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Highly Regio- and Stereoselective [2+3] Cycloadditions of Azomethine Ylides to [70]Fullerene

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Picolylamines and aromatic aldehydes were used as reagents to generate azomethine ylides that undergo highly regio- and stereoselective [2+3] cycloaddition reactions with [70]fullerene. Isolated pyrrolidinofullerenes were products of the ylide addition across the most reactive 8,25-double bond in the carbon cage; other regioisomers were observed in small amounts or did not form at all. These reactions demonstrated unusually high stereoselectivity: 2′,5′-disubstituted pyrrolidinofullerenes were represented almost entirely by *cis* isomers, whereas obtained 1′,2′,5′-trisubstituted products were shown to be *trans* isomers. Cyclic voltammetry studies of the synthesised pyrrolidinofullerenes showed the existence of some electronic communication between the substituents in the pyrrolidine ring and the [70]fullerene cage.

Introduction

Organic derivatisation of fullerenes now plays a very important role in the design of novel carbon-based materials for nanoelectronics and water-soluble fullerene compounds that can find pharmaceutical applications.[1,2] The impact of fullerene chemistry on material science is reflected in the appearance of a number of companies that produce specific fullerene derivatives or use them in the development of organic electronic components such as solar cells, field-effect transistors, logical circuits and so on.[3,4] Therefore, the search for novel methods that can be used in the preparation of specific types of fullerene compounds is still a relevant task.

Organic chemistry of [60]fullerene is deeply explored and a number of convenient routes were suggested for the preparation of a variety of different compounds.[5] However, this is not the case for [70]fullerene, which is less abundant and less symmetrical in comparison with C_{60}. The most typical protocols that are applicable to C_{60} yield almost inseparable mixtures of regioisomeric products with C_{70}.[6] In just a few cases, isomerically pure products were obtained by reagent addition across the most reactive 8,25-double bond (1,2-bond according to Taylor nomenclature).[7] Among them, the addition of sulfonium ylides to C_{70} gave the best results.[8] Radical additions of peroxide groups and halogen atoms to C_{70} also proceed with high selectivity to yield mainly multiaddition products such as $C_{70}R_8$ and $C_{70}R_{10}$ (R = Cl, Br, *t*BuOO, etc).[9] However, all these reactions appear impractical for wide synthetic utilisation. To the best of our knowledge, stereoselective cycloaddition reactions have not been reported for C_{70}.

Recently, we found that various substituted and nonsubstituted picolylamines in combination with aldehydes can be used for the generation of azomethine ylides in [2+3] cycloaddition reactions with [60]fullerene.[10] This method gives pyrrolidinofullerenes with unusually high yields and stereoselectivity. Some of the synthesised *cis*-2′,5′-disubstituted and *trans*-1′,2′,5′-trisubstituted pyrrolidinofullerenes bearing chelating pyridyl groups were utilised as materials for solar cells.[11] Fullerene C_{70} and its derivatives have stronger and wider absorptions in the visible range of the spectrum relative to their C_{60}-based congeners; therefore, materials based on [70]fullerene are more interesting for solar cell applications.[12] In this paper we used picolylamine for the functionalisation of C_{70} to obtain specific derivatives possessing chelating pyridyl groups that can be useful as materials, in particular, for photovoltaic devices.

Results and Discussion

First, nonsubstituted 2- and 3-picolylamines were tested as reagents for the synthesis of symmetrically substituted pyrrolidinofullerenes (Scheme 1). The reaction of 2-picolylamine with 2-pyridinecarbaldehyde and C_{70} was accomplished within just a few minutes and afforded pyrrolid-

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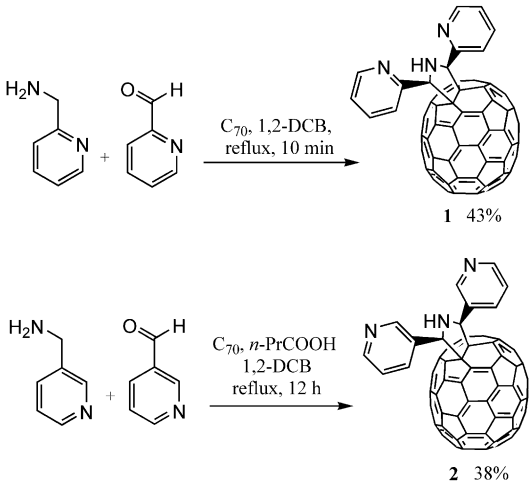
inofullerene **1** in 43% yield. The reaction of 3-picolylamine with 3-pyridinecarbaldehyde required the addition of butyric acid as a catalyst and continuous heating at reflux in 1,2-dichlorobenzene. A similar trend in the reactivities of 2- and 3-picolylamines was observed previously when C_{60} was used as the substrate.[10]



Scheme 1.

The NMR spectroscopic characterisation of the isolated 2′,5′-disubstituted pyrrolidinofullerenes revealed the presence of just one major component in each sample and the content of impurities (presumably isomers of **1** and **2**) was less than 10%. Previously known [2+3] cycloaddition reactions involving [70]fullerene afforded three isomeric products that were unsubstituted at the 2′- and 5′-positions by azomethine ylide additions across the 8,25-, 9,10- and 11,12-double bonds of the cage. For 2′,5′-disubstituted pyrrolidinofullerenes, many more isomers can be expected. Even if enantiomers are not considered, nine stereoisomers can be drawn for products with 8,25-, 9,10- and 11,12-addition patterns (Figure 1). These include two diastereomers (*cis* and *trans*) for the 8,25-addition product, three for the 9,10- and four for the 11,12-addition products. As shown in Scheme 1, reactions yield just one major product, and therefore, such selectivity is quite remarkable. ^{1}H NMR spectra revealed the presence of some other isomers as minor impurities in the samples that could not be separated from the major product.

Pyrrolidinofullerenes **1** and **2** were characterised by ^{1}H NMR and ^{13}C NMR spectroscopy. The ^{1}H NMR spectra showed that the two pyridyl groups are nonequivalent in pyrrolidinofullerenes **1** and **2**. The ^{13}C NMR spectra revealed 75–78 signals due to the sp^2 carbons of the fullerene cage and the pyridyl units as well as four peaks corresponding to the sp^3 carbon signals (two fullerene bridgehead carbon atoms and two pyrrolidine ring *C*-H). The assignment of some signals in the spectra was confirmed by 2D H–C NMR spectra (HSQC). On the basis of the spectroscopic data obtained, a conclusion about C_1 molecular symmetry of the isolated compounds was made. This allows one to

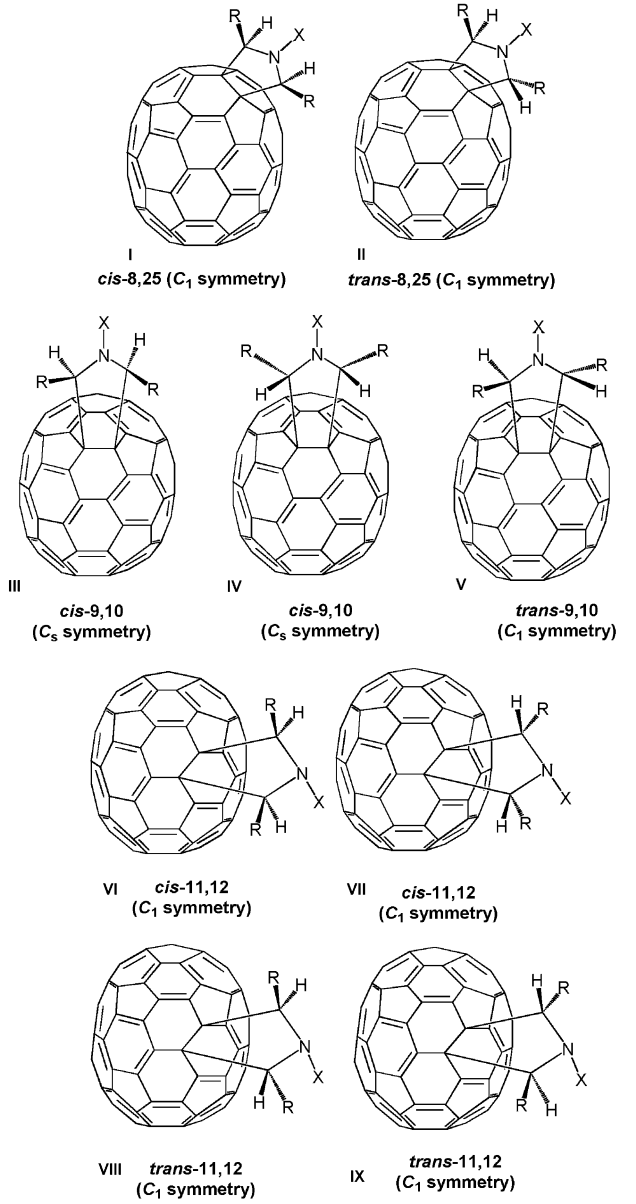


Figure 1. Molecular structures of the eight isomers of 2′,5′-disubstituted pyrrolidine derivatives of C_{70} that can potentially be formed in the studied reactions.

rule out some C_S-symmetrical structures shown in Figure 1. However, a question about the molecular structures of **1** and **2** remains unresolved.

UV/Vis spectra of isomeric C_{70} adducts are known to be very characteristic and uninfluenced by the nature of addends attached to the cage.[13] The UV/Vis spectra of **1** and **2** were very similar to the spectra of other known C_{70}-based compounds with an 8,25-addition pattern.[13] Therefore, it is very reasonable that **1** and **2** should also be considered as 8,25-addition products because the 8,25-bond is the most reactive one in the [70]fullerene cage.

Pyrrolidinofullerenes **1** and **2** can have a *cis* or *trans* arrangement of the pyridyl units with respect to the pyrrolidine ring (Figure 1, structures **I** and **II**). To determine con-

figuration of the substituents, 2D ROESY and NOESY NMR spectroscopic experiments were performed on **1** and **2**. As a result, a clear correlation was observed between two signals of nonequivalent methine protons of the pyrrolidine ring (Figure 2). This is a univocal proof of the *cis* arrangement of these two protons with respect to the pyrrolidine ring. Thus, pyrrolidinofullerenes **1** and **2** have molecular structures with a *cis* arrangement of the pyridyl groups represented by drawing **I** in Figure 1.

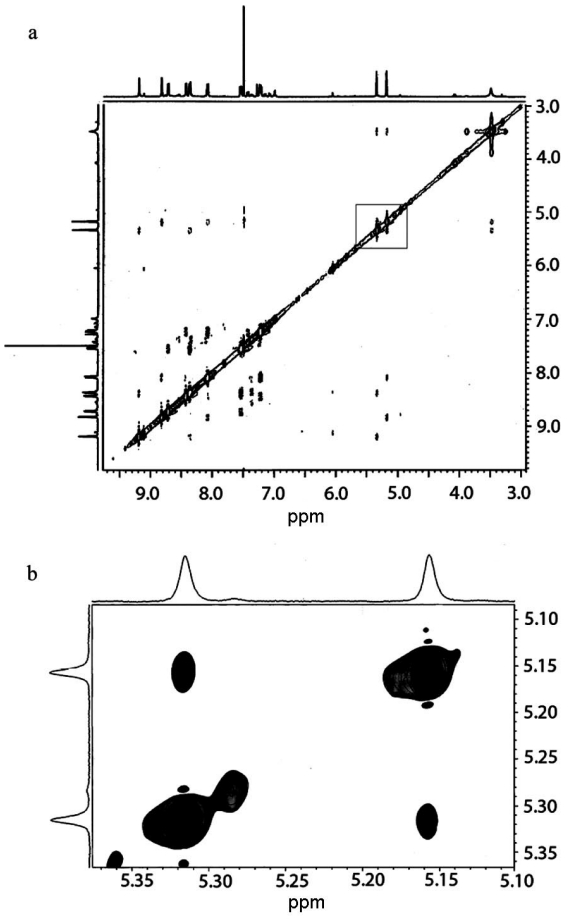
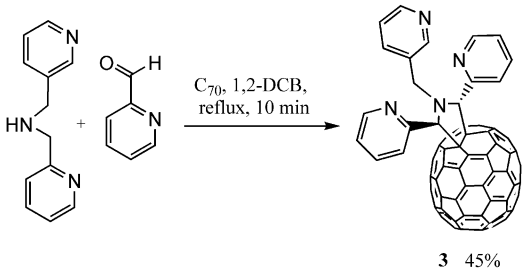


Figure 2. (a) Full-range H–H NOESY NMR spectrum of **2**; (b) enlarged part of the spectrum (marked by the rectangle on the full-scale spectrum) illustrating couplings between signals of the methine protons.

A 1,2,3-trisubstituted azomethine ylide generated in situ from 2-picolyl-3-picolylamine and 2-pyridinecarbaldehyde reacted smoothly with C_{70}. Chromatographic separation resulted in isolation of pyrrolidinofullerene **3** in 45% yield together with unreacted C_{70} and a mixture of polyaddition products (Scheme 2). NMR spectroscopic characterisation revealed that the isolated sample of pyrrolidinofullerene **3** contained a single component with a specific regio- and stereoisomeric pattern without any detectable impurities of other products. At the same time, no other products (such as other possible isomers of **3**) were observed as separately eluted fractions in the course of the chromatographic separation. This implies that the formation of pyrrolidinofullerene **3** is even more selective in comparison with the similar reactions yielding **1** and **2**.



Scheme 2.

The structure of **3** is more sterically crowded relative to those of **1** and **2**. Therefore, rotation around of any of the single bonds in the NCH_2–(3-pyridyl) moiety is restricted, which results in splitting of the signal from the CH_2 group into two doublets in the ^1H NMR spectrum (Figure 3). It seems that inversion of configuration of the pyrrolidine nitrogen atom is also restricted, which is reflected in some broadening of the signals due to the two methine protons (C*H* units of the pyrrolidine ring). More or less the same effects were observed for all previously prepared 1,2,5-trisubstituted pyrrolidine derivatives of C_{60}.[10]

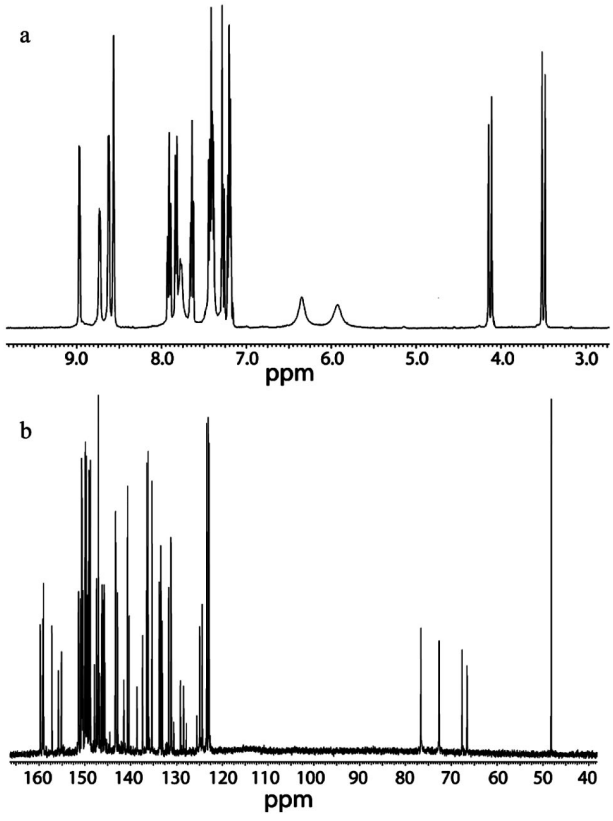


Figure 3. (a) ^1H NMR and (b) ^{13}C NMR spectra of **3**.

Both the ^1H and ^{13}C NMR spectra revealed C_1 molecular symmetry of pyrrolidinofullerene **3** and the confirmed high compositional purity of the material obtained. The

UV/Vis spectrum (not shown) of **3** was virtually identical to the spectra of **1** and **2**; therefore, a conclusion about the 8,25-addition pattern was made. To prove either the *cis* or *trans* addend configuration in **3**, 2D NOESY NMR spectroscopic experiments were performed. No correlation was detected between the two pyrrolidine ring methine protons in the spectrum obtained (empty rectangles in Figure 4). Therefore, pyrrolidinofullerene **3** most probably has a *trans* configuration of the pyridyl substituents in the pyrrolidine ring (Figure 1, structure **II**). It should also be noted that the *trans* configuration was previously assigned to 1′,2′,5′-trisubstituted pyrrolidine derivatives of C_{60} on the basis of the interpretation of the ^{1}H NMR spectroscopic data.[10] The signals due to the methine protons of the pyrrolidine ring are ca. 1.0 ppm downfield shifted for the *trans* isomers relative to those of the *cis* isomers. The same chemical shift difference is observed between compound **3** on the one side and **1** and **2** on the other. The preferable formation of the *cis*-2′,5′-disubstituted and *trans*-1′,2′,5′-trisubstituted pyrrolidinofullerenes was explained previously by using semiempirical theoretical calculations.[10]

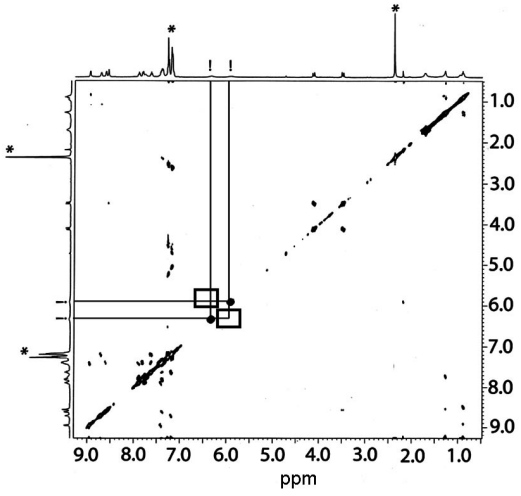


Figure 4. Full-range H–H NOESY NMR spectrum of **3**. Symbol "!" denotes signals of the pyrrolidine ring methine protons, symbol "*" denotes residual toluene signals (most probably, it was trapped in the crystal lattice of solid **3**). Rectangles show regions where correlations between signals of nonequivalent methine protons should appear.

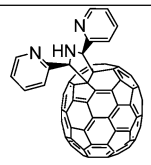
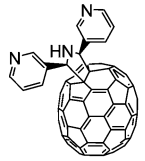
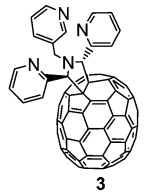
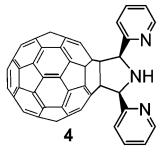
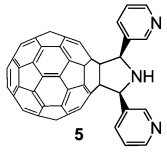
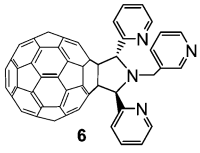
Summarising the obtained synthetic results, it should be noted that the use of picolylamines as reagents for the generation of the azomethine ylide allows both the regio- and stereoselectivity of the [2+3] cycloaddition reactions involving a C_{70} substrate to be controlled. It seems that the reason for such a high stereoselectivity of these reactions is in the thermodynamic equilibration of the intermediate azomethine ylide configurations.[10] Thus, it was shown before for similar reactions with C_{60} that the W-shaped conformation of the 1,3-disubstituted azomethine ylides is more stable than the S-shaped conformation. Therefore, the addition of the ylides in the W-form mainly takes place to afford *cis*-2′,5′-disubstituted pyrrolidinofullerenes. For 1,2,3-trisubstituted ylides, three configurations are possible and the S-shaped one is the most stable. The addition of the S-ylides to fullerene affords *trans*-1′,2′,5′-trisubstituted pyrrolidinofullerenes, which was indeed observed before with the use of C_{60} as the substrate[10] and in this work for reactions involving C_{70}. The origin of the high regioselectivity of the investigated reactions is not clear. Initially, we believed that the addition of the azomethine ylides to the [70]fullerene cage is thermodynamically controlled. However, AM1 semiempirical calculations showed that for compound **1**, for example, the most stable isomer is designated by **V** (Figure 1). The actually formed product (form **I**) was 15 kcal mol^{-1} less stable. Perhaps the AM1 calculations do not give relevant information on the relative stability of isomers **I-VIII** shown in Figure 1. In this case, some higher level calculations (DFT) should be applied in the future to clarify if the studied reactions reach thermodynamic equilibrium or not. Another explanation is that the ylide addition across the 8,25-double bond is kinetically much more favoured than additions across other double bonds.

Cyclic voltammetry studies were performed for compounds **1**–**3** and C_{60} derivatives **4**–**6** to compare their electronic properties. The cyclic voltammograms of **1**–**3** recorded in 1,2-dichlorobenzene exhibited three reversible and forth irreversible reduction waves. At the same time, only three reductions were observed for the C_{60}-based compounds. The calculated reduction potentials are given in Table 1 (values vs. SCE). It is notable that there is no observable difference in the first reduction potentials between equally substituted pyrrolidine derivatives of C_{70} and C_{60}. The difference becomes well pronounced only for third reduction potentials.

Previously, we performed cyclic voltammetry studies on a range of substituted pyrrolidine derivatives of C_{60} and found that introduction of a 2-pyridyl group to the 2′- or 5′-position of the pyrrolidine ring somewhat shifts the first reduction potential of the compound to more negative values.[10] As follows from Table 1, this is also true for investigated compounds **4** and **5** in this work as well as for their C_{70}-based relatives **1** and **2**. The reduction potentials of the compounds bearing two 3-pyridyl groups are ca. 20–30 mV more positive relative to those of the corresponding pyrrolidinofullerenes possessing two 2-pyridyl units. We explain this effect by steric proximity of the nitrogen atoms of the 2-pyridyl substituents to the carbon cage. This might result in some interaction of the nitrogen lone pair of electrons with the electron-deficient fullerene π system.

Interestingly, compounds **3** and **6** have even more negatively shifted reduction potentials than **1** and **4**, though they differ only by the substituent attached to the nitrogen atom (H or 3-picolyl) and the configuration of the two 2-pyridyl units at the 2′- and 5′-positions of the pyrrolidine ring. It seems that the 3-picolyl substituent cannot afford any electron donation through the sequence of single bonds, but perhaps the nitrogen lone pair of electrons can interact directly with the fullerene π system. Another explanation can be that by changing the *cis* configuration to a *trans* configu-

Table 1. Cyclic voltammetry data for pyrrolidinofullerenes **1**–**6** (values vs. SCE).

Compound	Reduction potentials			
	$E^1_{1/2}$	$E^2_{1/2}$	$E^3_{1/2}$	E^4_p [a]
 **1**	–0.76	–1.17	–1.54	–2.08
 **2**	–0.75	–1.15	–1.53	–2.00
 **3**	–0.78	–1.18	–1.57	–2.10
 **4**	–0.76	–1.14	–1.67	–
 **5**	–0.74	–1.14	–1.67	–
 **6**	–0.78	–1.18	–1.73	–

[a] The peak potentials are given for irreversible reductions.

ration somehow improves the electron communication between the electron lone pairs of the 2-pyridyl units and the fullerene cage.

Summarising the electrochemical data, the existence of some (though rather weak) electronic communication between the substituents in the pyrrolidine ring and the fullerene π-system was observed. This effect can be useful for the improvement of the characteristics of organic fullerene-based photovoltaic devices (increase in the open-circuit voltage).[14]

Conclusions

An efficient route for the highly regio- and stereoselective synthesis of organic derivatives of [70]fullerene was designed. This method can potentially be used for the synthesis of various C_{70}-based compounds for different kinds of applications. In particular, three novel pyrrolidinofullerenes reported here possess two or three chelating pyridyl groups that make them attractive precursors for the preparation of complexes with transition metals, noncovalently linked dyads with metallated porphyrins, phthalocyanines and so on. We have already utilised **1**–**3** as acceptor materials for organic solar cells, where these compounds showed appreciable performances.[15]

Experimental Section

Materials and Instrumentation: All reagents and solvents were purchased from Acros Organics and used as received. Absorption spectra were recorded with a SPECORD UV/Vis spectrophotometer. NMR spectra were recorded with AMX 400 or Avance 600 Bruker instruments with the solvent residual proton signal or tetramethylsilane (TMS) as a standard.

Cyclic Voltammetry: Measurements were performed for a solution of the fullerene derivative in 1,2-dichlorobenzene (ca. 1×10^{-3} M) in a cell equipped with a glassy carbon working electrode ($d = 2$ mm^2), platinum wires as counter electrode and SCE as a reference electrode. Scan rate was 200 mV s^{-1}. A solution of Bu_4NPF_6 (0.1 M) was used as a supporting electrolyte.

Pyrrolidinofullerene 1: Fullerene C_{70} (300 mg, 0.36 mmol) was heated at reflux with 2-picolylamine (50.2 mg, 0.46 mmol) and 2-pyridinecarbaldehyde (0.1 mL, 1.05 mmol) in 1,2-dichlorobenzene (50 mL) for 10 min. After cooling, the reaction mixture was diluted with toluene (50 mL) and poured onto a silica gel column (40–60 μ, 60 Å). Elution with toluene/MeOH (99.5:0.5) afforded **1** in 43% yield (159.2 mg). ^{1}H NMR [400 MHz; CS_2/$(CD_3)_2CO$, 9:1]: δ = 4.78 (t, J = 12.6 Hz, 1H), 5.30 (d, J = 12.6 Hz, 1 H), 5.42 (d, J = 12.6 Hz, 1 H), 7.21 (dt, J = 7.6, 2.3 Hz, 1 H), 7.49 (dt, J = 5.0, 1.2 Hz, 1 H), 7.51 (d, J = 8.3 Hz, 1 H), 7.66 (dt, J = 7.8, 1.6 Hz, 1 H), 7.96 (d, J = 7.8 Hz, 1 H), 8.03 (dt, J = 7.6, 1.6 Hz, 1 H), 8.61 (d, J = 4.6 Hz, 1 H), 8.88 (d, J = 4.6 Hz, 1 H) ppm. ^{13}C NMR [150 MHz; CS_2/$(CD_3)_2CO$, 9:1]: δ = 72.17, 73.97, 76.18, 78.97, 123.10, 124.37, 128.43, 130.82, 131.13, 131.16, 131.20, 131.26, 131.47, 132.97, 133.50, 133.60, 133.80, 136.03, 136.52, 137.25, 137.52, 140.23, 140.33, 140.44, 140.48, 142.68, 142.88, 143.02, 143.09, 143.23, 143.32, 143.48, 143.52, 144.90, 145.33, 145.74, 145.78, 146.04, 146.25, 146.37, 146.84, 147.00, 147.06, 147.11, 147.18, 147.34, 147.41, 147.45, 147.55, 148.01, 148.71, 148.87, 148.89, 148.97, 149.09, 149.14, 149.26, 149.50, 149.63, 149.65, 149.72, 149.74, 149.77, 150.08, 150.16, 150.44, 150.48, 150.51, 150.55, 150.61, 150.64, 150.70, 150.83, 151.14, 151.28, 151.43, 151.54, 154.94, 155.83, 156.21, 156.25, 160.39 ppm. MALDI TOF MS (sulfur matrix): m/z = 1038 [M + H]$^+$.

Pyrrolidinofullerene 2: Fullerene C_{70} (300 mg, 0.36 mmol) was heated at reflux with 3-picolylamine (50.2 mg, 0.46 mmol), 3-pyridinecarbaldehyde (0.1 mL, 1.05 mmol) and butyric acid (2 mL) in 1,2-dichlorobenzene (50 mL) for 12 h. Chromatographic separation (silica gel, 40–60 μ, 60 Å; toluene/MeOH, 98:2) gave **2** in 38% yield (141 mg). ^{1}H NMR [400 MHz; CS_2/$(CD_3)_2CO$, 9:1]: δ = 3.39 (br. s, ca. 1 H), 5.18 (s, 1 H), 5.34 (s, 1 H), 7.23 (dt, J = 4.8, 3.0 Hz, 1 H) 7.55 (dt, J = 4.8, 3.0 Hz, 1 H), 8.08 (dt, J = 8.0, 1.6 Hz, 1 H), 8.37 (dt, J = 7.8, 1.8 Hz, 1 H), 8.44 (dd, J = 4.8, 1.6 Hz, 1 H), 8.73 (dd, J = 4.8, 1.6 Hz, 1 H), 8.84 (d, J = 1.8 Hz, 1 H), 9.20 (d, J = 1.8 Hz, 1 H) ppm. ^{13}C NMR [150 MHz; CS_2/$(CD_3)_2CO$, 9:1]: δ = 68.72, 69.63, 70.11, 72.89, 72.97, 123.19, 127.80, 130.65, 131.19,

131.24, 131.28, 131.31, 131.35, 131.68, 133.12, 133.40, 133.54, 133.65, 133.88, 134.04, 135.19, 135.84, 137.43, 137.88, 138.44, 140.18, 140.59, 140.84, 141.27, 142.91, 143.06, 143.31, 143.39, 143.47, 144.26, 145.64, 145.85, 145.95, 146.19, 146.24, 146.43, 146.91, 147.00, 147.01, 147.14, 147.44, 147.50, 147.63, 148.67, 148.85, 148.98, 149.10, 149.16, 149.20, 149.23, 149.25, 149.34, 149.69, 149.81, 149.88, 149.93, 150.01, 150.17, 150.31, 150.47, 150.53, 150.54, 150.62, 150.67, 150.76, 150.78, 150.96, 151.28, 151.30, 151.36, 151.47, 154.94, 155.17, 155.96, 158.26 ppm. MALDI TOF MS (sulfur matrix): m/z = 1038 $[M + H]^+$.

Pyrrolidinofullerene 3: C_{70} (300 mg, 0.36 mmol), 2-picolyl-3-picolylamine (78.8 mg, 0.39 mmol) and 2-pyridinecarbaldehyde (0.1 mL, 1.05 mmol) were heated at reflux in 1,2-dichlorobenzene (50 mL) for 10 min. Chromatographic separation (silica gel, 40–60 μ, 60 Å; toluene/MeOH, 97.5:2.5) afforded isomerically pure product **3** in 45% yield (181 mg). ^{1}H NMR [600 MHz; $CS_2/(CD_3)_2CO$, 9:1]: δ = 3.41 (d, J = 14.1 Hz, 1 H), 4.07 (d, J = 14.1 Hz, 1 H), 5.86 (s, 1 H), 6.28 (s, 1 H), 7.24 (dt, J = 4.8, 2.9 Hz, 1 H), 7.32 (dt, J = 4.8, 2.9 Hz, 1 H), 7.37 (br. s, 1 H), 7.45 (dt, J = 4.8, 1.7 Hz, 1 H), 7.67 (dt, J = 7.8, 1.9 Hz, 1 H), 7.75 (d, J = 6.4 Hz, 1 H), 7.82 (d, J = 7.6 Hz, 1 H), 7.93 (dt, J = 7.6, 1.9 Hz, 1 H), 8.38 (s, 1 H), 8.51 (d, J = 4.6 Hz, 1 H), 8.74 (d, J = 2.7 Hz, 1 H), 8.95 (d, J = 4.4 Hz, 1 H) ppm. ^{13}C NMR [150 MHz; $CS_2/(CD_3)_2CO$, 9:1]: δ = 48.19, 66.57, 67.67, 72.68, 76.63, 122.89, 123.06, 123.45, 123.63, 124.39, 124.73, 124.93, 125.55, 127.84, 128.42, 129.14, 130.64, 131.18, 131.23, 131.30, 131.73, 132.97, 133.10, 133.43, 133.70, 133.79, 135.34, 136.19, 136.35, 136.50, 137.40, 137.44, 138.64, 140.37, 140.73, 142.82, 142.87, 143.15, 143.19, 143.24, 143.34, 145.69, 145.79, 146.04, 146.25, 146.40, 146.83, 147.04, 147.09, 147.33, 147.45, 147.51, 148.79, 148.89, 148.97, 149.06, 149.11, 149.26, 149.42, 149.57, 149.69, 149.91, 150.06, 150.45, 150.53, 150.63, 150.72, 151.00, 151.37, 151.42, 151.48, 155.15, 157.22, 159.06, 159.24, 159.76 ppm. MALDI TOF MS (sulfur matrix): m/z = 1129 $[M + H]^+$.

Supporting Information (see footnote on the first page of this article): NMR spectra of **1** and **2** and UV/Vis spectrum of **3**.

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