Tetrahedron Letters 54 (2013) 1607–1611

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Syntheses of N-bridged ferrocene/porphyrin-fullerene dyads and influence of iminofullerene isomers on the attached chromophores

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ARTICLE INFO

Article history:
Received 22 November 2012
Revised 6 January 2013
Accepted 15 January 2013
Available online 21 January 2013

Keywords:
[5,6]-Open azafulleroid
[6,6]-Closed aziridinofullerene
Ferrocene
Porphyrin

ABSTRACT

N-Ferrocene (**Fc**)/porphyrin (**Por**) [5,6]-open azafulleroids and [6,6]-closed aziridinofullerenes have been synthesized for the first time. Electrochemical measurements revealed that chromophores attached to [5,6]-open azafulleroids are more easily oxidizable than those attached to [6,6]-closed aziridinofullerenes. This was attributed to the delocalization degree of the nitrogen lone-electron pair involved in aziridinofullerene that is larger than that in azafulleroid.

[60]Fullerenes have attracted wide attention because of their excellent electronic properties such as high electron affinity, small reorganization energy, and high singlet oxygen quantum yield, and have been widely applied in photovoltaics, organic field-effect transistors, nonlinear optics, and biological area.[1] Great efforts are being continuously devoted to achieving new fullerene derivatives for specific function.[2] Many fullerene modification methodologies have been developed, including hydrogenation, transition metal complex formation, nucleophilic addition, radical addition, and cycloaddition.[3] Among them, treating fullerene with organic azide has been recognized as a convenient and practical way to complete the modification because of its easy preparation, and good tolerance to water and oxygen.[4,5]

A series of organic azides have been applied in the syntheses of iminofullerenes, such as alkyl azides,[6] simple aryl azides (phenyl, naphthyl, pyrenyl),[7] sulfonyl azides,[8] and tetrafluoroarylazides.[9] They can react facilely with fullerene to yield [6,6]-closed aziridinofullerenes or [5,6]-open azafulleroids through a nitrene addition or a 1,3-dipolar cycloaddition reaction.[10] In most cases, a mixture was obtained simultaneously, and the ratio of [6,6]-closed aziridinofullerenes to [5,6]-open azafulleroids is greatly dependant on the nature of the introduced substituent.[6f] Further exploring shows that the N-substituted group has a significantly remote control effect on the features of the excited states of fullerene.[7] Taking the mutual interaction into account, the distinction between the inherent electronic properties of [5,6]-open azafulleroids and [6,6]-closed aziridinofullerenes is reasonably suggested to result in a different influence on the electronic features of the N-substituted groups.[11] Shinkai and co-workers had found that a slight difference in the electron density of the nitrogen atom ([5,6]-open vs [6,6]-closed) can cause a dramatic change of its guest affinity.[12] But to the best of our knowledge, there is no more example to explore the influence of the fullerene π system ([5,6]-open and [6,6]-closed) on its attached molecule, which may guide us to find a broadened approach to improve the practical application of fullerene.

Herein, we report the syntheses of **Fc**- and **Por**-iminofullerene dyads through treating fullerene with the corresponding azides. Due to the rich electronic active properties of **Fc** and **Por** and their sensitivities to the adjacent substituents,[13] the constructed dyads provide us a convenient visualization tool to estimate the influence of the iminofullerene.

The ferrocenylazide was first introduced to react with fullerene in chlorobenzene at 130 °C according to the literature method,[6–9] but only insolubles were obtained probably because of the instability of ferrocenylazide.[14] The reaction temperature was then reduced to 60 °C, a main product with 16% yield was got and identified to be [6,6]-closed aziridinofullerene **1b** (Scheme 1). A molecule ion peak $[M]^+$ was observed at 919.013 *m*/*z* (MALDI), and the ^{13}C NMR spectrum reveals 17 signals between 146 and 124 ppm and one sp^3 resonance at 85.4 ppm (Fig. S9, **1b**) indicating a C_{2v}-symmetry of fullerene and a [6,6]-closed form.[6g,8] This structure might come from a [2+1] nitrene addition procedure instead of a [3+2] cycloaddition because the thermal instability of ferrocenylazide and a [5,6]-open form is usually the major product in a [3+2] cycloaddition reaction according to the reported work.[10]

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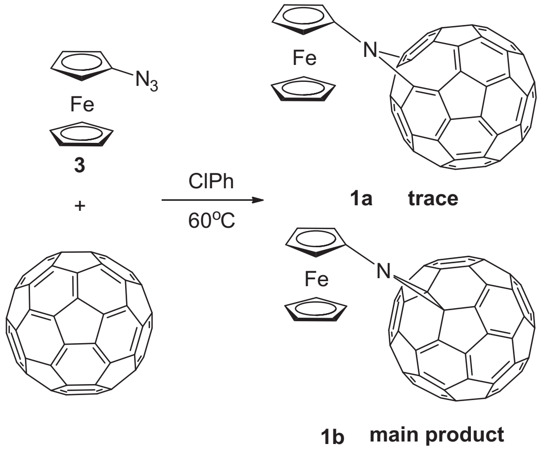
0040-4039/$ - see front matter
http://dx.doi.org/10.1016/j.tetlet.2013.01.061



Scheme 1. Preparation of *N*-ferrocene [5,6]-open azafulleroid **1a** and [6,6]-closed aziridinofullerene **1b**.

Besides aziridinofullerene **1b**, a trace amount of compound **1a** with a less polarity was also obtained. It has the same molecular ion signal $[M]^+$ at 919.009 as **1b**. Comparing to **1b**, there is no aliphatic carbon signal observed, and a total of 32 signals of fullerene appear at 148–124 ppm (Fig. S9, **1a**), indicating that product **1a** has a C_s-symmetry and should be a [5,6]-open azafulleroid. The [5,6]-open product may be generated through a direct addition of singlet nitrene to [5,6]-ring junctions proposed by the previous theoretical calculations.[10,15]

As shown in Scheme 2, the porphyrin-fullerene dyads **2a** and **2b** were obtained by the reaction of azidophenylporphyrin **4** and C_{60} in chlorobenzene at 130 °C for 9 h. The isomers **2a** and **2b** were both separated in 12% yield. The MALDI mass spectrometry gave $[M+H]^+$ peak of 1685.6266 for **2a** and 1685.6237 for **2b**. The ^{13}C NMR spectra reveal that **2a** and **2b** have a different C_{60}-symmetry, C_s-symmetry for **2a** and C_{2v}-symmetry for **2b**. A sharp peak at 82.9 ppm found in the aliphatic region of **2b** demonstrates that compound **2b** stands as a [6,6]-closed form. Unlike the [2+1] nitrene addition of **Fc**–N_3, **Por**–N_3 might prefer a 1,3-dipolar cycloaddition of azide to the 6,6 double bond of the fullerene to form the intermediate triazoline, subsequently thermal cleavage of N_2 to afford the [5,6]-open azafulleroid and [6,6]-closed aziridinofullerene.[10]

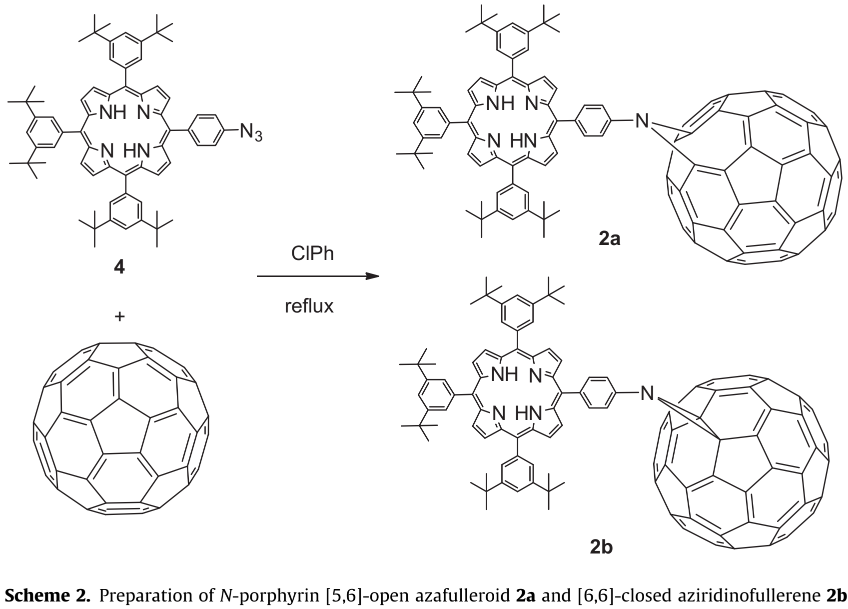
The UV/vis absorption spectra of **1** (1.5×10^{-5} M) and **2** (2×10^{-6} M) in toluene are shown in Figures S22 and S23, and the absorption data are listed in Table 1. The characteristic absorption for aziridinofullerene derivatives was observed at 427 nm for **1b**. The absorption of fullerene moiety in both azafulleroids **1a** and **2a** is bathochromically shifted compared to the corresponding aziridinofullerenes **1b** and **2b**. Meanwhile, the absorption of porphyrin moiety in **2a** shows slight but unambiguous 1 nm red shift than that of porphyrin in **2b**. This difference should result from the distinction of two iminofullerene types, since there is only a slight difference of structure between **2a** and **2b**.

Further examination was done by cyclic voltammetry to estimate the ground state electronic interaction between fullerene and the attached chromophore (**Fc** or **Por**). The cyclic voltammograms of porphyrin-fullerene dyads are shown in Figure 1. The experiments were carried out in benzonitrile at room temperature and the data are summarized in Table 2. The structures of reference compounds are shown in Scheme 3.

For **Fc**-fullerene dyads, three quasi reversible one-electron reduction waves were observed for **1a** (−0.931, −1.355, −1.805 V) and **1b** (−0.932, −1.368, −1.805 V) corresponding to the first three reduction processes of C_{60}. The porphyrin-fullerene dyads were found to have the similar fullerene reduction waves at −0.935, −1.337, −1.832 V for **2a** and −0.937, −1.303, −1.818 V for **2b**, and two additional reduction waves at −1.701, −2.076 V for **2a** and −1.685, −2.066 V for **2b** which were assigned to the reduction of porphyrin moiety by comparing with the reference compound **6**. The similar reduction potentials between azafulleroids and aziridinofullerenes can be rationalized by Wuld's result, the reduction potentials of functionalized C_{60} had been ascribed to come from a combinational effect of the nature of the bridge nitrogen and the binding mode of fullerene.[6f]

Interestingly, the oxidation potentials of the isomers show a dramatic change between [5,6]-open and [6,6]-closed forms. The one-electron oxidation potential of **1a** is observed at −0.056 V, 64 mV negative shift than that of **1b** at 0.008 V. Same tendency was also found in dyads **2a** and **2b**, and the oxidation potential of **2a** is evaluated to be 50 mV cathodic shift than that of **2b**. The electrochemical test reveals that chromophores attached to [5,6]-open azafulleroids are more easily oxidizable.

The oxidation potential of **Fc** and **Por** is strongly sensitive to the adjacent substituent, and has been broadly used as a detection



Scheme 2. Preparation of *N*-porphyrin [5,6]-open azafulleroid **2a** and [6,6]-closed aziridinofullerene **2b**.