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The conventional π -elongation of open-[60]fullerenes could only give unilaterally π -extended derivatives. Herein, we report the further π -elongation at another site to achieve bilateral π -elongation via a consecutive nucleophilic addition of 4,5-dimethyl-*o*-phenylenediamine. The thus-formed π -extended open-[60]fullerene bears two-fold diaza[*n*]helicene ($n = 5$ and 6) motifs in its skeleton. The crystallographic analysis revealed the characteristic helicene–fullerene interactions with close contacts of 3.09 and 3.14 Å.

Open-[60]fullerenes¹ contain a geodesic polyarene with a formula of C₅₀H₁₀, which was firstly synthesized as the shortest end-cap (5,5) carbon nanotube (CNT) by Scott and co-workers in 2012.² The (5,5) end-cap is a possible template molecule for CNT growth. The chemical vapor deposition in the presence of a mixed carbon source of CH₄/C₂H₄ indeed produced single-walled CNTs with an average diameter of 0.82 nm.³ The similar preprogrammed bottom-up synthesis of CNTs has been demonstrated using unimolecular seeds such as cycloparaphenylene,⁴ truxene derivative,⁵ and open-[60]fullerene,⁶ in which ethanol is usually employed as a carbon source. These methods enable the production of CNTs with atomically-controlled diameters. However, the bay regions in the (5,5) end-cap resist Diels–Alder cycloadditions, thus being far less reactive toward nitroethylene and benzyne.⁷ Therefore, organic synthesis of molecular CNTs with an atomically precise π -conjugation length still remains a formidable challenge.

The consecutive chemical scission of [60]fullerene gives an open-form with a large orifice.¹ This type of open-[60]fullerene could be regarded as a functional π -extended (5,5) end-cap (Fig. 1). Apart from the pristine (5,5) end-cap with a poor reactivity, open-[60]fullerenes are expected to be promising seeds for the growth of molecular CNTs.⁸ The unilateral

Bilateral π -extension of an open-[60]fullerene in a helical manner†

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π -extension of open-[60]fullerenes has been developed by Iwamatsu⁹ and us,¹⁰ independently, in which a fused quinoxaline was introduced to the geodesic π -conjugation (Fig. 1). The related conjugation motifs of such acceptor–acceptor (quinoxaline–open-[60]fullerene) hybrids were also prepared by Gan and co-workers.¹¹ Recently, we synthesized π -extended open-[60]fullerenes with a fused imidazole (Fig. 1),^{10b} showing a notable increase of the absorption coefficients in the visible region owing to donor–acceptor interactions.¹² As exemplified above, open-[60]fullerenes allow us to precisely elongate their π -skeleton in a step-by-step manner while the unilateral π -elongation provides molecular platforms not ideal for the construction of tubular nanostructures. Thereby, multilateral and/or uniform π -elongation from the rim is highly demanded to chemically synthesize molecular CNTs. Herein, we report a bilateral π -elongation of an open-[60]fullerene, giving access to a π -extended (5,5) end-cap with two-fold embedded hetero[*n*]helicene motifs.

Recently, we have reported a unilateral π -elongation of an open-[60]fullerene giving tricarbonyl derivative **1** (Scheme 1).^{10a} We had initially expected the further π -elongation from C(1)=O(1) and C(4)=O(4) groups as footholds via two-fold dehydrative condensation with a suitable aromatic diamine. Thus, the reaction of **1** with 4,5-dimethyl-*o*-phenylenediamine

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Unilateral π -extension

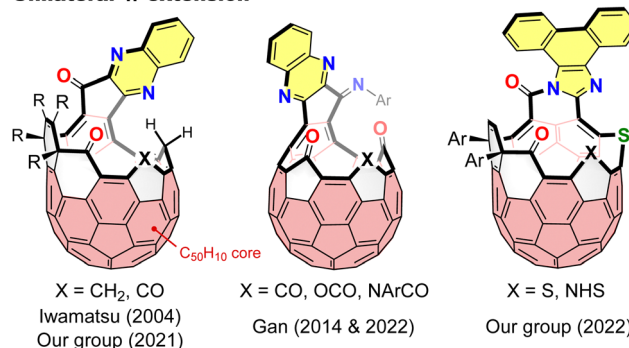
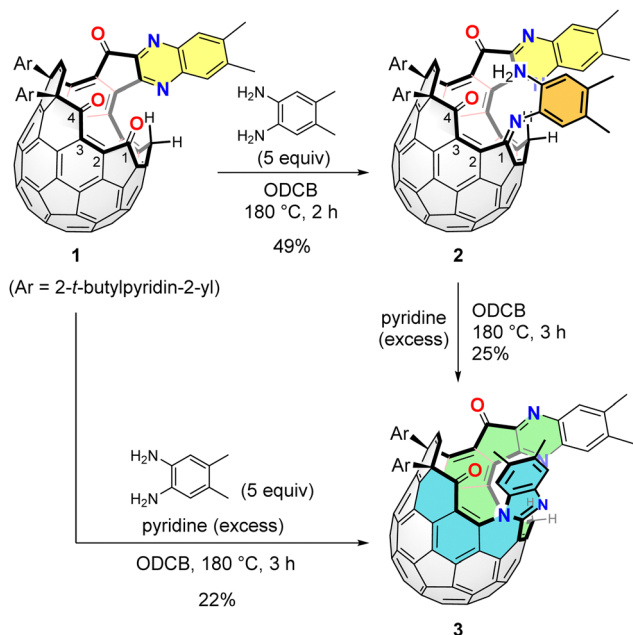


Fig. 1 Unilateral π -extension of open-[60]fullerenes.




 Scheme 1 Synthesis of **3**.

was conducted in *o*-dichlorobenzene (ODCB) at 180 °C for 2 h. As a result, **2** was obtained in 49% isolated yield by a single dehydrative condensation, while the further reaction did not proceed at all (Scheme 1). The high selectivity at the C(1)=O(1) group is simply due to its higher accessibility (Fig. 2a). With

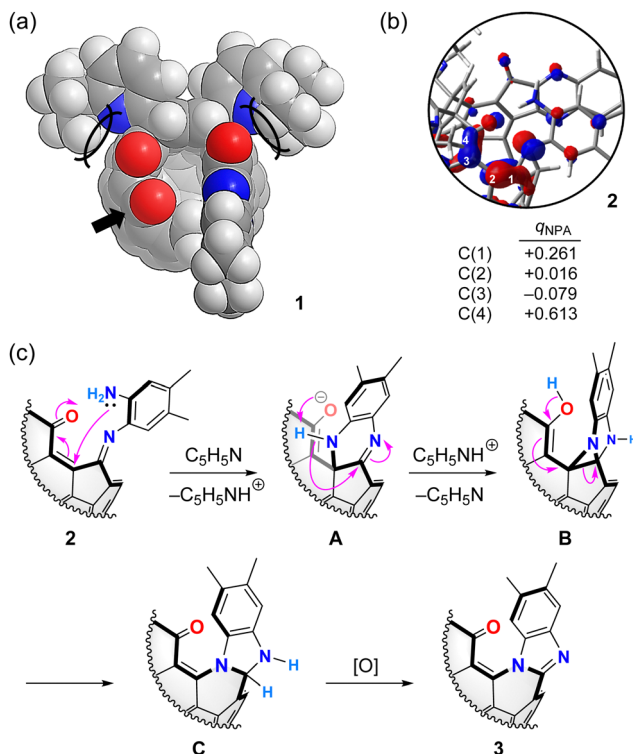


Fig. 2 (a) Optimized structure of **1**, (b) the LUMO+1 of **2** and natural charges q_{NPA} of selected carbon atoms, and (c) plausible mechanism. The calculations were performed at the B3LYP-D3/6-31G(d) level of theory.

the key precursor (**2**) in hand, we then tried the reaction in the presence of pyridine. The mass spectrometric analysis of the product (**3**) showed a molecular ion peak at m/z 1336.3477, which differs from the initially expected compound ($[\text{2-H}_2\text{O}]^{\bullet-}$) but was finally assignable to $[\text{2-2H}]^{\bullet-}$. The absence of the amino group was confirmed by ^1H NMR while ^{13}C NMR spectrum of **3** (201 MHz, acetone- d_6 /CS $_2$ (1 : 5)) clearly indicated the presence of two carbonyl groups at δ 192.00 and 187.42 ppm. These results imply that the reaction occurred at the rim of the orifice undoubtedly with the amino group. The structure of **3** was unambiguously determined by X-ray crystallographic analysis (Fig. 3) and found to have an imidazole ring generated through a nitrogen-insertion between the C(1)–C(2) bond. Upon seeing the LUMO+1, the large orbital coefficient was found at the α,β -unsaturated carbonyl group where the C(2) atom (q_{NPA} +0.016) is more positively charged rather than C(3) (q_{NPA} -0.079) according to the natural population analysis (NPA) (Fig. 2b). Note that the LUMO

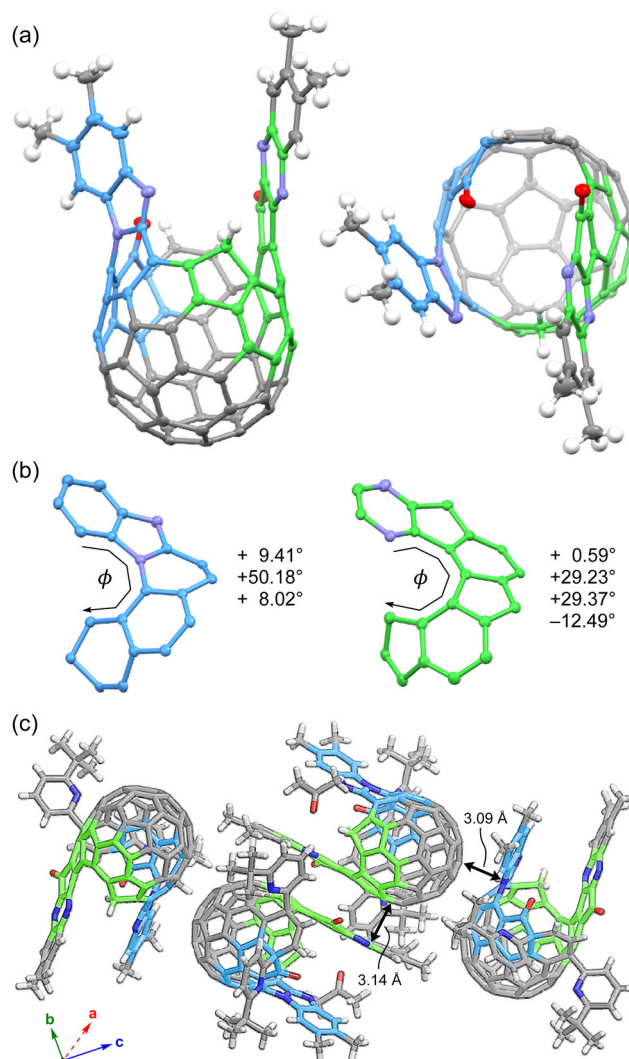


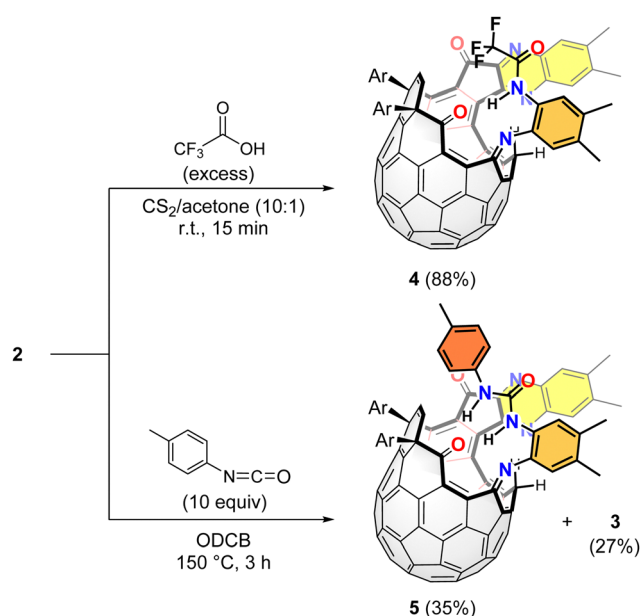
Fig. 3 Single crystal X-ray structures of **3**: (a) side and top views (the aryl groups are omitted for clarity), (b) embedded helical motifs with torsion angles ϕ along helical inner rims, and (c) packing view with contact distances. The solvent and encapsulated molecules are not shown for all views.



has large coefficients on the entire [60]fullerene skeleton. As is the case with the addition of the diamine to **1**, the amino group in **2** is not likely to attack the C(4)=O(4) group due to the steric demand while it undergoes a nucleophilic addition to the C(2) atom, thus giving intermediate **A** which is transformed into **B** via aziridination (Fig. 2c). The subsequent ring-opening reaction allows for the nitrogen atom to be inserted into the rim of the orifice. The thus-formed dihydroimidazole derivative (**C**) is then oxidized to afford imidazole-fused **3**.

The single crystals of racemic **3** were obtained from a CS₂/acetone solution. The solid-state structure for one of the two enantiomers is shown in Fig. 3. It is worth mentioning that the π -elongation was achieved on the geodesic [60]fullerene skeleton in a bilateral manner (Fig. 3a) where the two π -systems are embedded as diaza[*n*]helicenes ($n = 5$ and 6) with a single *P*-helicity (Fig. 3b), while another enantiomer consists of a single *M*-helicity. The torsion angles φ along the helical inner rims indicate the considerably larger distortion of the two helical motifs, when compared with non-substituted carbo[5] and [6]helicenes (16.4, 31.5, and 18.4° and 11.1, 30.1, 31.2, and 15.1°),¹³ reflecting the positive curvature of the [60]fullerene skeleton. Within the crystal, the molecules of **3** are arranged in close proximity with contact distances of 3.09 and 3.14 Å between the helically and spherically π -conjugated motifs (Fig. 3c).

We also examined the chemical transformation of **2** at the amino group (Scheme 2). The reaction of **2** with trifluoroacetic acid smoothly gave the corresponding amide **4** in 88% yield under catalyst-free conditions. Such condensation is known to occur only if aniline is substituted with an electron-deficient group, which prevents it from generating a salt with the acid.¹⁴ In our case, the strong electron-accepting character of the [60]fullerene moiety is considered to make catalysts unnecessary. As another electrophile, we used *p*-tolyl isocyanate, which furnished the corresponding urea derivative **5** in 35% isolated yield together with **3** (27%).



Scheme 2 Synthesis of **4** and **5**.

To get insights into the electronic properties of **1–5**, we measured absorption spectra in benzene (Fig. 4). Compound **6**,¹⁵ which bears two carbonyl groups, was also measured as a reference molecule for evaluating the effect of the π -elongation in **1** and **3**. As shown in Fig. 4a, the first π -elongation (**6** \rightarrow **1**) drastically modulates the absorption properties with increased coefficients over the measured range. The embedded diaza[6]helicene moiety in **1** is well-conjugated with the [60]fullerene skeleton as found in the HOMO–1 and LUMO (B3LYP/6-31G(d)) (Fig. 4c). The second π -elongation (**1** \rightarrow **3**) contributes to a slight increase in absorption at the visible region (Fig. 4a). According to theoretical calculations (Fig. 4c), the HOMO of **3** (–5.48 eV) is dominantly distributed on the aza[5]helicene moiety, which is less conjugated with the [60]fullerene core, while it overrides the level of the original HOMO (–5.69 eV) of **1** by the second π -elongation. The longest wavelength absorption of **3** originates from a charge transfer transition as opposed to **1** showing

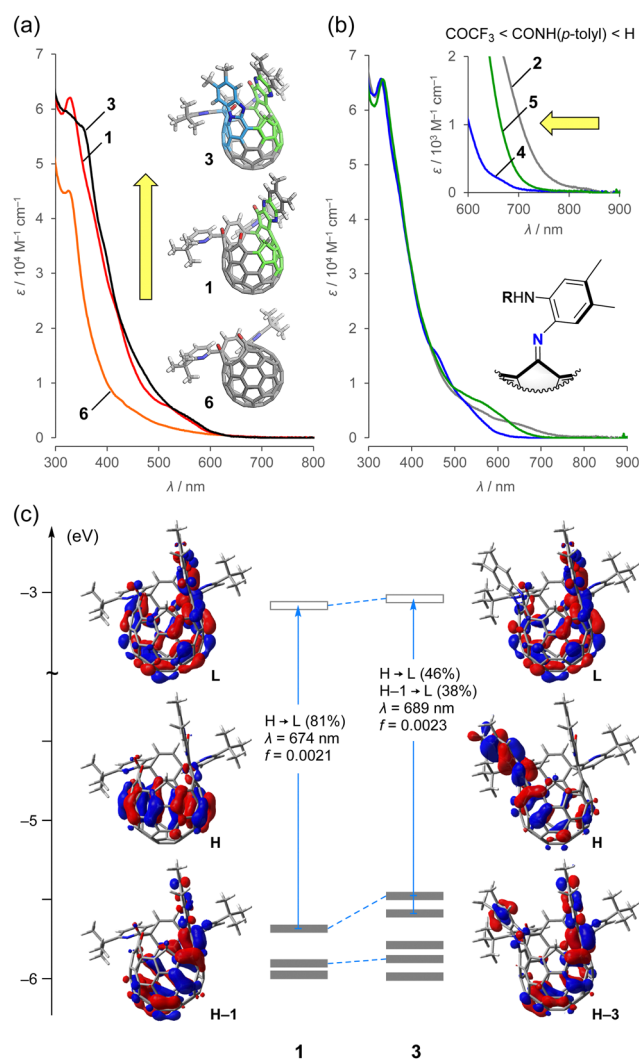


Fig. 4 UV-vis-NIR absorption spectra of (a) **1**, **3**, and **6** and (b) **2**, **4**, and **5** (50 μ M in benzene). (c) Kohn–Sham HOMO and LUMO levels of **1** and **3** with optical transitions (TD CAM–B3LYP/6-31G(d)//B3LYP/6-31G(d)). The transition energies were calibrated with a factor of 0.72.¹⁶



a π - π^* character. Note that the HOMO-3 (-5.88 eV) and LUMO (-3.04 eV) of **3** bear a close resemblance with the HOMO-1 (-5.91 eV) and LUMO (-3.09 eV) of **1**, respectively, without considerable perturbation to their energy levels by the second π -elongation.

The aniline-substituted derivative (**2**) exhibited a near-infrared (NIR) absorption, which tails to 870 nm (Fig. 4b). The absorption edges were hypochromically shifted by varying the substituents: amide (**4**, 750 nm) < urea (**5**, 800 nm) < amine (**2**, 870 nm). The theoretical calculations suggested that the HOMO level is lowered in the order of **2** (-4.96 eV) > **5** (-5.06 eV) > **4** (-5.65 eV), while the LUMO levels are comparable (**2**, -2.97 eV; **5**, -3.12 eV; **4**, -3.08 eV) (B3LYP/6-31G(d)). Thus, the observed hypsochromic shift is ascribed to the magnitude of the donor character on the aniline moiety in **2**, **4**, and **5**.

In summary, we achieved the second π -elongation of a unilaterally π -extended open-[60]fullerene (**1**) by the reaction with 4,5-dimethyl-*o*-phenylenediamine in the presence of pyridine. The structure of the product (**3**) was unambiguously determined by X-ray diffraction analysis, which revealed the bilateral π -elongation from the [60]fullerene core in a helical manner. The two embedded diaza[*n*]helicene (*n* = 5 and 6) moieties are severely distorted due to the positive curvature of the [60]fullerene skeleton. The close contacts between the helical and spherical π -motifs were found at distances of 3.09 and 3.14 Å. In this reaction, **2** is a key intermediate for the formation of **3** and its electronic structure was found to be modifiable by the reaction with electrophiles, thus observing the obvious hypochromic shift in the absorption spectra. Since **3** could be regarded as a π -extended (5,5) end-cap, this approach would open a way to create structurally well-defined molecular CNTs through stepwise chemical reactions.

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Conflicts of interest

There are no conflicts to declare.

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