixed supramolecular assemblies, which resulted in difficulties tuning the crystalline[6] and supramolecular morphologies,[7] respectively. On the basis of these findings,

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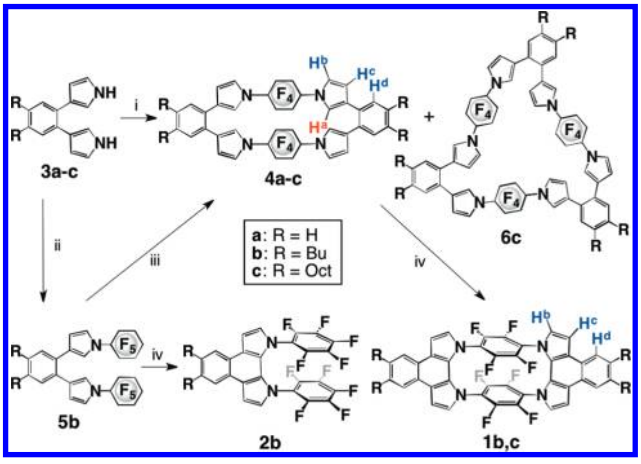
10.1021/ol400882q

we herein report the design and synthesis of a donor–acceptor segregated paracyclophane and its dimer as an initial step toward easily processable and well-defined segregated structures.

The molecular design of donor–acceptor segregated paracyclophane **1** is based on the orthogonally arranged naphthobipyrroles[8] as a donor and the stacked fluoroarenes[9] as an acceptor, where the inter N–N distances are calculated to be ca. 3.4 Å, which is almost the same as the $\pi-\pi$ stacking distance (Scheme 1). Compared to the numerous examples of electron-rich cyclophanes and some D–A cyclophanes,[10] there are only a few examples of electron-deficient cyclophanes composed of stacked or nearly stacked fluoroarenes are still limited.[11]

Scheme 1. Synthesis of Paracyclophane **1** and Clipped Structure **2**[a]



[a] Reagents and conditions: (i) NaH, C_6F_6 (1 equiv) in DMF and THF; (ii) NaH, excess C_6F_6 in DMF and THF; (iii) NaH, **3b** in DMF; (iv) DDQ, $Sc(OTf)_3$ in CH_2Cl_2.

The key step, the synthesis of cyclic precursor **4**, was accomplished by the aromatic nucleophilic substitution (S_NAr) reaction of pyrrolyl anions and hexafluorobenzene,[12] considering the reported examples of regioselective substitutions at the 1 and 4 positions.[9a,13] Utilizing the S_NAr reaction with dipyrrolylbenzene **3c** and hexafluorobenzene, the cyclic structures of both **4c** (17%) and **6c** (25%) were obtained in one-pot (Scheme 1),[14] which were easily isolated by column chromatography or recycling gel permeation chromatography system. Notably, the formation of **6c** seemed to be more favorable than that of **4c** (Figure S3, Supporting Information). Another possible synthetic approach for **4** is a stepwise synthesis via clipped-type compound **5b**. Although a large excess amount of fluoroarene was necessary to obtain **5b** in moderate yield (73%) because of the rapid S_NAr reaction,[12] the cyclic structure **4b** was obtained in 43% yield from **5b**.

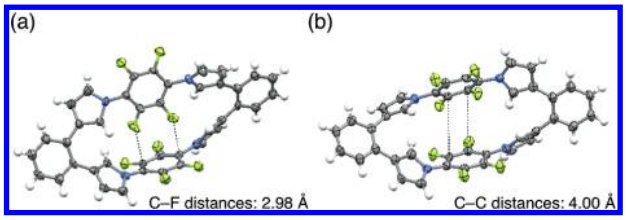


Figure 1. Crystal structures of the two independent conformers of **4a** in the unit cell. Thermal ellipsoids are at 50% probability.

Single-crystal structure analysis of **4a** showed two independent conformers in the unit cell. The fluorobenzene moieties in the two structures are orthogonally crossed with CF-π interactions and are pseudostacked (Figure 1).[15] Variable-temperature (VT) ^{19}F NMR measurements showed that the two fluorobenzene moieties can rotate freely even at −80 °C (Figure S4, Supporting Information).[16,17]

Subsequent cyclodehydrogenation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) and $Sc(OTf)_3$[18] under diluted conditions (0.5 mM) gave the target cyclophanes **1b** (55%) and **1c** (52%) in good yields. The ^1H NMR spectrum of **1c** revealed the absence of H^a protons at the inner α positions of the pyrroles; the other peaks, H^b, H^c, and H^d,

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(15) Single-point DFT calculations for the two geometries indicated that the "pseudo-stacked structure" was slightly more stable by 0.13 kcal mol^{-1} (B3LYP/6-31G(d,p)).

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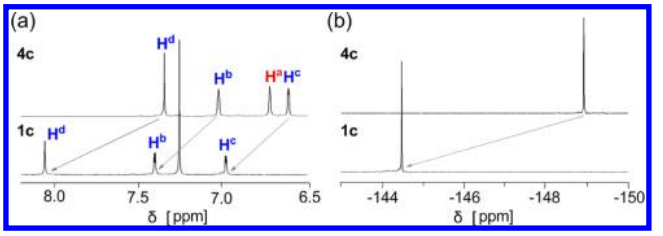

Figure 2. (a) ^{1}H and (b) ^{19}F NMR spectra of **1c** and **4c** in $CDCl_3$.

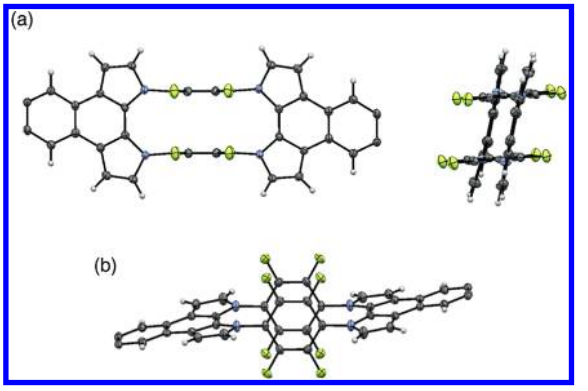

Figure 3. Crystal structure of cyclophane **1b**: (a) side views and (b) top view. Thermal ellipsoids are at 50% probability, and alkyl chains are omitted for clarity.

were shifted downfield, reflecting the expanded conjugation of the naphthobipyrrole moiety (Figure 2a). The ^{19}F NMR spectrum of **1c** also exhibited a low-field shift associated with the transannular reaction due to the effect of steric compression between the two fluorine atoms on the closely packed fluoroarenes (Figure 2b).[19] Similar spectral changes were observed for the clipped-type compounds going from **5b** to **2b**. The tightly stacked fluoroarene structure of **1b** with a D−A orthogonal arrangement was umambiguously revealed by X-ray crystallography (Figure 3). The closest C−C distance of the stacked fluoroarene moiety was 3.19 Å, which is smaller than the sum of the van der Waals radii (3.4 Å), and the dihedral angle between D and A was approximately 70°.

The normalized absorption spectra in THF of **1c**, **4c** and **2b**, **5b** are shown in Figure 4, which revealed broad charge-transfer (CT) absorption bands at 338 and 314 nm for only annulated **1c** and **2b**, respectively. The intramolecular CT nature of **1** and **2** was supported by molecular orbital (MO) calculations at the B3LYP/6-31G(d) level of theory, which showed that the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are substantially localized at the naphthobipyrrole and fluoroarene moieties, respectively (Figure 5). The CT band of **1** appeared at a longer wavelength mainly as a result of the low-lying LUMO of the stacked fluoroarene. Thus, the transannular reaction to form naphthobipyrrole units in both **1** and **2** not only increases the HOMO level but also greatly decreases the LUMO level with the packing of the two fluoroarenes.

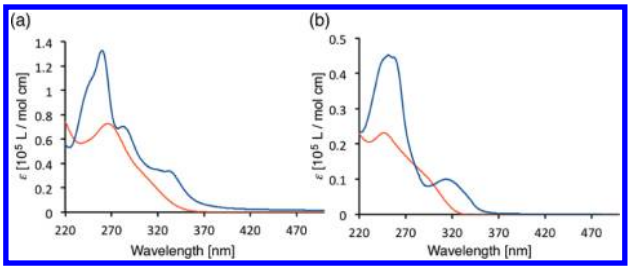

Figure 4. Absorption spectra of (a) cyclophane **1c** (blue) and **4c** (red) and (b) clipped structure **2b** (blue) and **5b** (red) in THF ($[c] = 5.0 \times 10^{-6}$ M).

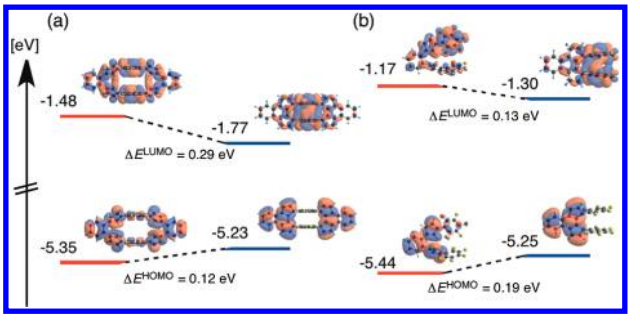

Figure 5. Frontier MO diagrams of (a) **1a**, **4a** and (b) **2a**, **5a** calculated at the B3LYP/6-31G(d) level of theory.

The redox properties of **1c**, **4c** and **2b**, **5b** were investigated using cyclic voltammetry (CV) in CH_2Cl_2 (Table 1). All compounds exhibited irreversible oxidation peaks (Figure S5, Supporting Information). As predicted from the DFT calculations, formation of the naphthobipyrrole unit increased the HOMO levels by 0.06 eV (**1c**) and 0.23 eV (**2b**) and decreased the LUMO levels by 0.30 eV (**1c**) and 0.25 eV (**2b**), which were evaluated based on the first oxidation potentials and the HOMO−LUMO gaps estimated from the absorption spectra, respetively. A much larger decrease

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(20) The rotation barrier was evaluated to be 11−12 kcal mol^{-1} (T_c = 0−25 °C in $C_2D_2Cl_4$) for the F^{a} fluorine atoms labeled in the structure.

Table 1. Redox Potentials of **1c**, **4c**, **2b**, **5b**, and **7c**

	E_{pa}^{ox} (V)[a]	HOMO[b] (eV)	LUMO[b] (eV)	E_g^{expc} (eV)	E_g^{cald} (eV)
1c	0.62, 0.75	−5.42	−2.38	3.04	3.46
4c	0.68	−5.48	−2.08	3.40	3.87
2b	0.71, 0.87	−5.51	−2.39	3.12	3.95
5b	0.94	−5.74	−2.14	3.60	4.27
7c	0.48,[e] 0.76	−5.28	−2.40	2.88	3.35

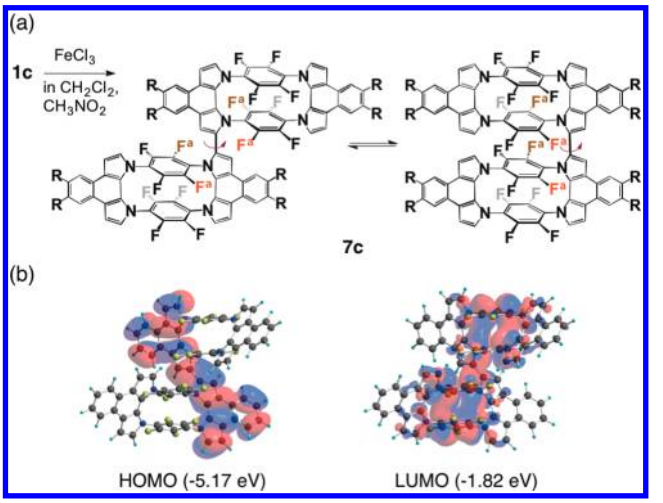
[a] Determined from the cyclic voltammograms in CH_2Cl_2 with 0.1 M n-Bu_4NPF_6 as the supporting electrolyte, $Ag/AgNO_3$ as the reference electrode, Pt as the working electrode, Pt wire as the counter electrode, and a scan rate of 20 mV/s. Potentials are referred to vs Fc/Fc^+ (V). [b] HOMO = $-(E_{ox} + 4.8)$ and LUMO = HOMO + E_g^{exp}. [c] Calculated from the cutoff of the absorption spectra. [d] Calculated at the B3LYP/6-31G(d). [e] Reversible peak.

in the LUMO level was observed in **1c** compared to **2b**, which is consistent with the DFT results (Figure 5).

To demonstrate the structural features of the D−A segregated cyclophane, dimer **7c** was synthesized with $FeCl_3$ in 27% yield (Scheme 2). Because the two cyclophane units are considered to rotate about the "new bond" as depicted in Scheme 2a, VT ^{19}F NMR measurements were conducted (Figure S7, Supporting Information). The splitting observed at lower temperatures indicates that twisted structures with partial stacking between the two stacked fluoroarene moieties are favorable.[20] The DFT optimized structure also showed a twisted structure with a dihedral angle for the two naphthobipyrroles of 96° (Figure S6, Supporting Information). Upon dimerization, one oxidation peak in the CV became reversible and appeared at a lower potential (Figure S5, Supporting Information), and the absorption spectrum showed a long tail into the lower energy region compared to the cyclophane monomer **1c** (Figure S8, Supporting Information, and Table 1). The extended π-conjugation of the HOMO and LUMO for the optimized structure (Scheme 2b) led to the raising and lowering of the HOMO and LUMO levels, respectively. These results clearly indicate that the integration of D−A moieties in a segregated manner was successful even with "mono-linkage" of the cyclophanes.

In summary, we have demonstrated a facile synthesis of donor−acceptor segregated cyclophane **1** in which the selective S_NAr reaction of hexafluorobenzene enabled the straightforward formation of cyclophane structures for the

Scheme 2. (a) Synthesis and Conformational Equilibrium of Cyclophane Dimer **7c** and (b) the Frontier MOs for the DFT-Optimized Structure at the B3LYP/6-31G(d) Level of Theory



first time. On the basis of the orthogonally arranged electron-rich naphthobipyrroles and electron-deficient fluoroarenes, intramolecular CT was demonstrated, and the dimerization of cyclophane **1** revealed the successful integration of D−A segregation. Further studies on synthesizing poly(oligo)meric structures toward *polypyrrole* will allow for realization of proccessable and well-defined D−A segregated structures; such investigations are currently underway.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (No. 23750045) from MEXT, Japan, and a research grant from the Kurata Memorial Hitachi Science and Technology Foundation. We thank Dr. K. Yamashita (Tokyo Metropolitan University) for help with the X-ray crystal structure analysis.

Supporting Information Available. Experimental details and the characterization data for all new compounds; Figure S3−S8; atomic coordinates of the optimized structures of **1a**, **2a**, **4a**, **5a** and **7a** (B3LYP/6-31G(d)); X-ray data for **1b** and **4a** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.