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Synthesis of novel methanofullerenes spiro-coupled with the indolinone fragment and prospects of their use in light-absorbing layers of plastic solar cells*

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A series of novel 2´-oxospiro[cyclopropafullerene-3,3´-indolines] was synthesized. Compounds of this type have a significant potential for use as electron-withdrawing components of light-absorbing layers of solar cells.

Key words: methanofullerenes, isatin, synthesis, structure, electrochemistry, absorption spectra, solubility, composite films, film morphology.

Efficiency of light conversion by solar cells based on crystalline silicon reaches 45—55%.[1] At the same time, toxicity, high cost of materials, and expensive technologies of cell preparation restrict the propagation of this type of power engineering. Therefore, search for novel materials and simplification of technologies of their production become more and more topical. Progress in the area of organic photovoltaics achieved within the recent decade indicates that organic materials can compete with inorganic materials.[2,3] The progress is caused, to a great extent, by the construction of plastic solar cells, whose light-absorbing layers represent composites of semiconducting conjugated polymers (electron donors) with fullerene derivatives (electron acceptors); the principle of their work is based on the theory of volume hypertransition.[4,5] Presently, plastic cells are inferior to inorganic cells in efficiency. Nevertheless, such their advantages as lightness, flexibility, prognosticated cheapness, and simpler technologies of preparation form significant prerequisites for the development of research in this area.[6—9] Devices, whose active layers represent composites of poly(3-hexylthiophene) with 1-(3-methoxycarbonylpropyl)-1-phenyl-[6,6]-methanofullerene (system P3HT/[60]PCBM), are pioneers among plastic solar cells during the recent decade. The efficiency of the first cells based on this composite was 2.5—2.7%.[10,11] After developing the technologies and modifying the structures of the cells based on P3HT/[60]PCBM, the cells with an efficiency of 4.5—6.7% are presently prepared.[5,12—14] However, relatively high cost of the composite, in particular, PCBM,[15] and an insufficient efficiency of the cells do not allow plastic solar cells to work up a market. Numerous attempts to substantially increase the efficiency of these cells due to the variation of the structure of methanofullerenes, including highest fullerenes, or to the combination of the polymer and fullerene fragments in one molecule are not too successful so far.[16—23] Nevertheless, in spite of modest success of organic photovoltaics, its advantages stimulate search for new approaches to design of fullerene derivatives. For instance, the first composite of trannulene $C_{60}F_{15}[C(COOMe)_3]_3$ with P3HT was described. Although the cells based on this composite are substantially inferior to the reference composite based on P3HT/[60]PCBM, the principal possibility of using trannulene for the construction of photovoltaic materials was shown for the first time.[24] We detected an unusual effect in phosphorus-containing methanofullerenes. An X-ray diffraction analysis showed the intermolecular interaction of a lone electron pair of the O atom of the phosphoryl group with the electronic system of fullerene in a molecule of *O*,*O*-diethyl-[1´-phenyl(cyclopropa[1,9](C_{60}-I_h)[5,6]-fulleren-1´-yl)] phosphonate.[25] Due to this effect, the phosphonate molecule, unlike all known phosphorylated methanofullerenes, does not decompose during accepting electrons, and photovoltaic cells based on its composite with P3HT have higher output characteristics of short-circuit current and open-circuit voltage than references cells.[26]

In the present work, we evaluated for the first time prospects of using spiro-coupled indolinonemethanofullerenes as electron-withdrawing components of active layers of solar cells. These compounds are interesting by simplicity of the synthesis and by the fact that the addend

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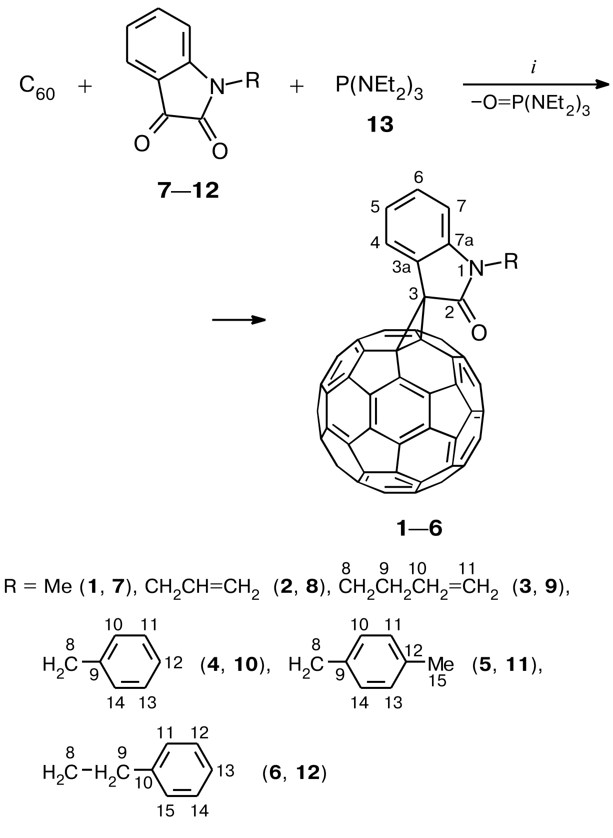
contributes to the absorbability of the molecule along with the fullerene sphere.

To add indolinone fragments to the fullerene sphere, we developed the reaction in the three-component system fullerene—dicarbonyl compound—hexaalkyltriaminophosphine.[27] The reaction occurs under mild conditions and, unlike the method for PCBM preparation, does not require heating or irradiation. As a result, only one monoadduct is formed in ~40% yield. Both quinones and isoxazoles undergo this reaction. It was assumed that during the reaction carbene is generated from the dicarbonyl compound under the action of aminophosphine, and the carbene adds to the C=C bond of the fullerene sphere to form methanofullerene.

Earlier[27] we have synthesized methanofullerenes **1** and **2** (Scheme 1) by the reaction of fullerene C_{60} with isatins **7** and **8**, respectively. Methanofullerenes **3**—**6** were synthesized by the addition of hexaethyltriaminophosphine **13** to a mixture of fullerene and corresponding isatin **9**—**12** at −10 °C followed by the temperature increase to ~20 °C. Compounds **1**—**6** were isolated from the reaction mixtures by column chromatography and were identified using a complex of physicochemical methods (IR and UV spectroscopy, ^1H and ^{13}C NMR spectroscopy, mass spectrometry). The mass spectra of these compounds exhibit peaks of molecular ions, and their IR and NMR spectra indicate that the addend adds to the C=C bond of fullerene at the atom C(3).

Scheme 1



i. o-DCB, −10—25 °C, 8 h.

To determine the absorbability of methanofullerenes **1**—**6** and the energies of their frontier orbitals, we studied their UV spectra and reduced the compounds by cyclic voltammetry.

The absorption spectra of methanofullerenes **1**—**6** recorded in dichloromethane are presented in Table 1. The data for fullerene C_{60} and [60]PCBM are also given for comparison. The spectra of methanofullerenes **1**—**6**, as the spectra of C_{60} and PCBM, in the region from 200 to 350 nm exhibit two intense absorption bands characteristic of π—π*-transitions in aromatic systems. The visible spectral region contains narrow bands at 427—431 nm, which are characteristic of [6,6]-closed monoadducts of fullerene, and broad bands at 500 and 690 nm. The position of bands in the spectrum of methanofullerene **1** does not substantially change relatively to the spectrum of [60]PCBM. As for the intensity of the absorption bands, the indolinone fragments most noticeably affect the absorption at 250 nm, where the bands of the initial isatins **7**—**12** are distinctly manifested. The data in Table 1 show that the intensity of this band in the spectra of methanofullerenes **1**—**6** increases with the replacement of the methyl substituent at the N atom, and for compounds **3**—**6** the band becomes an order of magnitude more intense than the similar absorption band in the spectrum of PCBM and approaches in intensity to the absorption band of unmodified fullerene. Initial isatins **9**—**12** also absorb in the visible region, but this absorption is less intensive. As compared with the spectrum of PCBM, the spectra of compounds **3** and **4** exhibit a slight increase in absorption at 500 nm, whereas for compounds **1** and **2** the absorption increase is observed at 690 nm. The absorption of methanofullerenes **1**—**6** in the visible region is an order of magnitude stronger than that of unmodified fullerene C_{60}.

The data on the electrochemical reduction of methanofullerenes **1**—**6** are presented in Table 2. The results of

Table 1. Absorption spectra of methanofullerenes **1**—**6**, C_{60}, and PCBM

Compound	λ_{max}/nm (logε)
C_{60}	257 (5.18), 329 (4.68), 403 (3.40), 407 (3.27), 534 (2.93), 592 (2.88), 687 (2.24)
1	257 (4.80), 326 (4.39), 427 (3.29), 490 (3.22), 694 (2.95)
2	256 (4.93), 326 (4.42), 427 (3.30), 490 (3.19), 679 (2.74)
3	258 (5.21), 329 (4.69), 430 (3.41), 500 (3.27), 690 (2.30)
4	258 (5.24), 330 (4.72), 429 (3.43), 500 (3.30), 694 (2.37)
5	258 (5.45), 329 (4.95), 430 (3.37), 500 (3.20), 690 (2.26)
6	257 (5.18), 326 (4.71), 428 (3.35), 498 (3.20)
PCBM	259 (4.07), 328 (4.56), 431 (3.42), 496 (3.20), 698 (2.45)

Table 2. Potentials of peaks detected on the cyclic voltammograms (E_p^{red}) and the LUMO energies (E_{LUMO}) of fullerene C_{60}, methanofullerenes **1**—**6**, and [60]PCBM

Compound	$-E_p^{red}$/V				$-E_{LUMO}$/eV
	C_1	C_2	C_3	C_4	
C_{60}	0.83	1.24	1.70	2.16	4.4
1	0.89	1.22	1.43	1.85	4.3
2	0.90	1.24	1.44	1.88	4.3
3	0.92	1.27	1.48	1.90	4.2
4	0.95	1.24	1.47	1.91	4.1
5	0.92	1.20	1.66	1.89	4.2
6	0.84	1.24	1.43		4.4
7	1.35	2.02			
8	1.31	1.99			
9	1.39	2.13			
10	1.34	1.98			
12	1.36	2.06			
11	1.32	1.96			
[60]PCBM					4.2

Note. Conditions: *o*-DCB—MeCN (3 : 1) mixture; 25 °C; concentration of solutions $5 \cdot 10^{-3}$ mol L^{-1}; background electrolyte 0.1 *M* Bu_4NBF_4; glassy carbon cathode (S_{work} = 3.14 mm^2); reference electrode Ag/0.01 *M* $AgNO_3$ in MeCN; v_{sweep} = = 50 mV s^{-1}.

electrochemical reduction of fullerene C_{60} and isatins **7**—**12** are also given for comparison.

Under the experimental conditions, four classical reversible one-electron peaks (C_1, C_2, C_3, and C_4) are detected in the cyclic voltammogram of fullerene C_{60} in the potential range from –0.83 to –2.16 V. Initial isatins **7**—**12** are reduced in the region of potentials close to those of the second and fourth reduction peaks of fullerene, and two reversible cathodic peaks are detected in each cyclic voltammogram. Methanofullerenes **1**—**6** are characterized by several reversible reduction peaks in the region of 0—2 V. A comparison of the reduction potentials of methanofullerenes **1**—**6**, C_{60}, and isatins **7**—**12** shows that the electron transfer to the fullerene sphere occurs at the first stage of reduction (cathodic peak C_1) of methanofullerenes **1**—**6**. At the next stages (cathodic peaks C_2, C_3, and C_4), both the fullerene sphere and heterocyclic fragments of the molecules are reduced. The first reduction peaks (C_1) of methanofullerenes **1**—**6** undergo shifts to the region of more negative values of potential relatively to fullerene C_{60}. The value of shift increases on going from methanofullerene with the methyl substituent at the N atom to methanofullerenes with unsaturated and aromatic substituents, and the closer the phenyl substituent to the N atom, the greater the shift; for compound **4** the shift reaches 120 mV. Note that the reduction of [60]PCBM is more difficult than that of fullerene C_{60} by 100 mV.[28]

The results of electrochemical reduction of methanofullerenes **1**—**6** formed a basis for the calculation of energies of their LUMO and prediction of the values of open-circuit voltage (V_{oc}), which one of parameters determining the efficiency of solar cells.[29] This factor depends on the energies of frontier orbitals of the electron donor and acceptor (Fig. 1).

It follows from the diagram presented in Fig. 1 that the LUMO level of spiro-coupled 2-oxoindolinonemethanofullerenes **3**—**5** is comparable with the level of the PCBM orbital, and these compounds can provide the value of V_{oc} not lower than PCBM provides.

Solubility in organic solvents of components of the active layer of solar cells is one of the main factors determining the efficiency of the latter.[24] This active layer is usually prepared as follows: a solution of a mixture of the components is deposited on the substrate by the coating method onto a rotating support followed by solvent removal *in vacuo*. Chlorobenzene well recommended itself in this process. At ~20 °C the solubility of methanofullerene [60]PCBM in chlorobenzene is 50 mg mL^{-1} and that of polymer P3HT is 50—70 mg mL^{-1} (see Ref. 24). Methanofullerene [60]PCBM with P3HT forms films in which phases polymer/fullerene derivative are separated and no pronounced clusters of fullerene compounds dispersed in the polymer matrix are observed.[13,30] The solubility in chlorobenzene of methanofullerenes **1**—**6** obtained by us is 3—5 mg mL^{-1}. Compounds having this solubility with P3HT form composite films with strong phase separation, which makes them poorly promising as materials for active layers of solar cells.

Other solvents, in particular, *o*-dichlorobenzene (*o*-DCB), are used along with chlorobenzene for the preparation of composite films. This solvent has a higher boiling point than chlorobenzene, and it is more difficult to remove it from the film, but the solubility of fullerene derivatives in it is higher, as a rule. For instance, the solubility of methanofullerenes **1**—**5** in *o*-DCB is 5—15 mg mL^{-1} and that of compound **6** is 20 mg mL^{-1}.

In order to determine the ability of spiro-coupled 2-oxoindolinonemethanofullerenes to mix with P3HT, we prepared a film of the composite of methanofullerene **6** with P3HT, whose solubility in *o*-DCB was maximum among the compounds prepared by us. The topography of the film surface was studied by atomic force microscopy (AFM). It is seen from Fig. 2 that domains are formed on

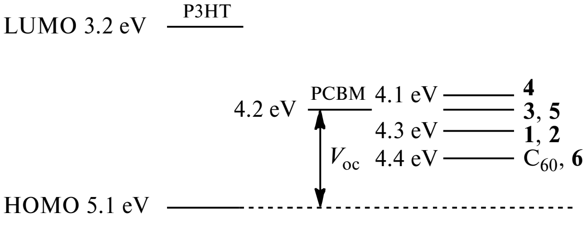


Fig. 1. Energy diagram of frontier orbitals for methanofullerenes **1**—**6**, fullerene C_{60}, and PCBM.

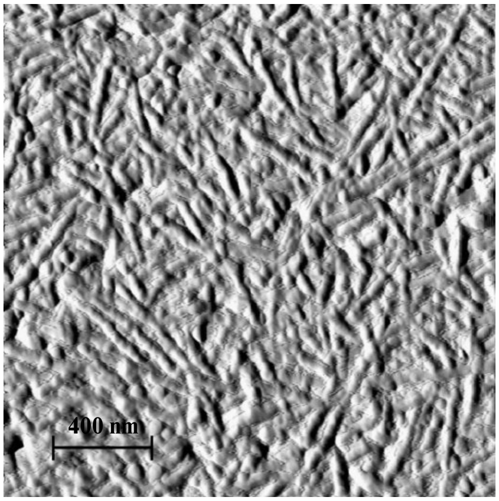


Fig. 2. AFM image of the film surface of composite P3HT/**6**.

the film surface. Their transversal sizes range from 50 to 150 nm and longitudinal sizes reach several hundreds of angström. This indicates that indolinone-substituted fullerenes are well miscible with polymer P3HT even at lower solubilities than [60]PCBM.

Thus, we obtained a series of new 2´-oxospiro[cyclopropafullerene-3,3´-indolines]. The study of their solubility, optical and electrochemical properties, and the ability to mix with polymer P3HT showed that these compounds possess a considerable potential for use as components of light-absorbing layers of plastic solar cells. The developed approach to the synthesis of methanofullerenes makes it possible to widely vary substituents at N atom: from alkyl to polycyclic substituents and, in particular, to fragments of dyes. In future spiro-coupled methanofullerenes can be the basis for the development of a new direction in search for solar cell materials.

Experimental

IR spectra were recorded on a Bruker IFS-113V FTIR spectrometer in KBr pellets. 1D and 2D NMR experiments were carried out in $CDCl_3$ solutions on a Bruker Avance-600 spectrometer (600 (^{1}H) and 150.926 MHz (^{13}C)) at 30 °C. The residual signal of $CDCl_3$ (δ_H 7.26 and δ_C 77.0) was used as an internal standard. UV spectra were recorded on a Specord UV-VIS instrument. Mass spectra were obtained on a Bruker Ultraflex III MALDI TOF/TOF SYSTEM instrument using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile as a matrix. HPLC analysis was carried out on an HPP 5001 chromatograph (UV detector, columns with the normal phase SC_1XC_{18}, toluene—MeCN (1 : 1, vol/vol) as an eluent, 0.3 mL min^{-1}, detector UV-Detector 308, λ = 328 nm).

In CV studies, the stationary disc glassy carbon electrode with the working surface (S_{work}) 3.14 mm^2 was used as a working electrode. Voltammograms (CV curves) were recorded using a PI-50-1 potentiostat with a PR-8 programmer switching the electrochemical cell by the three-electrode scheme. The CV curves were recorded on a two-coordinate recorder with a linear potential sweep (v_{sweep}) of 50 mV s^{-1}. The CV curves were detected in an *o*-DCB—MeCN (3 : 1) mixture against a background of 0.1 *M* Bu_4NBF_4. The system Ag/0.01*M* $AgNO_3$ in MeCN served as a reference electrode. A Pt wire was used as an auxiliary electrode. Measurements were carried out in a temperature-controlled (25 °C) cell under an argon atmosphere. The concentration in a solution of C_{60} was $2 \cdot 10^{-3}$ mol L^{-1}, and that of solutions of adducts was $5 \cdot 10^{-3}$ mol L^{-1}.

To prepare the film, polymer P3HT (Sigma Aldrich) and compound **6** were preliminarily dissolved in *o*-dichlorobenzene in a concentration of 20 g L^{-1} with permanent stirring for 12 h. Then the components were mixed and additionally stirred for 12 h. The obtained solution was deposited in the glass support 25×25 mm in size using the centrifuging (spin-coating) technique at 700 rpm for 2 min. An MTI TC100 centrifuge was used to rotate the support.

The solubility of methanofullerenes **1**—**6** was determined at ~20 °C by mixing a weighed sample of the compound (25 mg) with 1 mL of an absolute solvent. After 24 h of stirring of the mixture, the non-dissolved part of methanofullerene was separated on an OPN-3.02 centrifuge (Dastan) with a rotation frequency of 1000 min^{-1}. The solvent was removed from the filtrate in vacuum of an oil pump, and the residue was weighed.

Anhydrous chlorobenzene, *o*-DCB, and MeCN were prepared by distillation over P_2O_5. [60]Fullerene was bought at the Fullerene Center company (Nizhnii Novgorod).

Isatins **10**—**12** were synthesized according to procedures described earlier.[31,32]

1-(But-4-en-1-yl)isatin (9). Sodium hydride (1.32 g, 33 mmol) as a 60% suspension in mineral oil was gradually added to a solution of isatin (3.73 g, 25 mmol) in absolute DMF (40 mL) at 0 °C. A bright orange solution gradually turned violet. After 30 min of stirring, 4-bromobut-1-ene (4.45 mL, 33 mmol) was added dropwise to the reaction mixture. The resulting bright red solution was stirred for 2.5 h. The reaction mixture was poured into a mixture of water (50 mL) and ice (100 g). The precipitate formed was filtered off and dried in vacuum of a water-jet pump. Isatin **3** was obtained in a yield of 2.97 g (89%) as a bright orange powder, m.p. 61 °C. IR (Nujol), ν/cm^{-1}: 1743, 1599, 1352, 1291, 1178, 1128, 1090, 1045, 997, 955, 923, 870, 818, 769, 639, 591, 476. ^{1}H NMR (DMSO-d$_6$), δ: 7.65 (ddd, 1 H, C(6)H, *J* = 7.6 Hz, *J* = 7.9 Hz, *J* = 1.3 Hz); 7.52 (dd, 1 H, C(4)H, *J* = 7.6 Hz, *J* = 1.0 Hz); 7.18 (br.d, 1 H, C(7)H, *J* = 7.9 Hz); 7.12 (br.ddd, 1 H, C(5)H, *J* = 7.3 Hz, *J* = 7.6 Hz, *J* = 0.6 Hz); 3.73 (t, 2 H, C(8)H$_2$, *J* = 7.0 Hz); 2.37 (td, 2 H, C(9)H, *J* = 7.0 Hz, *J* = 7.0 Hz); 5.80 (m, 1 H, C(10)H); 5.04, 4.99 (m, 2 H, C(11)H$_2$). ^{13}C NMR (DMSO-d$_6$), δ: 158.12 (C(2)); 183.61 (C(3)); 117.36 (C(3a), overlaps with C(11)); 110.99 (C(4)); 123.38 (C(5)); 138.51 (C(6)); 124.64 (C(7)); 150.72 (C(7a)); 39.07 (C(8)); 31.26 (C(9)); 135.10 (C(10)); 117.47 (C(11)). MS, *m/z*: 201.2 [M]$^+$ ($C_{12}H_{11}NO_2$).

1´-(But-4-en-1-yl)-2´-oxospiro[cyclopropa[1,9](C_{60}-I_h)-[5,6]fullerene-3,3´-indoline] (3). Triaminophosphine **13** (0.112 g, 0.454 mmol) was added dropwise to a mixture of fullerene C_{60} (0.109 g, 0.151 mmol) and isatin **9** (0.031 g, 0.454 mmol) at −10 °C. The temperature was gradually increased to ~20 °C during 8 h. The solvent was removed in vacuum of an oil pump at the bath temperature 30 °C, and the residue was chromatographed on a column with silica gel using a toluene—petroleum ether (3 : 1) mixture as an eluent. Fullerene C_{60} (0.011 g, 10%)

and fractions containing mono- and polyadducts were obtained. After repeated chromatography, methanofullerene **3** was obtained in a yield of 0.064 g (47% based on the amount of fullerene taken in the reaction). HPLC (column with the normal phase): retention time 7.9 min. TLC (Sorbfil, eluent toluene): R_f 0.8. IR (KBr), ν/cm^{-1}: 2922, 2850, 1722, 1610, 1466, 1355, 1186, 742, 526. ^{1}H NMR ($CDCl_3$—CS_2, 2 : 1), δ: 8.31 (d, 1 H, C(4)H, J = 7.5 Hz); 7.53 (ddd, 1 H, C(6)H, J = 7.5 Hz, J = 7.5 Hz, J = 1.0 Hz); 7.18 (m, 2 H, C(5)H, C(7)H); 5.98 (m, 1 H, C(10)H); 5.24, 5.21 (dd, 2 H, C(11)H_2, J = 24.4 Hz, J = 23.2 Hz); 4.09 (t, 2 H, C(8)H, J = 7.5 Hz); 2.69 (td, 2 H, C(9)H, J = 7.1 Hz, J = 7.1 Hz). ^{13}C NMR ($CDCl_3$—CS_2, 2 : 1), δ: 168.62 (C(2)); 142.00 (C(7a)); 129.28 (C(6)); 125.12 (C(3a)); 124.95 (C(4)); 123.81 (C(5)); 122.42 (C(10)); 117.56 (C(11)); 108.63 (C(7)); 41.84 (C(3)); 40.11 (C(8)); 31.98 (C(9)); 145.29 (2 C), 145.25 (2 C), 144.99 (2 C), 144.95 (4 C), 144.81 (4 C), 144.75 (2 C), 144.52 (6 C), 144.28 (2 C), 144.18 (2 C), 144.01 (1 C), 143.92 (2 C), 143.89 (2 C), 143.52 (2 C), 143.36 (2 C), 142.90 (3 C), 142.84 (2 C), 142.75 (2 C), 142.58 (2 C), 142.01 (2 C), 141.96 (2 C), 141.33 (2 C), 141.15 (2 C), 141.08 (2 C), 140.73 (2 C), 138.64 (2 C), 75.09 (2 C) (fullerene fragment). MS, m/z: 905 ($C_{72}H_{11}NO$), 720 (C_{60}).

1´-Benzyl-2´-oxospiro[cyclopropa[1,9](C_{60}-I_h)[5,6]fullerene-3,3´-indoline] (4). Triaminophosphine **13** (0.101 g, 0.409 mmol) was added dropwise to a mixture of fullerene C_{60} (0.101 g, 0.14 mmol) and isatin **10** (0.033 g, 0.14 mmol) in anhydrous *o*-DBC (50 mL) at –10 °C. The temperature was gradually increased to ~20 °C during 8 h. The solvent was removed in vacuum of an oil pump at the bath temperature 30 °C, and the residue was chromatographed on a column with silica gel using a toluene—petroleum ether (4 : 1) mixture as an eluent. Fullerene C_{60} (0.006 g, 6%) and fractions containing mono- and polyadducts were obtained. After repeated chromatography, methanofullerene **4** was obtained in a yield of 0.040 g (35%). HPLC (column with the normal phase): retention time 4.7 min. TLC (Sorbfil, eluent toluene—petroleum ether (4 : 1)): R_f 0.69. IR (KBr), ν/cm^{-1}: 1724, 1610, 1468, 1359, 1185, 744, 728, 709, 526. ^{1}H NMR ($CDCl_3$—CS_2, 2 : 1), δ: 8.36 (d, 1 H, C(4)H, J = 7.8 Hz); 7.58 (m, 1 H, C(6)H); 7.27 (m, 1 H, C(5)H); 7.15 (d, 1 H, C(7)H, J = 7.8 Hz); 5.27 (s, 2 H, C(8)H_2); 7.38—7.30 (m, 5 H, C(10)H, C(11)H, C(12)H, C(13)H, C(14)H). ^{13}C NMR ($CDCl_3$—CS_2, 2 : 1), δ: 168.11 (C(2)); 142.74 (C(7a)); 135.30 (C(9)); 129.03 (C(10), C(14)); 128.68 (C(6)); 127.68 (C(11), C(13)); 127.41 (C(3a)); 124.68 (C(12)); 123.53 (C(4)); 122.34 (C(5)); 109.19 (C(7)); 44.23 (C(8)); 41.68 (C(3)); 145.23 (2 C), 145.16 (2 C), 144.88 (2 C), 144.83 (4 C), 144.68 (3 C), 144.41 (6 C), 144.36 (2 C), 144.15 (2 C), 144.09 (2 C), 143.90 (1 C), 143.83 (2 C), 143.70 (2 C), 143.42 (2 C), 143.28 (2 C), 142.79 (2 C), 142.76 (2 C), 142.63 (2 C), 142.46 (2 C), 142.21 (2 C), 141.91 (2 C), 141.86 (2 C), 141.20 (2 C), 141.00 (2 C), 140.88 (2 C), 140.59 (2 C), 138.52 (2 C), 75.01 (2 C) (fullerene fragment). MS, m/z: 941 ($C_{75}H_{11}NO$), 720 (C_{60}).

1´-(4-Methylbenzyl)-2´-oxospiro[cyclopropa[1,9](C_{60}-I_h)-[5,6]fullerene-3,3´-indoline] (5). Triaminophosphine **13** (0.123 g, 0.497 mmol) was added dropwise to a mixture of fullerene C_{60} (0.100 g, 0.138 mmol) and isatin **11** (0.036 g, 0.146 mmol) in anhydrous *o*-DBC (50 mL) at –10 °C. The temperature was gradually increased to ~20 °C during 8 h. The solvent was removed in vacuum of an oil pump at the bath temperature 30 °C, and the residue was chromatographed on a column with silica gel using a toluene—petroleum ether (3 : 1) mixture as an eluent. Fullerene C_{60} (0.010 g, 10%) and fractions containing mono- and polyadducts were obtained. After repeated chromatography, methanofullerene **5** was obtained in a yield of 0.052 g (40%). HPLC (column with the normal phase): retention time 7.1 min. TLC (Sorbfil, eluent toluene): R_f 0.86. IR (KBr), ν/cm^{-1}: 2919, 2846, 1722, 1609, 1466, 1346, 1185, 743, 526. ^{1}H NMR ($CDCl_3$—CS_2, 2 : 1), δ: 8.33 (d, 1 H, C(4)H, J = 7.5 Hz); 7.43 (m, 1 H, C(6)H); 7.45 (d, H, C(10)H, C(14)H, J = 7.5 Hz); 7.24—7.21 (m, 2 H, C(5)H, C(7)H); 7.12 (d, 2 H, C(11)H, C(13)H, J = 7.5 Hz); 5.19 (s, 2 H, C(8)H_2); 2.38 (s, 3 H, C(15)H_3). ^{13}C NMR ($CDCl_3$—CS_2, 2 : 1), δ: 169.41 (C(2)); 142.17 (C(7a)); 137.56 (C(9)); 132.44 (C(12)); 129.58 (C(10), C(14)); 129.31 (C(6)); 127.71 (C(11); C(13)); 125.06 (C(3a)); 123.82 (C(4)); 122.67 (C(5)); 109.69 (C(7)); 44.36 (C(8)); 42.08 (C(3)); 145.48 (2 C), 145.44 (2 C), 145.19 (2 C), 145.15 (2 C), 144.14 (2 C), 145.01 (1 C), 144.98 (2 C), 144.71 (6 C), 144.49 (2 C), 144.38 (2 C), 144.20 (1 C), 144.11 (4 C), 143.72 (2 C), 143.53 (2 C), 143.09 (2 C), 143.03 (4 C), 142.95 (2 C), 142.79 (2 C), 142.19 (2 C), 142.16 (4 C), 141.53 (2 C), 141.41 (2 C), 141.26 (2 C), 140.94 (2 C), 138.88 (2 C), 75.30 (2 C) (fullerene fragment). MS: m/z 955 ($C_{76}H_{13}NO$).

1´-(2-Phenylethyl)-2´-oxospiro[cyclopropa[1,9](C_{60}-I_h)-[5,6]fullerene-3,3´-indoline] (6). Triaminophosphine **13** (0.101 g, 0.409 mmol) was added dropwise to a mixture of fullerene C_{60} (0.100 g, 0.138 mmol) and isatin **11** (0.034 g, 0.140 mmol) in anhydrous *o*-DBC (50 mL) at –10 °C. The temperature was gradually increased to ~20 °C during 8 h. The solvent was removed in vacuum of an oil pump at the bath temperature 30 °C, and the residue was chromatographed on a column with silica gel using a toluene—petroleum ether (4 : 1) mixture as an eluent. Fullerene C_{60} (0.012 g, 12%) and fractions containing mono- and polyadducts were obtained. After repeated chromatography, methanofullerene **6** was obtained in a yield of 0.053 g (40%). HPLC (column with the normal phase): retention time 7.0 min. TLC (Sorbfil, eluent toluene): R_f 0.71. IR (KBr), ν/cm^{-1}: 2921, 2851, 1722, 1611, 1446, 1352, 1174, 1159, 742, 700, 526. ^{1}H NMR ($CDCl_3$—CS_2, 2 : 1), δ: 8.23 (d, 1 H, C(4)H, J = 7.5 Hz); 7.45 (dd, 1 H, C(6)H, J = 7.5 Hz, J = 7.5 Hz); 7.25 (d, 1 H, C(7)H, J = 7.5 Hz); 7.16 (dd, 1 H, C(5)H, J = 7.6 Hz, J = 7.6 Hz); 7.12 (dd, 2 H, Ph, H_m, J = 7.5 Hz, J = 7.5 Hz); 7.07 (d, 2 H, Ph, H_p, J = 7.8 Hz); 7.04 (d, 2 H, Ph, H_p, J = 7.8 Hz); 4.16 (t, 2 H, C(8)H_2, J = 6.0 Hz); 3.13 (t, 2 H, C(9)H_2, J = 6.0 Hz). ^{13}C NMR ($CDCl_3$—CS_2, 2 : 1), δ: 167.81 (C(2)); 142.60 (C(7a)); 137.36 (C(10)); 128.65 (C(13)); 128.53 (C(11), C(15)); 129.14 (C(6)); 128.48 (C(12), C(14)); 126.61 (C(3a)); 123.66 (C(4)); 122.17 (C(5)); 108.26 (C(7)); 41.87 (C(8)); 41.56 (C(9)); 41.56 (C(3)); 145.18 (2 C), 145.10 (2 C), 144.80 (2 C), 144.79 (3 C), 144.65 (2 C), 144.55 (2 C), 144.38 (6 C), 144.33 (2 C), 144.12 (2 C), 144.02 (2 C), 143.85 (1 C), 143.79 (2 C), 143.71 (2 C), 143.38 (2 C), 143.25 (2 C), 142.76 (2 C), 142.70 (2 C), 142.60 (2 C), 142.42 (2 C), 142.00 (2 C), 141.87 (2 C), 141.82 (2 C), 141.17 (2 C), 140.99 (2 C), 140.93 (2 C), 140.54 (2 C), 138.47 (2 C), 74.91 (2 C) (fullerene fragment). MS: m/z 955 ($C_{76}H_{13}NO$).

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