Reactions of [60]fullerene with 2-azidopyrimidines

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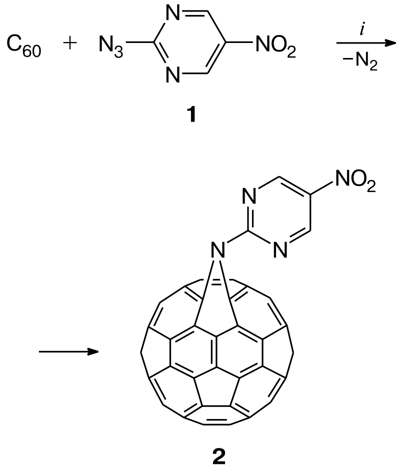
The reaction of [60]fullerene with 2-azidopyrimidines affords fullerenoimidazopyrimidines, whose electron affinity is higher than that of nonmodified C_{60}.

Key words: [60]fullerene, 2-azidopyrimidines, [60]fullereno[1´,2´:4,5]imidazo[1,2-*b*]pyrimidines, electrochemistry.

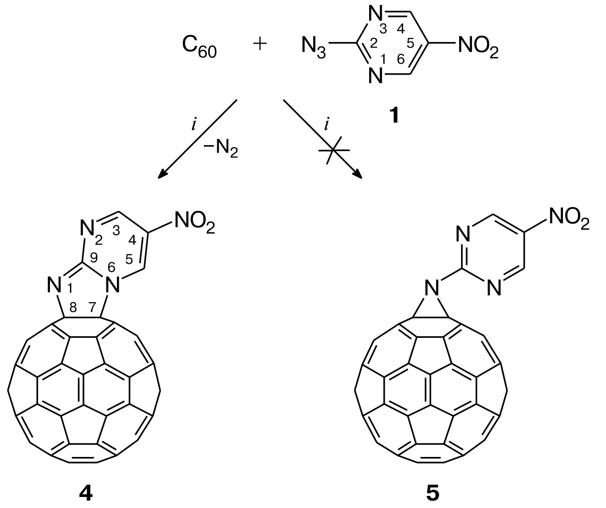
Synthesis of strong electron-withdrawing organofullerenes retaining unique properties of nonmodified fullerenes provides new possibilities for studying spherical carbon molecules in electron transfer processes. Such organofullerenes can be synthesized by the addition of electron-withdrawing atoms, groups, or fragments to fullerenes.[1,2] We proposed to modify C_{60} by the electron-withdrawing pyrimidine fragments using for this purpose the intensely studied reaction of fullerene with organic azides.[3] This reaction affords several types of monoadducts different in structure of the fullerene cage and out-of-sphere cycles. This extends search for electron-withdrawing organofullerenes. From one to three electron-withdrawing nitrogen atoms can be added directly to the fullerene sphere. This is an advantage over the reaction of C_{60} with pyrimidine-*o*-quinodimethanes,[4] which gave fulleropyrimidines known in the literature.

We have previously[5] shown that the reaction of C_{60} with 2-azido-5-nitropyrimidine (**1**) in *o*-dichlorobenzene (DCB) at 180 °C affords 2-(azahomo[60]fullereno)-5-nitropyrimidine (**2**), which is the adduct at the open 5,6-bond of fullerene with sphere extension by one nitrogen atom. The electrochemical reduction of adduct **2** occurred more easily that the reduction of nonmodified fullerene, and the peak of the first reduction wave shifted by 80 mV to the anodic region compared to the peak of the first wave of C_{60} reduction.

Our study of the reactions of [60]fullerene with isocyanurate-substituted azides has shown[6] that the result



i. DCB, 180 °C, 4.5 h.



i. DCB, 100 °C, 26 h.

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of similar reactions is determined by both the structural features of azides and external factors, in particular, temperature of the process. In this work we present the results of the reactions of C_{60} with azido-5-nitropyrimidine **1** at 100 °C and its substituted analog **3** at 100 and 180 °C.

The reaction of C_{60} with azide **1** at 100 °C was carried out in DCB. After heating for 16 h, the reaction mixture was separated by column chromatography on silica gel using toluene as eluent. As a result, we isolated the unreacted fullerene and product **4**, whose mobility on TLC (R_f 0.93) differed from that of earlier obtained azahomo[60]fullerene **2** (R_f 0.76).[5] An increase in the eluent polarity in the column did not lead to isolation of other fullerene-containing adducts, although, according to mass spectrometric data, the reaction mixture contained bisadducts. The yield of product **4** was 10% of the amount of fullerene involved in the reaction and 23% of the reacted amount of C_{60}. The mass spectrum of product **4** exhibits the peak of a molecular ion with *m/z* 858, which corresponds to the $C_{64}H_2N_4O_2$ molecule. The UV and ^{13}C NMR spectra of product **4** indicated the closure of the out-of-sphere heterocycle at the closed 6,6-bond of fullerene. The UV spectrum of this compound contained absorption bands of the fullerene cage: intense bands with λ_{max} 257 and 326 nm and low-intense bands with λ_{max} 514 nm (broad) and 420 nm (narrow). The latter is characteristic of 6,6-closed structures.[7]

The monoadducts at the close 6,6-bond of C_{60} with molecular weight 858 can bear the aziridine (structure **5**) or imidazopyrimidine (structure **4**) fragments on the fullerene sphere surface. The choice between these structures was made from the ^{13}C and ^{1}H NMR spectroscopic data.

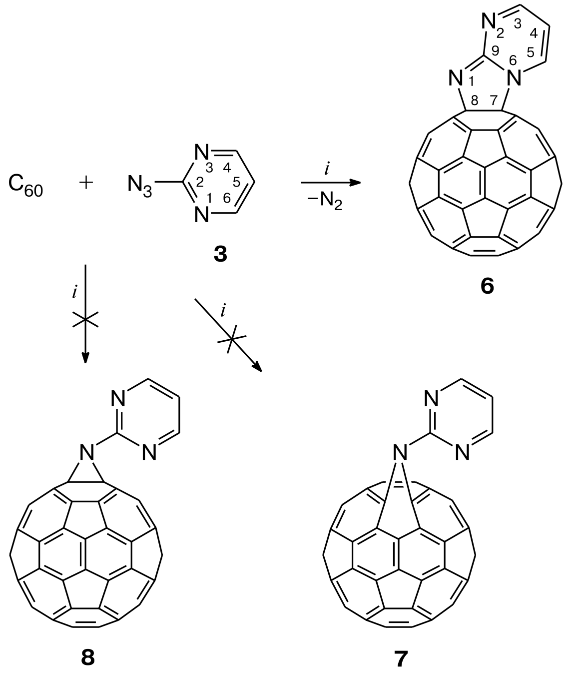
The specific feature of the ^{13}C NMR spectra for adducts at the closed 6,6-bond of fullerene is that they should have signals in the region of δ 70—90 [6,7] corresponding to the sp^3-hybridized carbon atoms of the fullerene sphere. Each of structures **4** and **5** has two such carbon atoms, which are equivalent in structure **5**. Structure **4** assumed that these carbon atoms are nonequivalent. The considered region of the ^{13}C NMR spectrum for the obtained adduct exhibits only one broadened signal with δ 82.6. In our opinion, this does not indicate the equivalence of the sp^3-hybridized carbon atoms of the fullerene sphere and can be caused, most likely, by a small difference in chemical shifts (CS) of the signals. The sp^2-hybridized carbon atoms of the fullerene sphere, which were not involved in the reaction, were characterized by 29 signals (26 signals with the 2C intensity, 1 signals with the 4C intensity, and 2 signals with 1C) in the region of δ 133—146. The number of lines in the spectrum and their relative intensities indicate the C_s symmetry of the fullerene sphere in the product molecule when the symmetry plane includes the bond between two sp^3-hybridized carbon atoms. The structure of adduct **4** satisfies this condition. In the case of structure **5**, the set of signals and their relative intensities would be different (27 signals with the 2C intensity 2C and 4 signals with the 1C intensity) because the symmetry plane in this structure is perpendicular to the bond between the sp^3-hybridized carbon atoms.

The structure of compound **4**, unlike structures **2** and **5**, assume that the C(3) and C(5) carbon atoms of the pyrimidine fragment of the molecule are also nonequivalent. Signals from these atoms in the ^{13}C NMR spectra were detected at δ 155.33 and 155.09 as a doublet of multiplets. In addition, for these carbon atoms in the ^{13}C NMR spectrum obtained without proton decoupling, different multiplet structures of the left and right components of doublets with $^1J_{CH}$ = 193.0 and 191.4 Hz were observed. This indicates that the $^3J_{H,}$ values, whose sum is 3.0 Hz, are not equal. Signals from the C(9) and C(4) atoms in these spectra are detected as multiplets with centers at δ 140.14 and 138.73, respectively.

The ^1H NMR spectrum of compound **4** exhibits signals from protons at the C(3) and C(5) atoms as two singlets with δ 9.38 and 9.54, indicating their magnetic nonequivalence. The IR spectrum of compound **4** evidences that its structure contains the nitro group and imidazo[1,2-*a*]pyrimidine and fullerene fragments.

Thus, all spectral data indicate the formation of 4-nitro-[60]fullereno[1´,2´:4,5]imidazo[1,2-*b*]pyrimidine (**4**) in the reaction of [60]fullerene with azide **1** at 100 °C.

According to HPLC, heating C_{60} with 2-azidopyrimidine **3** in DCB for 26 h at 100 °C does not produce any products in significant amounts. The temperature rise to 180 °C drastically changed the situation. According to



i. DCB, 180 °C, 3 h.

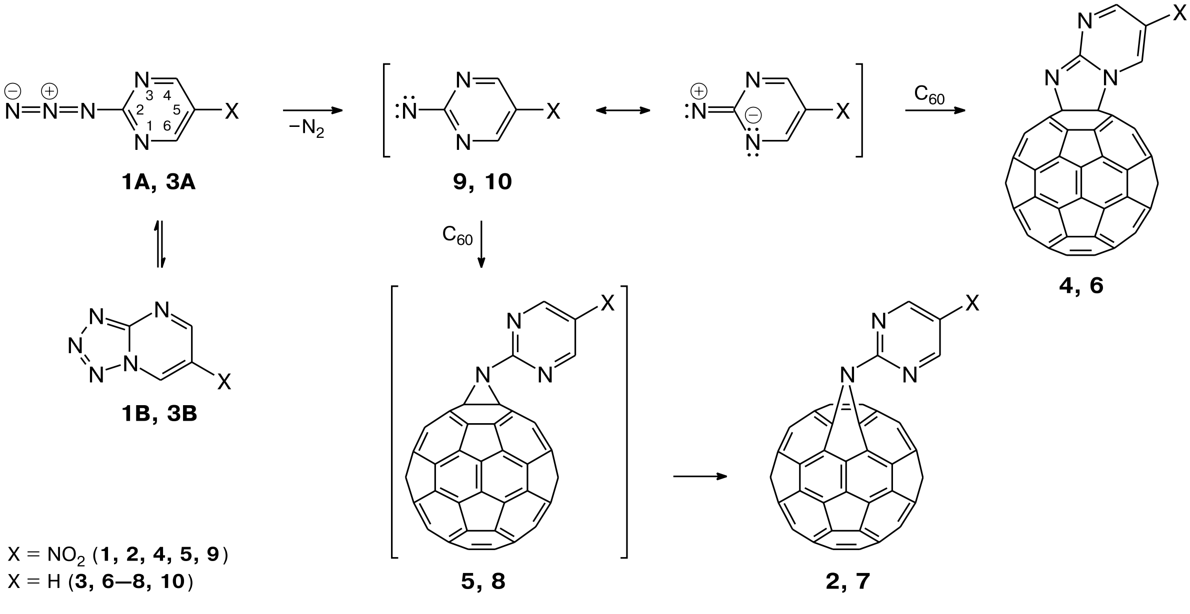
the HPLC and mass spectrometric data, after heating the reaction mixture for 3 h, the unreacted fullerene (*m/z* 720) and monoadduct (*m/z* 813) were detected along with polyadducts (bisadducts with *m/z* 906 and trisadducts with *m/z* 999). The reaction mixture was chromatographed on a column packed with silica gel and yielded fullerene (50% with respect to the amount of C_{60} involved in the reaction), individual monoadducts **6**, and unseparated mixtures of bis- and trisadducts. The HPLC and TLC data evidenced the individual nature of product **6**. Its structure was established by a complex of physicochemical methods.

The yield of adduct **6** was 12% of the initial amount of fullerene. The UV spectrum of adduct **6** exhibited the intense bands at λ 250—400 nm characteristic of fullerenes and, in addition, a narrow band with λ_{max} 422 nm and a broad band with λ_{max} 498 nm indicating out-of-sphere cycle closure at the 6,6-bond of C_{60}, which excludes the formation of azahomofullerene **7**. Unlike nitro-substituted adducts **2** and **4**, adduct **6** was less soluble in organic solvents, which prevented obtaining a good ^{13}C NMR spectrum for this compound. The structure of adduct **6** was established from the ^1H NMR spectrum. The resonance signals of protons at the C(3), C(4), and C(5) carbon atoms represent the spectrum of the ABX spin system with the following parameters: an insignificant difference in chemical shifts of the A and B protons (δ(A) 8.84, δ(B) 8.83, and δ(X) 7.45) but with noticeably different vicinal spin-spin coupling constants $^3J_{H,H}$ ($^3J_{AX}$ = 3.4 Hz, $^3J_{BX}$ = 5.0 Hz, and $^3J_{AB}$ = 0.5 Hz). The IR spectrum of adduct **6** showed that the molecule contained the nitrous and fullerene fragments. Based on these data, we do not consider that azahomo[60]fullerene **7** and [60]fullereno[1,2-*b*]azidirine **8** are formed in the reaction of C_{60} with azide **3** at 180 °C and believe that adduct **6** is [60]fullereno[1′,2′:4,5]imidazo[1,2-*b*]pyrimidine, *i.e.*, its structure is similar to that of adduct **4**. Remind that the reaction of C_{60} with azide **1** at 180 °C afforded 5,6-open adduct, *viz.*, azahomo[60]fullerene **2**.[5]

Unfortunately, available experimental data do not allow unambiguous explanation of formation of various types of adducts in the reactions of C_{60} with 2-azidopyrimidines **1** and **3**. However, we can make several suppositions. Two schemes of interactions are presently discussed in the literature. The first[8] of them includes the step of 1,3-dipolar cycloaddition of azide to the C=C bond of fullerene to form [60]fullereno[1,2-*c*]triazoline, whose thermal decomposition produces azahomo[60]fullerene. However, in the case of the reaction of C_{60} with 2-azidopyrimidines **1** and **3**, this scheme explains only the formation of azahomo[60]fullerene **2**. The second scheme[9] is based on the fact that in the reaction organic azides decompose to nitrenes, which add to fullerene. The formation of nitrenes **9** and **10** from azides **1** and **3** is also probable.[10] The addition of the latter can occur in two ways (Scheme 1).

First, nitrenes **9** and **10** can isomerize to biradicals or 1,3-dipoles and give adducts **4** and **6**. Second, nitrenes **9** and **10** can directly add to C_{60} to form [60]fullereno[1,2-*b*]aziridines **5** and **8**, which isomerize to azahomo[60]fullerenes **2** and **7**, respectively. The latter explanation contains a contradiction with the earlier[6] data for isocyanorate-substituted fullerenes, which undergo the inverse sequence of thermal transformations, *i.e.*, azahomo[60]fullerenes (5,6-adducts) isomerized to [60]fullereno[1,2-*b*]aziridines (6,6-adducts). To resolve this contradiction, the heats of formation of adducts **2** and **4—8**

Scheme 1



X = NO$_2$ (**1, 2, 4, 5, 9**)
X = H (**3, 6—8, 10**)

Table 1. Heats of formation (ΔH/kcal mol^{-1}), relative energies (ΔE/kcal mol^{-1}), and electron affinities (EA_{calc}/eV) calculated by the PM3 and AM1 methods and obtained from the first wave potentials of electrochemical reduction (EA_{exp}/eV) of C_{60} and adducts **2** and **4—8**

Compound (type of adduct)	PM3			AM1			EA_{exp}
	ΔH	ΔE	EA_{calc}	ΔH	ΔE	EA_{calc}	
C_{60}	811.7	—	2.65	973.3	—	—	2.65
$C_{60}NC_4N_2H_3$							
6 (6,6)	848.2	−13.8	2.70	1042.7	−7.4	2.64	2.70
7 (5,6)*	862.0	0.0	2.60	1050.0	0.0	2.58	—
7 (6,5)*	862.1	0.1	2.59	1050.2	0.2	2.57	—
8 (6,6)	865.2	3.2	2.60	1053.5	3.5	2.58	—
$C_{60}NC_4N_2H_3NO_2$							
4 (6,6)	839.2	−15.1	2.93	1047.3	−8.45	2.88	2.76
2 (5,6)*	854.3	0.00	2.72	1056.8	0.00	2.81	2.73
2 (6,5)*	854.6	0.32	2.73	1056.3	0.47	2.81	—
5 (6,6)	858.5	4.16	2.70	1067.4	4.56	2.79	—

* The digits indicate the orientation of the exocyclic bond at the nitrogen atom of azahomo[60]fullerenes **2** and **7** above the pentagon or hexagon, respectively.

were calculated by the quantum-chemical PM3 and AM1 methods. The calculations showed (Table 1) that the most stable adducts are **4** and **6** followed by azahomo[60]fullerenes **2** and **7** (regardless of the orientation of the exocyclic bond) and then [60]fullereno[1,2-*b*]aziridines **5** and **8** follow. No formation of adducts **7** and **8** was experimentally observed. Based on the experimental and calculated data, we can assume that the formation of a biradical or a dipole is preferable for nitrene **10** at 180 °C, while the intermediate formation of adduct **5** under similar conditions cannot be excluded for nitrene **9**.

Thus, the variation of the temperature of the reactions of [60]fullerene with 2-azidopyrimidines **1** and **3** resulted in the formation of various types of cyclic adducts, which is related, most likely, to a change in the schemes of interactions of these reactants.

To estimate the electron affinity of adducts **4** and **6**, we studied their electrochemical behavior by cyclic voltammetry. The obtained results were compared with the data of electrochemical reduction of the starting reactants: C_{60}, azides **1** and **3**, and adduct **2**. Under the conditions studied, the voltammogram of C_{60} exhibits four classical reversible reduction waves with the potentials of the peaks presented in Table 2. Azides **1** and **3** were reduced in the same potential interval (see Table 2). The voltammograms of compound **1** [5] contained four reduction waves, two of which with the highest currents were irreversible, whereas the voltammogram of azide **3** exhibited only one reversible reduction wave. It is known for pyrimidines[11] bearing electron-withdrawing substituents at the C(2) carbon atom (atom numbering scheme for isomer **A** is shown in Scheme 1) that in aprotic solvents during electrochemical reduction these pyrimidines accept one electron to form the radical monoanion accompanied by opening of the bond between the N(3) and C(4) atoms. A similar process can occur in azide **3A**. However, it should be taken into account that at room temperature in a DBC solution isomer **3B** can appear,[12] whose tetrazole cycle can compete with the pyrimidine cycle in electrochemical reduction. The electrochemical reduction of azide **1** is more complicated. Both the pyrimidine cycle and nitro group are reduced in the potential interval from 0.7 to 2.5 V but the reduction potential value of azide **3** suggests that the first wave in the voltammogram of azide **1** corresponds to the reduction of the nitro group. The subsequent waves can be attributed to both nitro group reduction and the reduction of the pyrimidine fragment of the molecule. The azido group is not reduced in the studied potential interval.[5] The relative irreversibility of the reduction waves for the nitro group is explained by the fact that the process is carried out at the potential scan from −0.7 to −2.5 V accompanied by accepting four electrons resulting in the decomposition of the molecule.

The cyclic voltammogram of adduct **6** (see Table 2) exhibits only four reversible one-electron waves of reduction of the fullerene cage corresponding to the final formation of the tetraanion. The reduction of adduct **6** was easier than the reduction of nonmodified fullerene. The absolute value of the difference in potentials of the first reduction peaks of fullerene and adduct **6** was 50 mV.

As in the case of adduct **2** reduction,[5] the cyclic voltammogram of adduct **4** had six reduction waves, four of which (waves I, III, IV, and VI) were reversible and corresponded to the reduction of the fullerene cage. The potentials of peaks of irreversible reduction waves II and V indicated the reduction of the organic fragment. Wave II

Table 2. Potentials (E_p^{red}/V) and currents (I_p^{red}/μA) at the wave peaks in the cyclic voltammograms of C_{60} and compounds **1—3**, **4**, and **6** [a]

Compound	E_p^{red} (I_p^{red})							
C_{60}	−0.83 (4.2)		−1.24 (3.8)		−1.70 (3.9)		−2.16 (4.6)	
1		−1.11 (24.5)[b]		−1.51 (2.5)		−2.02 (25)[b]		−2.20 (4.0)
2	−0.75 (3.5) (I)	−1.11 (2.3)[b] (II)	−1.22 (1.3) (III)		−1.68 (3.3) (IV)	−1.88 (3.5)[b] (V)	−2.18 (3.6) (VI)	
3						−1.81 (21.0)		
4	−0.73 (3.0) (I)	−1.07 (1.1)[b] (II)	−1.20 (1.1) (III)		−1.68 (3.5) (IV)	−1.82 (2.5)[b] (V)	−2.21 (5.7) (VI)	
6	−0.78 (2.5) (I)		−1.10 (1.8)		−1.65 (2.5)		−2.12 (4.8)	

[a] An DCB—MeCN (3 : 1) mixture at 25 °C; concentration of solutions $1 \cdot 10^{-3}$ mol L^{-1}; 0.1 *M* Bu_4NBF_4 as supporting electrolyte; glassy-carbon (GC) cathode (S_{work} = 3.14 mm^2), Ag/0.01 *M* $AgNO_3$ in MeCN as reference electrode, v_{scan} = 50 mV s^{-1}.

[b] Irreversible wave.

corresponds, most likely, to the reduction of the nitro group. It is difficult to draw unambiguous conclusions about the nature of wave V. All reduction waves of the fullerene cage are in the more anodic region compared to the positions of the reduction waves of C_{60}. The absolute difference in potentials of the first reduction peaks of fullerene and adduct **4** was 100 mV.

Based on the potential values for the first peaks of electrochemical reduction of C_{60} and adducts **2**, **4**, and **6**, we estimated their electron affinities (EA) (see Table 1). Thus obtained EA values for the adducts exceeded the EA of fullerene. The calculation of EA (see Table 1) by the PM3 and AM1 methods also showed that adducts **2**, **4**, and **6** should have higher EA than those of nonmodified fullerene and fullereno[1,2-*b*]aziridines **5** and **8**. Thus, the modification of fullerenes by azidopyrimidines can become a promising direction of synthesis of new fullerene-containing electron acceptors.

Experimental

IR spectra were obtained on a Bruker IFS-113V FTIR spectrometer in pellets with KBr. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker MSL-400 instrument at ν_0 400.13 MHz and 100.62 MHz, respectively. The δ values were calculated relatively to $CDCl_3$. UV spectra were recorded on a Specord UV-VIS instrument. The HPLC analysis was carried out on a Laboratorni pristoje Praha chromatograph (Czechia) (column Separon SGX C_{18}, 7 μm, a PhMe—MeCN (1 : 1) mixture as eluent, 0.3 mL min^{-1}, a UV-VIS Detector LCD 2253 instrument as detector, λ 365 nm). Mass spectra were obtained on a MALDI TOF MS instrument (Dynamo) using the *p*-nitroaniline matrix. A stationary disk glassy-carbon (GC) electrode with a working surface of 3.14 mm^2 was used as working electrode in studies by cyclic voltammetry (CV). Voltammograms (CV curves) were recorded using a PI-50-1 potentiostat with a PR-8 programmer and an electrochemical cell connected according to the three-electrode scheme. The CV curves were detected on a two-coordinate recorder at a linear potential sweep rate of 50 mV s^{-1}. The CV curves were obtained in a DBC—MeCN (3 : 1) mixture against a 0.1 *M* solution of Bu_4NBF_4. The Ag/0.01 *M* $AgNO_3$ system in MeCN served as reference electrode. A Pt wire 1 mm in diameter was used as auxiliary electrode. Measurements were carried out in a cell with the temperature maintained at 25 °C in argon. Anhydrous *o*-dichlorobenzene (DCB) was obtained by distillation over P_2O_5. [60]Fullerene was presented by the G. A. Razuvaev Institute of Organometallic Chemistry of the RAS (Nizhny Novgorod).

Processing of results of voltammetric studies. The error of measurement of potentials of wave peaks was not higher than 10 mV. The electron affinity (EA_{exp}) was calculated using the approximating formula $E_p^{red} = 1.0 \cdot EA_{exp}$ + const ($EA_{exp} = 3.48 + E_p^{red}$ for the Ag/0.01 *M* $AgNO_3$ system in MeCN).

2-Azido-5-nitropyrimidine (1) was prepared using a previously described procedure.[13] UV (CH_2Cl_2), λ_{max}/nm: 290. IR (KBr), ν/cm^{-1}: 2297, 2142, 1574, 1520, 1443, 1264, 1143, 978, 873, 840, 792. IR (DCB), ν/cm^{-1}: 2162, 2138, 1587, 1570, 1443, 1413, 1343, 1330, 1159, 1089, 791. ^{1}H NMR ($CDCl_3$), δ: 9.35 (s, 2 H). ^{13}C—{^{1}H} NMR ($CDCl_3$), δ: 139.06 (C(5)); 155.30 (C(4); C6)); 166.15 (C(2)).

2-Azidopyrimidine (3) was synthesized by a previously described procedure.[13] UV (CH_2Cl_2), λ_{max}/nm: 246.5, 270. IR (KBr), ν/cm^{-1}: isomer **3B** — 1620, 1534, 1510, 1397, 1335, 1266, 1161, 1097, 988, 800, 785. IR (DCB), ν/cm^{-1}: 2923, 2853 (CH_2), 2132 (N_3), 1627, 1508, 1461, 1430, 1313, 1252, 1128, 1088, 1035, 820, 755, 746. ^{1}H NMR ($CDCl_3$), δ: isomer **3B** — 9.13 (d, 1 H, *J* = 7.0 Hz); 9.06 (d, 1 H, *J* = 3.0 Hz); 7.33 (m, 1 H); isomer **3A** — 8.60 (d, 2 H, *J* = 4.6 Hz); 7.05 (t, 1 H, *J* = 3.1 Hz). ^{13}C—{^{1}H} NMR ($CDCl_3$), δ: isomer **3B** — 117.15 (C(3)); 160.23 (C(2)); 162.52 (C(4)); 160.59 (C(9)); isomer **3A** — 116.94 (C(5)); 159.08 (C(4), C(6)); 162.85 (C(2)).

4-Nitro-[60]fullereno[1,2-*b*]-1,3a,7-imidazopyrimidine (4). Azide **1** (0.26 mmol) was added to a solution of C_{60} (0.2 mmol) in anhydrous DCB (40 mL), and the mixture was heated with stirring for 16 h at 100 °C. The solvent was removed *in vacuo*, and the residue was chromatographed on a column with silica gel using toluene as eluent. Fullerene C_{60} (82 mg, 57%) and compound **4** (17 mg, 10%) were isolated. TLC data (R_f, Silufol plates, toluene as eluent): 0.93. UV (CH_2Cl_2), λ_{max}/nm: 257, 326, 420, 514. IR (KBr), ν/cm^{-1}: 1574, 1337, 884, 849 (NO_2), 1560, 1427 (heterocyclic system), 526 (C_{60}). ^{1}H NMR ($CDCl_3$), δ: 9.38 (s, 1 H); 9.54 (s, 1 H). ^{13}C NMR ($CDCl_3$), δ: 138.09 (m, C(4)); 140.14 (m, C(9)); 155.33 (dm, C(5), J = 191.4 Hz); 155.10 (dm, C(3), J = 193.1 Hz); C_{60} — 2C: 145.33, 145.03, 145.01, 145.26, 144.64, 144.58, 144.53, 144.49, 144.14, 143.84, 143.81, 143.63, 143.28, 143.03, 142.90, 142.29, 142.12, 141.73, 141.28, 140.21, 138.72, 138.03, 137.42, 135.83, 135.25, 134.26, 82.6; 4C: 143.28; 1C: 144.96, 143.39. MS: *m/z* 858.

[60]Fullereno[1´,2´:4,5]imidazo[1,2-*b*]pyrimidine (6). Azide **3** (0.11 mmol) was added to a solution of C_{60} (0.1 mmol) in anhydrous DCB (25 mL), and the mixture was heated with stirring for 1.5 h at 180 °C. According to the mass spectrometric data, the reaction mixture contained unreacted fullerene (*m/z* 720), monoadduct (*m/z* 813), bisadducts (*m/z* 906), and trisadducts (*m/z* 999). The solvent was removed *in vacuo*, and the residue was chromatographed on a column with silica gel. When toluene was used as eluent, C_{60} (41 mg, 50%), compound **7** (11 mg, 12%), and a mixture of bis- and trisadducts were isolated. TLC data for compound **7** (R_f, Silufol plates, toluene as eluent): 0.44. HPLC data (retention time/min): 5.5. UV (CH_2Cl_2), λ_{max}/nm: 258, 324, 422, 498. IR (KBr), ν/cm^{-1}: 1561, 1410, 811 (heterocyclic system), 526 (C_{60}). ^{1}H NMR ($CDCl_3$), δ: 7.45 (m, C(4)H); 8.85, 8.84 (m, C(3)H, C(5)H), $^4J_{H(2),H(4)}$ = 0.5 Hz, $^3J_{H(2),H(3)}$ = 5.6 Hz, $^4J_{H(4),H(3)}$ = 3.7 Hz).

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