Substituent Effects on Redox Properties and Photoinduced Electron Transfer in Isoxazolo-Fullerenes

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Keywords: Fullerenes / Cycloadditions / Donor−acceptor systems / Cyclic voltammetry / Photoinduced electron transfer

The new C60 and C70 adducts **1b**, **1d**−**1k**, **1m**, **6d**, **7d**, and **8d** have been synthesized by [2+3] cycloadditions of the appropriate nitrile oxides. Variations in the distance and geometry of the donor and acceptor substituents are seen to have an influence on the redox behavior of the fullerene adducts in cyclic voltammetry experiments. The isoxazolo-fullerenes **1c**, **1d**, and **1i** show shifts of about 30 mV or 40 mV to more negative values compared with the reference compound **1a**. On the other hand, strong acceptor properties are detected in the case of compound **1e**, which shows a positive shift of 30 mV relative to **1a**. Moreover, time-resolved fluorescence spectroscopy has shown that upon excitation of the fullerene moiety in the polar solvent benzonitrile, an electron is transferred from the donor substituent to the first excited singlet state of the fullerene, thereby reducing the excited-state lifetime. Our data demonstrate that the electron-transfer rate in donor-substituted fullerenes can be controlled by the electron-donating property of the substituent as well as the electronic structure and/or length of the spacer used. The C70 regioisomers **6d**, **7d**, and **8d** exhibit differences in their spectroscopic characteristics.

Introduction

Due to their unique electrochemical and photophysical properties, fullerenes may be useful for the construction of supramolecular assemblies and new materials. Therefore, the spectroscopic characteristics of fullerenes have been extensively studied during the last few years.[1a,1b] Recently, inter- and intramolecular electron-transfer interactions between fullerenes (C_{60}, C_{70}) and aromatic electron-donating groups in solution have been studied by fluorescence techniques.[2a−2f] We carried out such investigations in the case of isoxazolo-fullerenes **1**. A whole series of examples of this class of compounds has been synthesized by cycloadditions of nitrile oxides[3a−3p] or trimethylsilylnitronates[4a,4b] to [60]- and [70]fullerene. In the present communication, we report on investigations into electron-transfer interactions in new isoxazolo-fullerenes by cyclic voltammetry (CV) and time-resolved fluorescence spectroscopy. Distance, orientation, and electron-donor and -acceptor properties of the substituents R^1 of the R^1CNO addends have been systematically varied to gain insight into the influence of R^1 on the electronic behavior of the cycloadducts **1** (Scheme 1). Since both fullerenes exhibit photophysical properties that are independent of the excitation energy[2b] and show absorption bands up to 700 nm, we decided to use a pulsed diode laser emitting at 630 nm as excitation source in our time-resolved studies.

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Results and Discussion

Synthesis and Analysis

The syntheses of the isoxazolo-fullerenes **1a**, **1c**, **1l**, and **1n** have been described in earlier publications by our group.[3b,3g,3h] The cycloadducts **1b**, **1d**, **1f**−**1k**, and **1m** were prepared by cycloadditions of the appropriate nitrile oxides, which, in turn, could be obtained by chlorination of the oximes **2** and subsequent in-situ dehydrochlorination. In the case of **1c**, the stable nitrile oxide **3c** could be isolated and used directly. For preparing isoxazolo-fullerene **1e**, the addition of the tosylated sodium nitronate **4e**[5] proved successful. The oximes **2b**, **2f**−**2h**, and **2m** have been described previously[6,7,8,9,10] (Scheme 1). The new oxime **2d** was obtained from the corresponding aldehyde **5**, which was synthesized for the first time by a Wittig reaction of 2,4,6-trimethoxybenzaldehyde[11] with formylmethylene-triphenylphosphorane.[12] The new aldoximes **2i** and **2k** were synthesized from the known aldehydes[13][14] (Scheme 2).

All compounds have been fully characterized by IR, UV/Vis, ^{1}H-NMR, and ^{13}C-NMR spectroscopy, as well as by high-resolution mass spectrometry or elemental analysis. For all cycloadducts **1**, the reduced number of NMR signals in the fullerene region proves the mirror symmetry of the products and hence confirms the expected addition to the [6,6] bonds of the fullerene. The synthesis of the [70]fullerene adducts **6d**, **7d**, and **8d** (Scheme 3) was performed in analogy to that of the C_{60} pendant **1d**.

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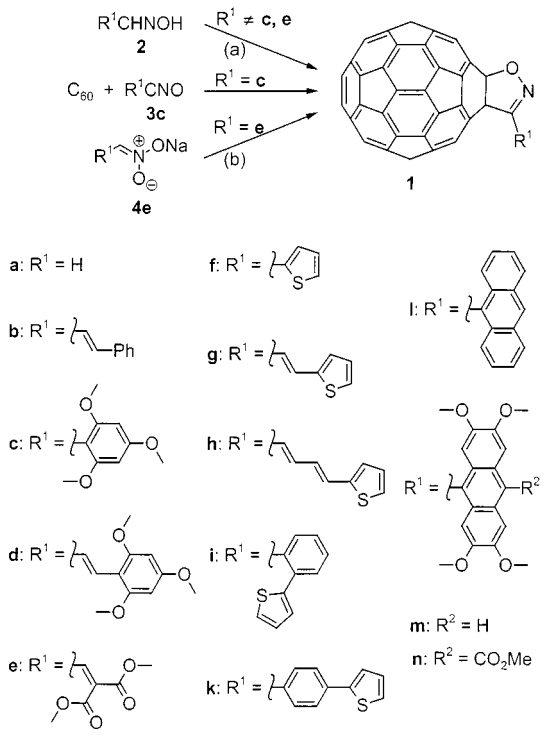
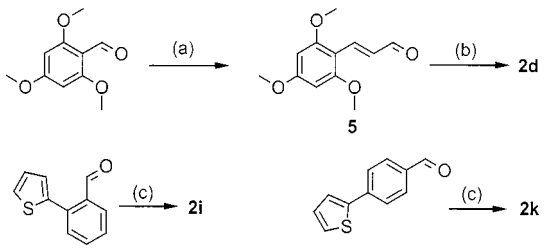
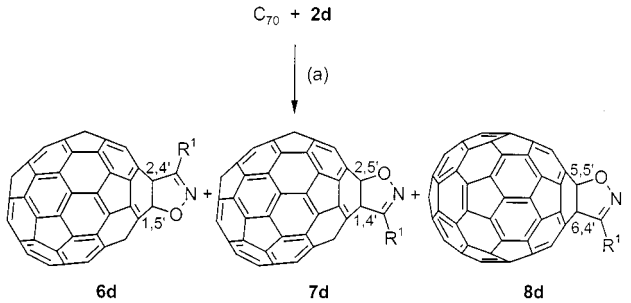


Scheme 1. (a) (i) NCS, $CHCl_3$; (ii) C_{60}, Na_2CO_3 or NEt_3, PhMe; (b) (i) TsCl, DMF; (ii) C_{60}, PhMe



Scheme 2. (a) $Ph_3PCHCHO$, PhMe; (b) $H_2NOH{\cdot}HCl$, C_5H_5N, EtOH; (c) $H_2NOH{\cdot}HCl$, Na_2CO_3, EtOH



Scheme 3. (a) (i) NCS, $CHCl_3$; (ii) C_{60}, NEt_3, PhMe; for **8d** only one enantiomer is drawn

HPLC yielded three fully characterized fractions, which could be assigned to the structures shown in Scheme 3 on the basis of NMR spectroscopic data.

Assignment of the C_{70} Regioisomers 6d, 7d, and 8d

In [70]fullerene, four [6,6] bonds at the 1,2-, 5,6-, 7,21-, and 20,21-positions[15] are available. Only addition to the 1,2- and 20,21-bonds yields achiral cycloadducts, which should be distinguishable by ^{13}C-NMR. In the 1,2-adduct, four fullerene atoms are located on the mirror plane (C^1, C^2, C^{41}, C^{58}). All the others are in enantiotopic pairs. Consequently, $(70 - 4)/2 = 33$ signals with double intensity should be detected for the fullerene core. Ten carbon atoms reside on the symmetry plane in the case of a 20,21-adduct (C^{20}, C^{21}, C^{24}, C^{25}, C^{35}, C^{36}, C^{46}, C^{47}, C^{50}, C^{51}). Consequently, $(70 - 10)/2 = 30$ signals for the enantiotopic fullerene carbons should appear in the ^{13}C-NMR spectrum. In view of the more extended fullerene region in comparison with the NMR spectra of [60]fullerene adducts, the signals for the carbon atoms on the symmetry plane and for the $C^{3'}$ of the heterocycle are not separated from the signals with double intensities. Therefore, $33 + 3 = 36$ signals following 1,2-addition and $30 + 9 = 39$ signals following 20,21-addition are to be expected in the fullerene region. On the other hand, for the two chiral possibilities, $70 - 2 = 68$ signals should be expected in the sp^2 fullerene region.

The cycloaddition of **2d** to C_{70} yields three adducts. Taking into account multiple intensities for signals that are coincidentally identical, we find 2×36 and 1×68 signals in the fullerene region, including that for the $C^{3'}$ of the heterocycle. Clearly, the latter signals correspond to a chiral adduct and we assume an addition to the more reactive 5,6-bond (**8d**) on the second most curved surface of the C_{70} instead of a 7,21-adduct at the relatively unreactive flat mid-section of the fullerene.[16] For the achiral cases, the number of signals (36 rather than 39) proves that the addition occurred at the more reactive 1,2-bond at the most curved surface of the fullerene. The two adducts obtained reflect the two possibilities for the orientation of the substituent R^1 (**6d**, **7d**). In distinguishing between these two orientations, the ^1H-NMR spectrum is helpful. In **7d** and **8d**, the substituent R^1 is positioned over the same five-membered ring in the equatorial region of the surface, while in the case of **6d**, R^1 is located over the apical ring at the pole. It is reasonable to assume that **7d** and **8d** should exhibit very similiar ^1H-NMR shifts for R^1, while the remaining isomer **6d** should show deshielded signals for R^1, where this moiety resides over the apical five-membered ring. This is indeed found to be the case for the isolated adducts. These findings and the order of elution confirm former investigations with other [70]fullerene adducts.[3c,3h,17]

Electrochemistry

Several variously functionalized organofullerenes have been extensively investigated.[1a] The work of Suzuki et al. on the influence of directly attached groups on C_{60} led to the conclusion that saturation of a double bond of the fullerene shifts the reduction potentials to more negative values as compared with the pristine C_{60}.[18] Very little is known about the influence of the nitrile oxide addend on

the electrochemical behavior of isoxazolo-fullerenes.[3c] In this context, we describe here the influence of the unsubstituted addend in **1a** on the reduction behavior of this reference compound. In spite of the saturation of one double bond, we found a shift (50 mV for E^1_{red}) of the reduction potentials to more positive values in **1a** as compared with C_{60} due to the strong electron-withdrawing effect of the heterocycle. To investigate the influence of the substituent R^1 on the isoxazolo system, we considered the first reversible reduction potential. The CV measurements were carried out in 1,2-dichlorobenzene at room temperature with tetrabutylammonium hexafluorophosphate as the supporting electrolyte. The results of these measurements are presented in Figure 1.

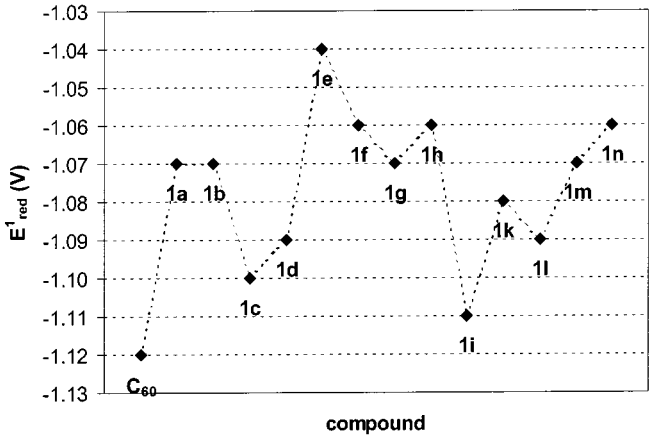


Figure 1. First reversible reduction potentials in the cyclic voltammograms of C_{60} and isoxazolo-fullerenes **1** (V vs. ferrocene/ferrocenium); conditions: 0.1 M nBu_4NPF_6 in 1,2-dichlorobenzene, room temp. (± 0.01 V), scan rate: 0.05 V s^{-1} (**1a**−**1h**) and 0.1 V s^{-1} (**1i**−**1n**); the reverse scan potential was adjusted shortly after the first reduction half-wave to exclude any influence by the oxidation half-wave of conceivable side-products that could have been formed by further reduction

The model compound **1a** was then modified by the introduction of electron donors such as 2-thienyl, 2,4,6-trimethoxyphenyl, and 2,3,6,7-tetramethoxyanthryl substituents and a diester as an electron acceptor. A combination of electron-donating and -withdrawing effects was considered in compound **1n**. In isoxazolo-fullerenes **1c**, **1d**, **1f**−**1h**, the distance between the donor moiety and the fullerene core increases systematically as a result of the introduction of up to two (*E*)-double bonds. Using an *o*-phenylene spacer, as in **1i**, it is possible for the 2-thienyl donor to closely approach the fullerene surface. The compounds **1a**, **1b**, **1k**, and **1l** were used as references in this investigation. Thus, comparison of the reference compound **1b** with **1c** and **1d** confirmed the slightly electron-donating effect of the 2,4,6-trimethoxyphenyl substituent. The influence of the double bond proved not to be significant. That the 2-thienyl heterocycle in compounds **1f**−**1h** and **1k** has no significant effect in comparison with reference **1a** was a somewhat unexpected result. In contrast, the 2-(2-thienyl)phenyl moiety in **1i** has a remarkable influence on the redox behavior. The 40 mV shift to more negative potentials in comparison with model compound **1a** can be explained in terms of through-space interactions between the heterocycle and the fullerene surface, which are favored by the orientation of the addend. A remarkable shift in the other direction is seen for the diester **1e**. The introduction of the two electron-withdrawing groups leads to a 30 mV more positive redox value relative to reference **1a**. This corresponds to a shift of 80 mV in comparison with pristine C_{60}. Clearly, the introduction of two ester groups in **1e** results in the most positive reduction potential in this series. The ester group in the (*Z*)-position is favorably orientated in relation to the fullerene surface, as was the case with the electropositive thiophene substituent in compound **1i**. It is striking that these two fullerene adducts, **1e** and **1i**, exhibit reduction potentials at the two extremes found in this investigation (Figure 1). In the anthryl derivatives, the substituents R^1 are forced to adopt a perpendicular orientation in relation to the heterocycle. The reason for the observed shift of the reduction potential of **1m** into the positive region compared to that of **1l** cannot as yet be adequately explained.

The reduction potentials of the [70]fullerene adducts **6d**, **7d**, and **8d** were found not to be significantly distinguishable from that of pristine fullerene. This confirms earlier findings for comparable isoxazolo-[70]fullerenes.[3c]

Spectroscopy

The fullerenes C_{60} and C_{70} are characterized by strong absorption bands in the UV region and weak but broad absorption bands in the visible wavelength region. The long-wavelength absorption can be attributed to symmetry-forbidden transitions. In contrast to C_{60}, the absorption spectra of functionalized [60]fullerene molecules typically exhibit a sharp absorption band at about 425 nm and an additional band at around 690 nm that can be assigned to the electronic transition from the ground state S_0 to the first excited state S_1 (Figure 2).

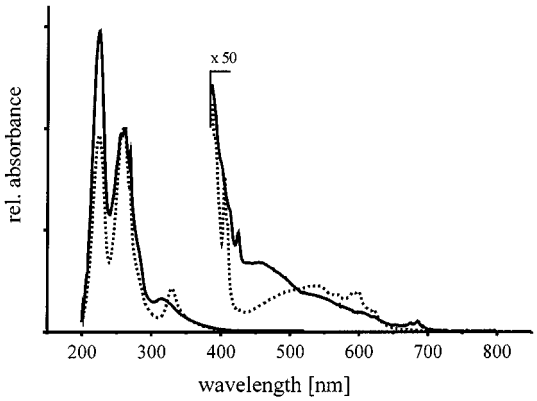


Figure 2. Absorption spectra of pure C_{60} (···) and derivative **1a** (−) in toluene

The absorption and emission spectral characteristics of our new C_{60} and C_{70} derivatives in toluene solution are listed in Table 1.

Table 1. Absorption and emission bands of C_{60}, C_{70}, and their derivatives in toluene; compound **1m** was excited at 370 nm

Compound	Absorption bands [nm]							Fluorescence bands [nm]
C_{60}		621	599	536		405	329	728
1a	693	685	676		455	425	314	699
1b		684				425	317	–
1c		693				492	426	704
1d	693	683	600		492	425	316	705
1e	685	673	602			425	315	–
1f	693	684				492	424	703
1g	687	676	605			425	321	702
1h	685	675			459	425	333	703
1i		690			458	429	323	705
1k		685				427	323	702
1l	689	678	470	450	395	374	316	705
1m		691				420	323	445, 712
1n		693						709
C_{70}		637	611	469	378	360	330	671
6d					464	399	331	685
7d					462	397	330	686
8d					444	400	331	694

The absorption spectra of compounds **1a**–**1n** are quite similar to those reported previously for mono-functionalized fullerenes.[2b,2e,2f] The observed deviations between the UV/Vis spectra of some adducts and the superpositions of the absorption spectra of the isolated components are indicative of weak electronic interactions between the substituents and the C_{60} moieties in the ground state. However, no additional charge-transfer bands were found in the solvents used. Similar results were obtained for C_{70} and its derivatives. Interestingly, differences are seen in the absorption spectra of the three isomers **6d**, **7d**, and **8d** (Figure 3).

The absorption maximum of **8d** in the 450 nm region shows a hypsochromic shift of ca. 20 nm. Additionally, all absorption bands of adduct **8d** are seen to be comparably broad. The other two isomers (**6d**, **7d**) exhibit almost identical absorption properties.

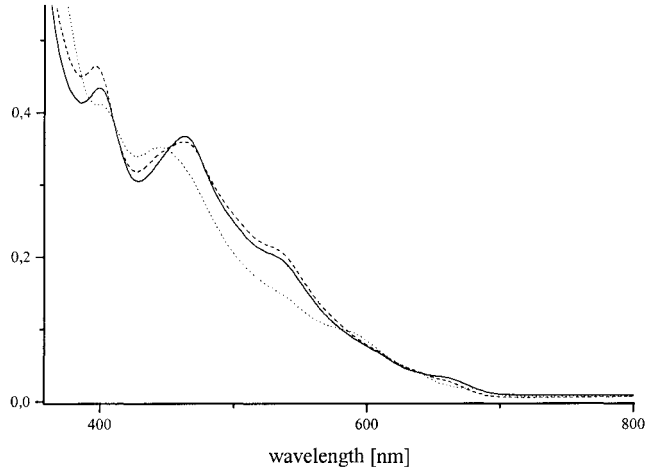


Figure 3. Absorption spectra of **6d** (–), **7d** (---), and **8d** (···) in toluene

Due to weak electronic interactions between S_1 and S_0, fullerenes exhibit low fluorescence quantum yields of Φ_f (C_{60}) = $3.2 \cdot 10^{-4}$ and Φ_f (C_{70}) = $5.7 \cdot 10^{-4}$, but have high inter-system crossing rates into excited triplet states irrespective of the experimental conditions used.[2e] The reduced symmetry in isoxazolo-substituted fullerenes increases their fluorescence quantum yield by a factor of about three compared to the naked fullerenes C_{60} and C_{70}, respectively. The fluorescence spectra of the fullerene derivatives studied here were found to be all very similar, but different from those of C_{60} and C_{70}. While the C_{60} derivatives show emission maxima at around 705 nm with a shoulder at 770 nm, the emission maxima of the C_{70} adducts appear at around 690 nm with a shoulder at 750 nm (Table 1). Upon excitation at 370 nm (excitation of the anthracene subunit), the bichromophoric compound **1m** exhibits an additional fluorescence band with a maximum at 445 nm, which can be assigned to fluorescence of the anthracene moiety. However, due to the short distance involved and efficient spectral overlap, the fluorescence is strongly quenched by Förster energy transfer.[19] These results, as well as a slight enhancement in the fullerene fluorescence band at 705 nm, correspond well to results reported previously for anthracenyl-substituted fullerenes.[2f] Increasing the electron-donating properties of the anthracene subunit by adding further methoxy substituents (compare derivatives **1l**, **1n**, and **1m**), the fluorescence emission maxima shift from 705 to 712 nm (Table 1).

The fluorescence emission maxima of the C_{70} adducts **6d**, **7d**, and **8d** are strongly dependent on the position of the 1,3-dipolar addition of the substituent on the fullerene. While those isomers having the substituent attached at the 1,2-bond closest to the pole (**6d** and **7d**) show almost identical spectral properties, the fluorescence emission maximum of the 5,6-adduct **8d** shows a bathochromic shift of 8 nm.

Fluorescence Lifetimes

Fluorescence decay times of the isoxazolo-fullerenes in toluene (ε = 2.38) and benzonitrile (ε = 25.2) were measured at room temperature by means of time-correlated single-photon counting (TCSPC), using a pulsed laser diode as a source to excite the fullerene subunits at 630 nm. The measured fluorescence decay time of 1.04 ns for C_{60} in toluene is corroborated by literature values ranging from 650 to 1450 ps.[2d] The fluorescence decay times of our new fullerene derivatives in toluene were found to be in the range of 1.49 to 1.76 ns (Table 2).

As can be seen from Table 2, the anthracenyl adducts **1l**, **1m**, and **1n** in particular exhibit longer fluorescence decay times in toluene. These decay times are slightly longer (ca. 200 ps) than those reported in the literature for differently substituted C_{60} derivatives.[2d,2e] As is also apparent from Table 2, the new fullerene derivatives can be roughly divided

Table 2. Fluorescence decay times τ_{S1} of the investigated fullerenes in toluene and benzonitrile measured using TCSPC with a pulsed diode laser; electron transfer rates k_{ET} in benzonitrile were calculated according to Equation 1

Compound	τ_{S1} (Toluene) [ns]	τ_{S1} (Benzonitrile) [ns]	k_{ET} [s^{-1}]
C_{60}	1.04	1.01	
1a	1.55	1.57	
1b	1.53	1.51	
1c	τ_1: 1.40, a_1: 0.90 τ_2: 2.94, a_2: 0.10	1.64	
1d	1.49	< 0.4	> $1.9\cdot10^9$
1e	1.55	1.62	
1f	1.52	1.39	
1g	1.54	1.56	
1h	1.53	1.01	$3.5\cdot10^8$
1i	1.54	1.53	
1k	1.55	1.56	
1l	1.60	1.66	
1m	1.66	< 0.4	> $1.9\cdot10^9$
1n	1.76	0.47	$1.5\cdot10^9$
C_{70}	0.70	0.67	
6d	0.91	0.44	$1.2\cdot10^9$
7d	0.96	0.42	$1.3\cdot10^9$
8d	0.72	0.49	$1.0\cdot10^9$

into those with long fluorescence decay times that are unaffected by the solvent polarity (**1a−c**, **1e−g**, and **1i−l**) and those with decay times influenced by the polarity of the medium (**1d**, **1h**, **1m**, **1n**, **6d**, **7d**, and **8d**). The observed solvent dependence of the fluorescence kinetics for some adducts indicates that in polar solvents an additional deactivation pathway of the excited S_1 state becomes available. Comparison of the structures of compounds **1c** and **1d**, **1f** and **1h**, or **1l** and **1n**, **1m**, respectively, and the measured decay times confirms the idea that non-radiative deactivation is linked with the electron-donating properties of the substituents. Therefore, we attribute the observed fluorescence quenching in benzonitrile to an intramolecular photoinduced electron-transfer reaction between fullerenes C_{60} and C_{70} and the aromatic substituents. Upon excitation of the fullerenes at 630 nm, an electron is transferred from the ground-state aromatic substituent to the excited fullerene subunit, thus reducing the measured fluorescence decay time. As indicated by the shorter fluorescence decay times seen for compounds **1d** and **1h**, additional double bonds in the spacer seem to enhance the electron-donating influence of the thienyl- and trimethoxyphenyl substituents, respectively. The electron-transfer rates, k_{ET}, in benzonitrile were calculated according Equation 1.

$$k_{ET} = \tau^{-1} - \tau_{ref}{}^{-1} \quad (1)$$

Here, τ_{ref} denotes the fluorescence decay time of the reference compound **1a** in benzonitrile and τ denotes the decay time of the compound being quenched in the same solvent. For C_{70} fullerenes, the decay times measured in toluene were used as reference decay times τ_{ref} in order to calculate k_{ET}. Table 2 summarizes the fluorescence decay times and the corresponding electron-transfer rates in benzonitrile for all the investigated fullerene derivatives.

For C_{70}, a fluorescence decay time of 700 ps was measured in toluene, which is in good agreement with previously reported results.[2b] Upon substitution with trimethoxyphenyl groups, as in compounds **6d** and **7d**, the fluorescence decay times in toluene increase slightly. On the other hand, **8d** exhibits essentially the same decay time as C_{70} (Table 2), indicating only weak electronic perturbation of the fullerene. However, we observe relatively large bathochromic shifts in the emission maxima of all the donor-substituted C_{70} fullerenes (Table 1), especially for compound **8d**. Moreover, the calculated electron-transfer rates of **6d**, **7d**, and **8d** in benzonitrile are similar. At present, we are unable to attribute the observed deviations in the spectroscopic properties to different coupling positions or interaction geometries between the two subunits.

Conclusion

The new C_{60} and C_{70} adducts **1b**, **1d−1k**, **1m**, **6d**, **7d**, and **8d** have been synthesized by [2+3] cycloadditions of the appropriate nitrile oxides. In the case of compound **1e**, a tosylated sodium nitronate was used as a precursor for an isoxazolo-fullerene for the first time. All adducts have been fully characterized. Variation of the distances and geometries of the donor and acceptor substituents has an influence on the redox behavior of the fullerene adducts, as shown by CV experiments. The two 2,4,6-trimethoxyphenyl-substituted isoxazolo-fullerenes **1c**, **1d**, as well as compound **1i** with a 2-thienyl donor connected via an *o*-phenylene spacer, show shifts of about 30 to 40 mV to more negative values as compared with the reference compound **1a**. On the other hand, strong acceptor properties are seen in compound **1e**, which shows a positive shift of 30 mV relative to **1a** due to the presence of two ester groups. The fullerene derivatives were also studied by time-resolved fluorescence spectroscopy. Upon excitation of the fullerene moiety in the polar solvent benzonitrile, an electron is transferred from the donor substituent to the first excited singlet state of the fullerene, thereby reducing the excited-state lifetime. Our data demonstrate that the electron-transfer rate in donor-substituted fullerenes can be controlled by the electron-donating property of the substituent as well as by the electronic structure and/or length of the spacer used. Whereas the reduction potentials of the C_{70} regioisomers **6d**, **7d**, and **8d** are not significantly different in the ground state, it is an interesting finding that they exhibit differences in their spectroscopic characteristics. However, the observed differences cannot be attributed to different coupling positions or interaction geometries of the two subunits. In order to gain further insight into the latter features, reference substances will have to be synthesized, separated, and carefully investigated.

Experimental Section

General Remarks: FT-IR: Bruker IFS-66. − UV/Vis: Hewlett Packard 8452 diode-array spectrophotometer. − ^{1}H- and ^{13}C-NMR: Bruker AC 300 or DRX 300. − FAB-MS: Jeol JMS-700 (positive-ion mode). − MALDI-TOF MS: Bruker Biflex MALDI-TOF (ma-

trix: 9-nitroanthracene, negative-ion mode). − Flash column chromatography: Aldrich silica gel, 32−63 μm, 60 Å. − HPLC/UV detection: Abimed Gilson 118, 201, 305, 806; columns: Macherey−Nagel silica gel: 25 × 250 mm, 7 μm, 50 Å; buckyclutcher I® (see phase "X" in ref.[20]): Regis Technologies, 21.1 × 250 mm, 10 μm, 100 Å. − CV: HEKA potentiotstat/galvanostat 285/IEC, HEKA.-POT 3.01; working electrode: glassy carbon; counter- and compensation electrode: platinum; reference electrode: calomel (Metrohm); solvent: 1,2-dichlorobenzene; electrolyte: nBu$_4$NPF$_6$ (0.1 M); internal calibration: ferrocene/ferrocenium couple, apart from C_{70} and derivatives, which were measured against SCE, assumed as 0 V. − Spectroscopic measurements: All measurements were made at room temperature in non-degassed HPLC-grade toluene or benzonitrile (Aldrich), which were not purified further, in standard quartz cuvettes with a pathlength of 1 cm. Absorption spectra were measured with a Perkin−Elmer Lambda 18 UV/Vis spectrophotometer. Fluorescence spectra were recorded in the wavelength range of 600 to 800 nm upon excitation at 477 nm in toluene solution using a Photon Technology Int. LS100 fluorescence spectrophotometer. The spectra of the pure solvents were subtracted from those of the samples. Fluorescence decay times were measured using a time-correlated single-photon counting technique (TCSPC). The samples were excited at 630 nm with a pulsed laser diode (Hamamatsu PLP 01, 10 μW, 100 ps FWHM, 10 MHz repetition rate). The fluorescence decay was monitored at the emission maximum using 512 time channels at 50 ps. For each fluorescence decay, at least 2000 photon counts were collected in the maximum channel. The photomultiplier tube (PMT) from the life-time spectrometer LS100 (PTI) was used for detection in combination with the necessary electronic equipment. The measurements were carried out in the reversed mode, i.e. the start pulses were provided by the PMT. The instrument response function required for deconvolution was obtained from a scattering solution. The quality of the decay fits were assessed by means of the reduced chi-squared statistical parameter (χ^2). Most of the decays could be described satisfactorily by a mono-exponential model with $\chi^2 < 1.3$. In the cases where a second component was necessary, a bi-exponential model was used to fit the decay (Equation 2):

$$I(t) = a_1 \exp(-t\ \tau_1{}^{-1}) + a_2 \exp(-t\ \tau_2{}^{-1}) \quad (2)$$

Here, a_1 and a_2 are pre-exponential factors, which describe the ratio of the excited species ($a_1 + a_2 = 1$), and τ_1 and τ_2 denote their lifetimes.

Isoxazolo[4′,5′:1,2][60]fullerene[21] **(1a):** This isoxazolo-fullerene has been synthesized previously in our laboratory.[3g] CV (0.05 V s^{-1}): E_{red} [V]: $E^1 = -1.09$, $E^2 = -1.45$, $E^3 = -1.89$.

(2*E*)-3-Phenyl-2-propenal Oxime (2b): The synthesis was carried out according to a literature procedure.[6]

3′-(2,4,6-Trimethoxyphenyl)isoxazolo[4′,5′:1,2][60]fullerene (1c): This isoxazolo-fullerene has been synthesized previously in our laboratory.[3h] CV (0.05 V s^{-1}): E_{red} [V]: $E^1 = -1.11$, $E^2 = -1.47$, $E^3 = -1.96$.

(*E*)-3-(2,4,6-Trimethoxyphenyl)propenal (5): The synthesis was based on a procedure for arylpropenals.[22] 6.20 g (20 mmol) of formylmethylene-triphenylphosphorane[12] was almost entirely dissolved in 570 mL of dry toluene with the help of an ultrasonic bath and slight heating. After the addition of 4.00 g (20 mmol) of 2,4,6-trimethoxybenzaldehyde,[11] the mixture was heated to reflux under argon for 4 d [TLC (SiO_2, EtOH): R_f (product) = 0.70, R_f (starting material) = 0.64, R_f (ylene) = 0.53]. After removal of the solvent, the aldehydes were dissolved in diethyl ether and separated from the residue, in which most of the triphenylphosphane oxide remained [TLC (SiO_2, AcOEt): R_f (product) = 0.61, R_f (starting material) = 0.42, R_f (phosphane oxide) = 0.26]. After removal of the ether, the residual orange solid was redissolved in a little warm ethyl acetate and purified by chromatography (silica gel). The product was dried over silica to yield 2.54 g (11 mmol, 56%) of **5**. Further purification by recrystallization from 400 mL of petroleum ether (60/70) yielded 1.52 g (6.6 mmol, 60%) of the product as an orange microcrystalline powder; m.p. 131.4−133.1°C. The remainder could only be recovered as an oil. − IR (KBr): $\tilde{\nu}$ = 1655 cm^{-1} (C=O), 1600, 1575, 1471, 1456, 1423, 1340, 1235, 1212, 1164, 1146, 1103. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 222 nm (3.93), 248 (3.99), 334 (4.41). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.83 (s, 3 H, 4-OCH_3), 3.86 (s, 6 H, 2,6-OCH_3), 6.09 (s, 2 H, arom. CH), 7.03 (dd, ^3J = 16.0 Hz, ^3J = 8.2 Hz, 1 H, H^2), 7.24 (s, $CHCl_3$, solv.), 7.82 (d, ^3J = 16.0 Hz, 1 H, H^3), 9.55 (d, ^3J = 8.2 Hz, 1 H, H^1). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.41 (1 C, 4-OCH_3), 55.73 (2 C, 2,6-OCH_3), 77.00 (t, $CDCl_3$, solv.), 90.48 (2 C, arom. 3,5-CH), 105.89 (arom. 1-C), 129.05 (olef. CH, C^2), 144.71 (olef. CH, C^3), 161.38 (2 C, arom. 2,6-C), 163.98 (arom. 4-C), 196.42 (CHO). − MS (EI, 70 eV): *m/z* (%): 222 (100) [M$^+$], 191 (88) [M$^+$ − OCH_3], 179 (16) [M$^+$ − C_2H_3O], 168 (51), 163 (7), 151 (6), 139 (16), 121 (9), 91 (4), 77 (3), 69 (3), 51 (1). − $C_{12}H_{14}O_4$ (222.2): calcd. C 64.85, H 6.35; found C 64.90, H 6.44.

(2*E*)-3-(2,4,6-Trimethoxyphenyl)propenal Oxime (2d): The synthesis was based on a procedure for aryl-substituted acrolein oximes.[8] 250 mg (1.1 mmol) of **5** and 390 mg (5.6 mmol, 5.1 equiv.) of hydroxylammonium chloride were dissolved in 50 mL of dry ethanol. After the addition of 0.45 mL (5.6 mmol) of dry pyridine, the mixture was heated to reflux for 12 h. After removal of the solvent, the crude product was redissolved in ethyl acetate and separated from the precipitated pyridine salt. After chromatography on silica gel eluting with ethyl acetate, the product was dried over silica to yield 200 mg (0.8 mmol, 73%) of **2d** as a lemon-yellow powder. For analytical purposes, a portion was recrystallized from water. The off-white product thus obtained was found to be a mixture of the (*E*)- and (*Z*)-oximes; m.p. 154.6−156.6°C. − TLC (SiO_2, AcOEt): R_f [(*E*)- and (*Z*)-isomers] = 0.65, 0.60. − IR (KBr): $\tilde{\nu}$ = 3249 cm^{-1} (OH), 3001, 2966, 2942, 2840, 1600 (C=N), 1458, 1434, 1415, 1348, 1326, 1233, 1204, 1158, 1113, 1060, 1037, 981, 952, 811. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 232 nm (4.07), 244 (4.14), 317 (4.46). Workup of one batch yielded the pure (*E*)-oxime: ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.49 (quint., [D$_5$]DMSO, solv.), 3.80 (s, 3 H, 4-OCH_3), 3.82 (s, 6 H, 2,6-OCH_3), 6.26 (s, 2 H, arom. CH), 7.01 (d, ^3J = 16.5 Hz, 1 H, H^3), 7.13 (d, ^3J = 9.6 Hz, 1 H, H^1), 7.46 (dd, ^3J = 16.5 Hz, ^3J = 9.6 Hz, 1 H, H^2), 10.80 (s, 1 H, OH); $\delta_{OH} - \delta_{CHN}$ = 3.67, (*E*)-isomer.[23] The rest of the batches yielded a mixture of the oximes: ^{1}H NMR (300 MHz and two signals at 200 MHz as indicated, [D$_6$]DMSO): δ = 2.49 (quint., [D$_5$]DMSO, solv.), 3.79 [s, 3 H, 4-OCH_3, (*Z*)-oxime], 3.80 [s, 3 H, 4-OCH_3, (*E*)-oxime], 3.81 [s, 6 H, 2,6-OCH_3, (*Z*)-oxime], 3.82 [s, 6 H, 2,6-OCH_3, (*E*)-oxime], 6.25 [s, 2 H, arom. CH, (*Z*)-oxime], 6.26 [s, 2 H, arom. CH, (*E*)-oxime], 6.97 [d, overlapped, 1 H, H^1, (*Z*)-oxime], 6.99 [d, ^3J = 7.5 Hz (at 200 MHz), 1 H, H^3, (*Z*)-oxime], 7.02 [d, ^3J = 16.5 Hz, 1 H, H^3, (*E*)-oxime], 7.14 [d, ^3J = 9.6 Hz, 1 H, H^1, (*E*)-oxime], 7.47 [dd, ^3J = 16.5 Hz, ^3J = 9.6 Hz, 1 H, H^2, (*E*)-oxime], 7.77 [dd, ^3J = 7.5 Hz, ^3J = 2.0 Hz (at 200 MHz; apparently "d" with "J = 8.1 Hz" at 300 MHz), 1 H, H^2, (*Z*)-oxime], 10.72 [s, 1 H, OH, (*Z*)-oxime], 10.81 [s, 1 H, OH, (*E*)-oxime]; $\delta_{OH} - \delta_{CHN}$ [(*Z*)-oxime] = 3.75, $\delta_{OH} - \delta_{CHN}$ [(*E*)-oxime] = 3.67, (*Z*)-oxime/(*E*)-oxime 2.7:1. − ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 39.70 (sept., [D$_6$]DMSO, solv.), 55.49 [1 C, 4-OCH_3, (*Z*)-oxime], 55.52 [1 C, 4-OCH_3, (*E*)-oxime], 55.96 [2 C, 2,6-OCH_3, (*Z*)-oxime], 56.02 [2

C, 2,6-OCH_3, (*E*)-oxime], 91.15 (double int.), 106.14, 106.24, 117.26, 123.44, 127.95, 129.06, 149.96, 152.52, 159.48, 159.98, 161.15, 161.63 (each arom. C or olef. C). − MS (EI, 70 eV): *m/z* (%): 237 (12) [M^+], 235 (13) [$M^+ - 2$ H], 220 (15), 219 (61) [$M^+ - H_2O$], 206 (30) [$M^+ - CH_3O$], 196 (17), 195 (29), 191 (22), 190 (100), 189 (22), 179 (42), 175 (20) [$M^+ - 2\ CH_3O$], 151 (17), 146 (14), 121 (22), 103 (11), 92 (11), 91 (16) [$C_7H_7^+$], 77 (16) [$C_6H_5^+$], 69 (23), 63 (10), 51 (9) [$C_4H_3^+$]. − $C_{12}H_{15}NO_4$ (237.3): calcd. C 60.75, H 6.37, N 5.90; found C 60.96, H 6.31, N 5.52.

Sodium 1,1-Bis(methoxycarbonyl)prop-1-ene-3-nitronate (4e): The synthesis was carried out according to a literature procedure.[5]

Thiophene-2-carbaldehyde Oxime (2f): The synthesis was carried out according to a literature procedure.[7]

(2*E*)-3-(2-Thienyl)propenal Oxime (2g): The synthesis was carried out according to a literature procedure.[8]

(2*E*,4*E*)-5-(2-Thienyl)penta-2,4-dienal Oxime (2h): A literature procedure was supplemented by chromatography (silica gel, AcOEt) to obtain this product.[9]

2-(2-Thienyl)benzaldoxime (2i): 350 mg (1.9 mmol) of 2-(2-thienyl)-benzaldehyde[13] was dissolved in 50 mL of ethanol. The solution was heated under reflux, whereupon 1.3 g (19 mmol, 10 equiv.) of hydroxylammonium chloride, dissolved in 5 mL of water and neutralized to pH 7 with $NaHCO_3$, was added. After heating for 1 h under reflux, cold water was added to the hot solution until precipitation of the product commenced. The precipitate was collected, washed with water, and dried in air to afford 290 mg (1.4 mmol, 74%) of **2i** as colourless crystals; m.p. 134°C. − IR (KBr): $\tilde{\nu}$ = 3422 cm^{-1} (OH), 3215 (OH), 1632 (C=N), 1487, 1317, 1199, 978, 957, 871, 848, 763, 683. − UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 232 nm (4.98), 248 (5.12), 274 (4.90). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.04 (dd, ^3J = 3.5 Hz, ^4J = 1.5 Hz, 1 H, thiophene), 7.13 (dd, ^3J = 5.1 Hz, ^3J = 3.3 Hz, 1 H, thiophene), 7.36−7.51 (m, 4 H, 3 × arom. CH, 1 × thiophene), 7.89 (dd, ^3J = 7.5 Hz, ^4J = 1.8 Hz, 1 H, arom. CH), 8.12 (s, 1 H, OH), 8.36 (s, 1 H, CHN). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 126.43, 126.58, 127.53, 128.12, 128.15, 129.73, 130.21, 130.85, 134.51, 140.60 (each arom. C), 149.64 (CHN). − MS (EI, 70 eV): *m/z* (%): 203 (10) [M^+], 202 (12), 187 (15), 186 (100) [M^+ − OH], 185 (15), 142 (13), 140 (10), 115 (47), 89 (14), 75 (12), 74 (11), 69 (11), 63 (20), 58 (14), 51 (14), 50 (13), 45 (45), 39 (27), 28 (11). − MS (HR EI): *m/z*: 203.040 [M^+, calcd. 203.040]. − $C_{11}H_9NOS$ (203.26): calcd. C 65.00, H 4.46, N 6.89, S 15.78; found C 65.02, H 4.73, N 6.84, S 15.77.

4-(2-Thienyl)-benzaldoxime (2k): 500 mg (2.7 mmol) of 4-(2-thienyl-)benzaldehyde[14] was dissolved in 75 mL of ethanol. The solution was heated under reflux, whereupon 1.85 g (27 mmol, 10 equiv.) of hydroxylammonium chloride, dissolved in 5 mL of water and neutralized to pH 7 with $NaHCO_3$, was added. After heating for 1 h under reflux, cold water was added to the hot solution until precipitation of the product commenced. The precipitate was collected, washed with water, and dried in air to afford 525 mg (2.6 mmol, 96%) of **2k** as colourless crystals; m.p. 156°C. − IR (KBr): $\tilde{\nu}$ = 3285 cm^{-1} (OH), 1602 (C=N), 1501, 1426, 1323, 1304, 1214, 1183, 973, 937, 872, 850, 820, 692, 475. − UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 234 nm (3.92), 314 (4.37). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.11 (dd, ^3J = 5.1 Hz, ^3J = 3.7 Hz, 1 H, thiophene), 7.33 (dd, ^3J = 5.1 Hz, ^4J = 1.1 Hz, 1 H, thiophene), 7.38 (dd, ^3J = 3.5 Hz, ^4J = 1.1 Hz, 1 H, thiophene), 7.60 (d, ^3J = 8.8 Hz, 2 H, arom. CH), 7.66 (d, ^3J = 8.8 Hz, 2 H, arom. CH), 7.99 (s, 1 H, OH), 8.17 (s, 1 H, CHN). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 123.70, 125.50, 126.09, 127.56, 128.18, 130.98, 135.94, 143.55 (each arom. C), 149.95 (CHN). − MS (EI, 70 eV): *m/z* (%): 203 (100) [M^+], 187 (13), 186 (30) [M^+ − OH], 185 (41), 160 (34), 159 (49), 158 (13), 115 (64), 113 (10), 74 (10), 63 (10), 51 (22), 39 (11), 28 (79). − MS (HR EI): *m/z*: 203.040 [M^+, calcd. 203.040]. − $C_{11}H_9NOS$ (203.26): calcd. C 65.00, H 4.46, N 6.89, S 15.78; found C 64.83, H 4.67, N 6.85, S 15.51.

3′-(Anthr-9-yl)isoxazolo[4′,5′:1,2][60]fullerene (1l): This isoxazolo-fullerene has been synthesized previously in our laboratory.[3b,3g] CV (0.05 V s^{-1}): E_{red} (V): E^1 = −1.11, E^2 = −1.48, E^3 = −1.91.

2,3,6,7-Tetramethoxyanthr-9-yl-carbaldoxime (2m): The synthesis was carried out according to a literature procedure.[10]

3′-[2,3,6,7-Tetramethoxy-10-(methoxycarbonyl)anthr-9-yl]isoxazolo-[4′,5′:1,2][60]fullerene (1n): This isoxazolo-fullerene has been synthesized previously in our laboratory.[3g] CV (0.05 V s^{-1}): E_{red} [V]: E^1 = −1.06, E^2 = −1.43, E^3 = −1.89.

General Procedure for the Synthesis of the Isoxazolo-Fullerenes 1b, 1d, 1f−1k, 1m: The synthesis was based on a general method for the cycloaddition of in situ prepared nitrile oxides to olefins.[24−26] To a solution of 140 μmol of the appropriate oxime in 10 mL of dry chloroform, 10 μL of dry pyridine was added. At 0°C, this yellow solution was treated with 37 mg (280 μmol, 2 equiv.) of *N*-chlorosuccinimide (NCS) and the mixture was stirred for 15 min. The resulting chlorooxime solution was subsequently added to 100 mg (140 μmol) of C_{60} dissolved in 150 mL of dry toluene. After the addition of either 20 μL (150 μmol) of triethylamine or 147 mg (1.4 mmol, 10 equiv.) of Na_2CO_3 in 2.5 mL of water, the reaction mixture was stirred overnight at room temp. It was then washed with water and dried (Na_2SO_4). Flash chromatography on silica gel eluting with toluene yielded a crude mixture of the monoadduct and unchanged C_{60}, while the higher fullerene adducts remained on the column. In one case (**1d**), separation of the C_{60} was possible at this stage. In all other cases, subsequent purification by HPLC (silica gel, toluene) was required to the isolate the brown monoadduct. For compounds **1i** and **1k**, separation of the C_{60} by chromatography on silica gel with CS_2 proved practicable. Finally, bucky-clutcher® HPLC eluting with toluene and subsequent removal of the solvent yielded the pure product in 25−36% yield after drying with SiO_2/paraffin. One adduct (**1h**) was found to have gleaming surfaces.

(1*E*)-3′-(2-Phenylvinyl)isoxazolo[4′,5′:1,2][60]fullerene (1b): Yield: 31 mg (26%, 35 μmol). − IR (KBr): $\tilde{\nu}$ = 1698 cm^{-1} (C=N), 1628 (C=C), 1429 (C_{60}), 1182 (C_{60}), 957 (C=C), 744, 688, 557 (C_{60}), 526 (C_{60}). − UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 233 nm (5.03), 256 (5.18), 319 (4.86), 362 (4.27), 390 (4.05), 486 (3.71). − ^{1}H NMR (200 MHz, CS_2/$CDCl_3$, 9:1): δ = 7.06−7.41 (m, 3 H, arom. 3,4,5-CH), 7.24 (s, $CHCl_3$, solv.), 7.28 (d, ^3J = 16.5 Hz, 1 H, olef. CH, C^2), 7.53 (dd, ^3J = 7.6 Hz, ^4J = 2.0 Hz, 2 H, arom. 2,6-CH), 7.96 (d, ^3J = 16.5 Hz, 1 H, olef. CH, C^1). − ^{13}C NMR (75 MHz, 1-chloronaphthalene/$CDCl_3$, 9:1, 19028 scans): δ = 77.94 (*C*CN, aliph. C, C^1), 103.76 (CON, aliph. C, C^2), 124.03 (1-chloronaphthalene, high-field signal, solv.), 115.52, 128.60, 128.90, 135.46, 137.94, 145.50 (each arom. CH or olef. CH), 136.23, 136.47, 139.52, 139.93, 141.03, 141.34, 141.48 (each 2 C, fullerene), 141.66 (8 C, fullerene), 142.05 (6 C, fullerene), 142.19, 143.32, 143.61, 143.84, 144.06, 144.25, 144.39, 144.46, 144.52, 144.81, 144.89, 145.14, 145.23, 145.60 (each 2 C, fullerene), 146.50, 147.04 (each C, fullerene, C^{55} or C^{60}), 151.79 (C=N, $C^{3'}$); for the assignment of the signals at δ = 128.60 and 128.90, a ^{13}C-NMR reference spectrum of the solvent (10000 scans) was used. − MS (MALDI-TOF): *m/z* (%): 865 (98) [M^-], 720 (100) [C_{60}^-]. − MS (FAB): *m/z* (%): 866 (11) [M^+ + H], 865 (4) [M^+], 816 (4), 793 (6), 792 (5), 768 (8), 744 (9), 737 (11), 720 (100) [C_{60}^+]. − MS (HR FAB): *m/z* (± 0.01): 866.06 [M^+ + H, calcd. 866.06], 865.06 [M^+, calcd. 865.05], 721.00

[$^{12}C_{59}{}^{13}C^+$, calcd. 721,00], 720.00 [$C_{60}{}^+$, calcd. 720.00]. − CV (0.05 V s^{-1}): E_{red} (V): $E^1 = -1.09$, $E^2 = -1.45$, $E^3 = -1.87$.

(1*E*)-3′-[2-(2,4,6-Trimethoxyphenyl)vinyl]isoxazolo[4′,5′:1,2][60]-fullerene (1d): Yield: 34 mg (25%, 40 μmol). − IR (KBr): $\tilde{\nu}$ = 1602 cm^{-1} (C=N), 1579 (C=C), 1466, 1454, 1433 (C_{60}), 1329, 1204, 1180 (C_{60}), 1157 (s), 1121 (s), 585 (C_{60}), 527 (C_{60}). − UV/Vis (CH_2Cl_2): (a) d = 0.1 cm: λ_{max} (lg ε) = 224 nm (5.21), 254 (5.27), 322 (4.91); (b) d = 1 cm: λ_{max} (lg ε) = 400 nm (3.68), 413 (3.52), 425 (3.40), 486 (3.46). − ^{1}H NMR (300 MHz, CS_2/$CDCl_3$, 9:1): δ = 3.81 (s, 6 H, 2,6-OCH_3), 3.82 (s, 3 H, 4-OCH_3), 6.03 (s, 2 H, arom. 3,5-CH), 7.24 (s, $CHCl_3$, solv.), 7.67 (d, ^3J = 16.9 Hz, 1 H, olef. CH), 8.31 (d, ^3J = 16.9 Hz, 1 H, olef. CH). − ^{13}C NMR (75 MHz, 1-chloronaphthalene/[D_6]acetone, 9:1, 10000 scans): δ = 54.39 (4-OCH_3), 54.85 (2 C, 2,6-OCH_3), 78.55 (*C*CN, aliph. C, C^1), 90.30 (2 C, arom. 3,5-CH), 103.48 (CON, aliph. C, C^2), 106.83 (arom. 1-C), 116.31 (CH, olef. C), 124.03 (1-chloronaphthalene, high-field signal, solv.), 136.27, 136.33, 139.43, 139.52, 141.04, 141.40, 141.62, 141.64, 141.73, 141.84, 142.01, 142.12, 142.18, 143.41, 143.66, 144.26 (each 2 C, fullerene), 144.38 (4 C, fullerene, 1 olef. CH), 144.64, 144.89, 145.08, 145.10, 145.19, 145.38, 145.46, 145.48, 145.61, 145.92 (each 2 C, fullerene), 146.46, 146.98 (each C, fullerene, C^{55} or C^{60}), 153.71 (C=N, $C^{3'}$), 160.31 (2 C, *C*OCH_3, arom. 2,6-C), 161.99 (*C*OCH_3, arom. 4-C). − MS (MALDI-TOF): *m*/*z* (%): 955 (29) [M^-], 720 (100) [$C_{60}{}^-$]. − MS (FAB): *m*/*z* (%): 956 (38) [M^+ + H], 955 (12) [M^+], 924 (11) [$M^+ - OCH_3$], 720 (100) [$C_{60}{}^+$]. − MS (HR FAB): *m*/*z* (± 0.009): 956.090 [M^+ + H, calcd. 956.092], 955.087 [M^+, calcd. 955.084], 719.998 [$C_{60}{}^+$, calcd. 720.000]. − CV (0.05 V s^{-1}): E_{red} [V]: $E^1 = -1.11$, $E^2 = -1.45$, $E^3 = -1.90$.

3′-(2-Thienyl)isoxazolo[4′,5′:1,2][60]fullerene (1f): Yield: 39 mg (33%, 45 μmol). − IR (KBr): $\tilde{\nu}$ = 1634 cm^{-1} (C=N), 1429 (C_{60}), 1186 (C_{60}), 842, 702, 574 (C_{60}), 527 (C_{60}). − UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 232 nm (5.06), 255 (5.24), 316 (4.80). − ^{1}H NMR (200 MHz, CS_2/$CDCl_3$, 9:1): δ = 7.16 (dd, ^3J = 5.2 Hz, ^3J = 3.7 Hz, 1 H, thiophene 4-H), 7.24 (s, $CHCl_3$, solv.), 7.54 (dd, ^3J = 5.2 Hz, ^4J = 1.1 Hz, 1 H, thiophene 5-H), 8.02 (dd, ^3J = 3.7 Hz, ^4J = 1.1 Hz, 1 H, thiophene 3-H). − ^{13}C NMR (75 MHz, 1-chloronaphthalene/$CDCl_3$, 9:1, 10000 scans): δ = 77.58 (*C*CN, aliph. C, C^1), 104.30 (CON, aliph. C, C^2), 124.03 (1-chloronaphthalene, high-field signal, solv.), 128.63, 133.99 (each C, thiophene), 136.06, 136.37, 139.45, 139.47, 140.85, 141.12, 141.42 (each 2 C, fullerene), 141.44 (6 C, fullerene), 141.57, 141.62 (each 2 C, fullerene), 141.98 (C, thiophene), 142.03, 143.18, 143.53, 143.58 (each 2 C, fullerene), 143.82 (4 C, fullerene), 143.85, 144.28, 144.36, 144.40, 144.79, 145.07 (each 2 C, fullerene), 145.08 (C, thiophene), 145.12, 145.35, 145.41, 145.52 (each 2 C, fullerene), 146.44, 146.94 (each C, fullerene, C^{55} or C^{60}), 148.72 (C=N, $C^{3'}$); for the assignment of the signals at δ = 128.63 and 133.99, a ^{13}C-NMR reference spectrum of the solvent (10000 scans) was used. − MS (MALDI-TOF): *m*/*z* (%): 845 (100) [M^-], 720 (97) [$C_{60}{}^-$]. − MS (FAB): *m*/*z* (%): 846 (20) [M^+ + H], 845 (13) [M^+], 766 (18), 749 (12), 737 (16), 720 (100) [$C_{60}{}^+$]. − MS (HR FAB): *m*/*z* (± 0.01): 846.00 [M^+ + H, calcd. 846.00], 845.00 [M^+, calcd. 844.99], 721.01 [$^{12}C_{59}{}^{13}C^+$, calcd. 721,00], 720.00 [$C_{60}{}^+$, calcd. 720.00]. − CV (0.05 V s^{-1}): E_{red} [V]: $E^1 = -1.10$, $E^2 = -1.45$, $E^3 = -1.86$.

(1*E*)-3′-[2-(2-Thienyl)vinyl]isoxazolo[4′,5′:1,2][60]fullerene (1g): Yield: 42 mg (35%, 48 μmol). − IR (KBr): $\tilde{\nu}$ = 1644 cm^{-1} (C=N), 1621 (C=C), 1426 (C_{60}), 1203 (C_{60}), 947, 700, 560 (C_{60}), 527 (C_{60}). − UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 232 nm (4.96), 254 (5.14), 325 (4.81), 362 (4.42). − ^{1}H NMR (200 MHz, CS_2/$CDCl_3$, 9:1): δ = 7.04 (d, ^3J = 16.0 Hz, 1 H, olef. 2-CH), 7.04 (dd, ^3J = 4.9 Hz, ^3J = 3.7 Hz, 1 H, thiophene 4-H), 7.19 (d, ^3J = 3.7 Hz, 1 H, thiophene 5-H), 7.24 (s, $CHCl_3$, solv.), 7.31 (d, ^3J = 4.9 Hz, 1 H, thiophene 3-H), 8.04 (d, ^3J = 16.0 Hz, 1 H, olef. 1-CH). − ^{13}C NMR (75 MHz, 1-chloronaphthalene/[D_6]acetone, 9:1, 19017 scans): δ = 77.74 (*C*CN, aliph. C, C^1), 104.21 (CON, aliph. C, C^2), 124.03 (1-chloronaphthalene, high-field signal, solv.), 114.28 (olef. C, C^2), 136.08, 136.19, 139.29, 139.78, 140.70, 140.80, 141.16, 141.24, 141.40 (each 2 C, fullerene), 141.42 (C, thiophene, C^1), 141.44 (2 C, fullerene), 141.82 (4 C, fullerene), 141.95, 143.10, 143.37, 143.62, 143.82, 144.02, 144.15, 144.23, 144.28, 144.56, 144.65, 144.92, 145.00 (each 2 C, fullerene), 145.27 (4 C, fullerene), 145.36 (2 C, fullerene), 146.26, 146.83 (each C, fullerene, C^{55} or C^{60}), 151.42 (C=N, $C^{3'}$); for the assignment of the substituent signals, ^{13}C-NMR data of the starting material was used. The three "missing" signals of the substituent are expected to be obscured by the solvent signal. − MS (MALDI-TOF): *m*/*z* (%): 871 (92) [M^-], 720 (100) [$C_{60}{}^-$]. − MS (FAB): *m*/*z* (%): 872 (35) [M^+ + H], 871 (13) [M^+], 765 (8), 752 (18), 736 (36), 720 (100) [$C_{60}{}^+$]. − MS (HR FAB): *m*/*z* (± 0.01): 872.02 [M^+ + H, calcd. 872.02], 871.01 [M^+, calcd. 871.01], 721.00 [$^{12}C_{59}{}^{13}C^+$, calcd. 721,00], 720.00 [$C_{60}{}^+$, calcd. 720.00]. − CV (0.05 V s^{-1}): E_{red} (V): $E^1 = -1.10$, $E^2 = -1.46$, $E^3 = -1.86$.

(1*E*,3*E*)-3′-[4-(2-Thienyl)buta-1,3-dienyl]isoxazolo[4′,5′:1,2][60]-fullerene (1h): Yield: 36 mg (29%, 40 μmol). − IR (KBr): $\tilde{\nu}$ = 1646 cm^{-1} (C=N), 1612 (C=C), 1422 (C_{60}), 1180 (C_{60}), 977 (C=C), 768, 727, 694, 564 (C_{60}), 526 (C_{60}). − UV/Vis (CH_2Cl_2): (a) d = 0.1 cm: λ_{max} (lg ε) = 222 nm (5.01), 254 (5.06), 330 (4.71), 352 (4.68); (b) d = 1.0 cm: λ_{max} (lg ε) = 414 nm (3.84), 424 (3.71), 451 (3.68). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.80 (dd, ^3J = 14.3 Hz, ^3J = 10.7 Hz, 1 H, olef. CH, H^3), 6.84 (d, ^3J = 15.5 Hz, 1 H, olef. CH, H^1), 6.99 (d, ^3J = 14.3 Hz, 1 H, olef. CH, H^4), 7.00 (dd, ^3J = 5.0 Hz, ^3J = 3.7 Hz, 1 H, thiophene 4-H), 7.21 (s, 1 H, thiophene 5-H), 7.24 (s, $CHCl_3$, solv.), 7.26 (s, 1 H, thiophene 3-H), 7.73 (dd, ^3J = 15.5 Hz, ^3J = 10.7 Hz, 1 H, olef. CH, H^2); in $CDCl_3$, no splitting for the CH signals in 3- and 5-positions of the thiophene ring could be observed. − ^{1}H NMR (300 MHz, CS_2/[D_6]acetone, 9:1): δ = 2.04 (quint., [D_5]acetone, solv.), 6.80 (dd, ^3J = 15.4 Hz, ^3J = 10.7 Hz, 1 H, olef. CH, H^3), 6.85 (d, ^3J = 15.8 Hz, 1 H, olef. CH, H^1), 6.98 (dd, ^3J = 5.5 Hz, ^3J = 3.7 Hz, 1 H, thiophene 4-H), 7.06 (s, 1 H, thiophene 5-H), 7.06 (d, ^3J = 15.4 Hz, 1 H, olef. CH, H^4), 7.26 (d, ^3J = 5.5 Hz, 1 H, thiophene 3-H), 7.68 (dd, ^3J = 15.8 Hz, ^3J = 10.7 Hz, 1 H, olef. CH, H^2); in CS_2/[D_6]acetone, no splitting of the thiophene 5-H signal could be observed. − ^{13}C NMR (75 MHz, CS_2/[D_6]acetone, 9:1, 10000 scans): δ = 78.05 (*C*CN, aliph. C, C^1), 113.22 (CON, aliph. C, C^2), 118.14, 125.19, 127.41, 127.84, 127.89, 128.07 (each olef. C or thiophene C), 136.45, 136.65, 139.96, 140.35, 141.52, 141.81, 141.94, 142.02, 142.15 (each 2 C, fullerene), 142.17 (olef. C or thiophene C), 142.20 (2 C, fullerene), 142.56 (4 C, fullerene), 142.75, 143.89, 144.13, 144.49, 144.58, 144.87, 144.94, 144.99, 145.08 (each 2 C, fullerene), 145.40 (4 C, fullerene), 145.63, 145.72 (each 2 C, fullerene) 145.98 (4 C, fullerene), 146.09 (2 C, fullerene), 146.97, 147.50 (each C, fullerene, C^{55} or C^{60}), 150.78 (C=N, $C^{3'}$), 192.30 (CS_2, solv.). − MS (MALDI-TOF): *m*/*z* (%): 898 (15) [M^-], 720 (100) [$C_{60}{}^-$]. − MS (FAB): *m*/*z* (%): 898 (7) [M^+ + H], 897 (4) [M^+], 792 (6), 768 (9), 744 (9), 737 (11), 720 (100) [$C_{60}{}^+$]. − MS (HR FAB): *m*/*z* (± 0.01): 898.03 [M^+ + H, calcd. 898.03], 897.02 [M^+, calcd. 871.02], 721.01 [$^{12}C_{59}{}^{13}C^+$, calcd. 721,00], 720.00 [$C_{60}{}^+$, calcd. 720.00]. − CV (0.05 V s^{-1}): E_{red} [V]: $E^1 = -1.08$, $E^2 = -1.42$, $E^3 = -1.85$.

3′-[2-(2-Thienyl)phenyl]isoxazolo[4′,5′:1,2][60]fullerene (1i): TLC (SiO_2, CS_2): R_f (C_{60}) = 0.80, R_f (**1i**) = 0.10. − Yield: 47 mg (36%, 51 μmol). − IR (KBr): $\tilde{\nu}$ = 1508 cm^{-1}, 987, 898, 852, 756, 730, 695, 649, 570, 524 (C_{60}). − UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 232 nm (4.97), 256 (5.07), 318 (4.60), 362 (4.10), 380 (3.85), 414 (3.47), 426

(3.33), 454 (3.17). − ^{1}H NMR (300 MHz, $CDCl_3/CS_2$, 8:2): δ = 7.23 (d, ^3J = 3.5 Hz, 1 H, arom. CH), 7.44 (d, ^3J = 4.5 Hz, 2 H, arom. CH), 7.51−7.63 (m, 3 H, arom. CH), 7.79 (d, ^3J = 7.5 Hz, 1 H, arom. CH). − ^{13}C NMR (75 MHz, $CDCl_3/CS_2$, 8:2): δ = 81.19 (*C*CN, aliph. C, C^1), 100.16 (CON, aliph. C, C^2), 126.90, 128.16, 128.30, 128.38, 128.87, 130.74, 130.87, 131.39, 135.13 (each arom. C), 135.67, 136.94, 140.01 (each 2 C, fullerene), 140.18 (arom. C), 141.70, 141.96, 142.20, 142.23, 142.33, 142.40, 142.70, 142.73, 142.82, 143.42, 144.04, 144.19, 144.22, 144.79, 145.07, 145.14, 145.16, 145.22, 145.44, 145.81, 145.92, 146.16 (each 2 C, fullerene), 146.19 (4 C, fullerene), 146.64 (2 C, fullerene), 147.17, 147.77 (each C, fullerene, C^{55} or C^{60}), 155.34 (C=N, C$^{3'}$). − MS (MALDI-TOF): *m/z* (%): 921 [M^-], 720 [C_{60}^-]. − MS (HR FAB): *m/z*: 921.030 [M^+, calcd. 921.025]. − CV (0.05 V s^{-1}): E_{red} [V]: E^1 = −1.09, E^2 = −1.46, E^3 = −1.91.

3′-[4-(2-Thienyl)phenyl]isoxazolo[4′,5′:1,2][60]fullerene (1k): TLC (SiO_2, CS_2): R_f (C_{60}) = 0.80, R_f (**1k**) = 0.10. − Yield: 35 mg (28%, 38 μmol). − IR (KBr): ṽ = 1508 cm^{-1}, 1425 (C_{60}), 1301, 1185 (C_{60}), 978, 862, 816, 768, 729, 694, 603, 569, 525 (C_{60}). − UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 232 (3.78), 302 (3.88). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.12 (dd, ^3J = 4.8 Hz, ^3J = 3.7 Hz, 1 H, CH, thiophene), 7.34−7.36 (m, 1 H, CH, thiophene), 7.41 (dd, ^3J = 3.7 Hz, ^4J = 1.1 Hz, 1 H, CH, thiophene), 7.78 (d, ^3J = 8.5 Hz, 2 H, arom. CH), 8.25 (d, ^3J = 8.5 Hz, 2 H, arom. CH). − ^{13}C NMR (75 MHz, $CDCl_3/CS_2$, 1:10): δ = 78.68 (*C*CN, aliph. C, C^1), 104.72 (CON, aliph. C, C^2), 124.30, 126.18, 126.39, 128.07, 128.44, 129.47, 136.62 (each arom. C), 136.71, 137.18 (each 2 C, fullerene), 140.41 (4 C, fullerene), 141.80, 142.19, 142.37, 142.44, 142.56 (each 2 C, fullerene), 142.94 (4 C, fullerene), 143.09 (2 C, fullerene), 143.24 (arom. C), 144.16, 144.51, 144.70, 144.84, 144.85, 145.21, 145.30, 145.47, 145.72, 145.93, 146.00, 146.06, 146.31 (each 2 C, fullerene), 146.34 (4 C, fullerene), 146.47 (2 C, fullerene), 147.32, 147.81 (each C, fullerene, C^{55} or C^{60}), 152.50 (C=N, C$^{3'}$). − MS (MALDI-TOF): *m/z* (%): 921 [M^-], 720 [C_{60}^-]. − MS (HR FAB): *m/z*: 921.032 [M^+, calcd. 921.025]. − CV (0.05 V s^{-1}): E_{red} (V): E^1 = −1.09, E^2 = −1.45, E^3 = −1.89.

3′-(2,3,6,7-Tetramethoxyanthr-9-yl)isoxazolo[4′,5′:1,2][60]fullerene (1m): Yield: 51 mg (35%, 48 μmol). − IR (KBr): ṽ = 1633 cm^{-1} (C=N), 1492, 1460, 1432 (C_{60}), 1242, 1187 (C_{60}), 1012, 887, 834, 562, 527 (C_{60}). − UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 232 nm (4.99), 262 (5.19), 318 (4.56), 378 (4.16), 414 (3.69). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.06 (s, 6 H, OCH_3), 4.16 (s, 6 H, OCH_3), 7.22 (s, 2 H, arom. CH), 7.72 (s, 2 H, arom. CH), 8.23 (s, 1 H, arom. CH, H^{10}). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.88, 56.03 (each OCH_3), 77.91 (*C*CN, aliph. C, C^1), 101.73 (CON, aliph. C, C^2), 103.47, 105.43, 116.88, 125.79, 126.96, 127.34 (each arom. C), 135.60, 136.15, 140.28, 140.71, 141.54, 141.78, 142.10, 142.16, 142.38, 142.43, 142.72, 142.83, 142.86, 142.97, 142.99, 144.25, 144.62, 144.84, 145.10, 145.11, 145.14, 145.20, 145.89, 146.01, 146.31, 146.33, 146.34, 146.37 (each 2 C, fullerene), 146.51, 147.60 (each C, fullerene, C^{55} or C^{60}), 149.49, 150.27 (each arom. C), 153.81 (C=N, C$^{3'}$). − MS (MALDI-TOF): *m/z*: 1060 [M^-], 830, 720 [C_{60}^-]. − MS (HR FAB): *m/z*: 1059.117 [M^+, calcd. 1059.111]. − CV (0.05 V s^{-1}): E_{red} [V]: E^1 = −1.05, E^2 = −1.43, E^3 = −1.87.

3′-[2,2-Bis(methoxycarbonyl)vinyl]isoxazolo[4′,5′:1,2][60]fullerene (1e): 31 mg (140 μmol) of the nitronate **4e** was dissolved in 10 mL of dry DMF. At 0°C, 27 mg (140 μmol) of tosyl chloride (TsCl) was added portionwise and stirring was continued for 30 min at 0°C and then for 2 h at room temp. [TLC (SiO_2, PhMe): R_f (TsCl) = 0.59, R_f (Ts nitronate) = 0.41]. This mixture was then dropped into a solution of 100 mg (140 μmol) of C_{60} in 120 mL toluene over a period of 10 min and the resulting mixture was heated to reflux for 12 h. The brown reaction mixture [TLC (SiO_2, PhMe): R_f (C_{60}) = 0.72, R_f (**1e**) = 0.20] was separated from 72 mg of unchanged C_{60} and higher fullerene adducts by flash chromatography (silica gel, toluene). Finally, purification by silica gel and buckyclutcher® HPLC afforded 30 mg (33 μmol, 24%) of the pure monoadduct, which exhibited gleaming surfaces after drying with SiO_2/paraffin. − IR (KBr): ṽ = 1741 cm^{-1} (C=O), 1730 (C=N), 1719 (C=C), 1433 (C_{60}), 1277, 1230, 1181 (C_{60}), 1078, 726, 575 (C_{60}), 527 (C_{60}). − UV/Vis ($CHCl_3$): λ_{max} (lg ε): 254 nm (5.07), 318 (4.59), 364 (3.94). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.89 (s, 3 H, CH_3), 4.10 (s, 3 H, CH_3), 7.24 (s, $CHCl_3$, solv.), 7.75 (s, 1 H, olef. CH). − ^{13}C NMR (75 MHz, CS_2/[D_6]acetone, 9:1, 16000 scans): δ = 52.16 (CH_3), 52.33 (CH_3), 77.74 (*C*CN, aliph. C, C^1), 114.87 (CON, aliph. C, C^2), 124.79 (C=C, C^1), 133.46 (C=C, C^2), 136.65, 137.02, 139.99, 140.73, 141.76, 141.93, 142.01, 142.14, 142.17, 142.22, 142.56 (each 2 C, fullerene), 142.61 (4 C, fullerene), 142.78, 143.50, 143.87, 144.07, 144.42, 144.94, 144.98 (each 2 C, fullerene), 145.02 (4 C, fullerene), 145.61, 145.71, 145.80, 146.07, 146.09, 146.16 (each 2 C, fullerene), 147.02, 147.60 (each C, fullerene, C^{55} or C^{60}), 148.23 (C=N, C$^{3'}$), 161.80 (C=O), 163.33 (C=O), 192.30 (CS_2, solv.). − MS (MALDI-TOF): *m/z* (%): 905 (44) [M^-], 720 (100) [C_{60}^-]. − MS (FD): *m/z* (%): 1090 (47) [bis-adduct$^+$], 905 (87) [M^+], 720 (100) [C_{60}^+]. − MS (FAB): *m/z* (%): 906 (8) [M^+ + H], 905 (4) [M^+], 768 (9), 745 (9), 737 (11), 720 (100) [C_{60}^+]. − MS (HR FAB): *m/z* (± 0.008): 907.038 [$^{12}C_{66}{}^{13}CH_8O_5N$, calcd. 907.044], 906.036 [M^+ + H, calcd. 906.040], 905.034 [M^+, calcd. 905.032], 721.003 [$^{12}C_{59}{}^{13}C^+$, calcd. 721,003], 719.998 [C_{60}^+, calcd. 720.000]. − CV (0.05 V s^{-1}): E_{red} [V]: E^1 = −1.07, E^2 = −1.39, E^3 = −1.85.

[70]Fullerene: CV (0.05 V s^{-1}): E_{red} [V]: E^1 = −0.53, E^2 = −0.88, E^3 = −1.27.

[70]Fullerene Adducts (6d, 7d, 8d): The procedure used was analogous to that employed for the synthesis of the corresponding [60]fullerene adduct **1d**. Thus, 23 mg (95 μmol) of the oxime in 4 mL dry chloroform, 10 μL of pyridine, 25 mg (190 μmol) of NCS, 80 mg (190 μmol) of C_{70} in 150 mL of dry toluene, and 20 μL (150 μmol) of NEt_3 were used. Unreacted C_{70} could be separated by flash chromatography. Buckyclutcher® HPLC yielded three product fractions after 54.1, 57.2, and 61.8 min (elution rate: 4 mL min^{-1}). The colors of the diluted HPLC fractions were distinguishable according to the two different bond types involved in the reaction. In order of elution, the fractions contained the regioisomers **6d**, **8d**, and **7d** in 10% (10.5 mg, 10 μmol), 10% (10.4 mg, 10 μmol), and 12% (12.5 mg, 12 μmol) yields.

(1*E*)-3′-[2-(2,4,6-Trimethoxyphenyl)vinyl]isoxazolo[4′,5′:2,1][70]-fullerene (6d): IR (KBr): ṽ = 2961 cm^{-1}, 2923, 1603 (C=N), 1580 (C=C), 1453, 1428, 1415, 1262, 1204, 1156, 1099, 1032, 807. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 222 nm (4.83), 236 (4.86), 329 (4.38), 393 (3.96), 462 (3.76), 491 (3.36). − ^{1}H NMR (300 MHz, CS_2/[D_6]acetone, 9:1): δ = 2.04 (quint., [D_5]acetone, solv.), 3.90 (s, 3 H, 4-OCH_3), 4.03 (s, 6 H, 2,6-OCH_3), 6.20 (s, 2 H, arom. 3,5-CH), 7.83 (d, ^3J = 16.9 Hz, 1 H, olef. CH), 8.85 (d, ^3J = 16.9 Hz, 1 H, olef. CH). − ^{13}C NMR (75 MHz, 1-chloronaphthalene/[D_6]-acetone, 9:1, 16000 scans): δ = 54.60 (4-OCH_3), 55.19 (2 C, 2,6-OCH_3), 72.95 (*C*CN, aliph. C, C^1), 90.56 (2 C, arom. 3,5-CH), 107.11 (CON, aliph. C, C^2), 113.57 (arom. 1-C), 116.59 (olef. CH), 116.60 (olef. CH), 124.03 (1-chloronaphthalene, high-field signal, solv.), 132.54, 132.69, 137.19, 137.31, 139.56, 139.79, 142.95, 143.05, 143.16, 143.21, 144.39, 145.04, 145.23, 145.92, 146.46, 146.49, 146.53, 146.71, 146.74, 146.82, 146.85, 147.66 (each 2 C, fullerene), 148.26 (4 C, fullerene), 148.44, 148.75, 148.81, 148.84, 149.06, 149.77, 149.95, 149.96, 150.10, 150.63, 155.10, 155.39 (each

2 C, fullerene or 1 C=N, C$^{3'}$), 160.66 (2 C, *C*OCH$_3$, arom. 2,6-C), 162.27 (*C*OCH$_3$, arom. 4-C); for the assignment of the signals at δ = 132.54 and 132.69, a ^{13}C-NMR reference spectrum of the solvent (10000 scans) was used. − MS (MALDI-TOF): *m/z* (%): 1075 (19) [M$^-$], 840 (100) [C$_{70}^-$]. − MS (FAB): *m/z* (%): 1076 (17) [M$^+$ + H], 1075 (7) [M$^+$], 840 (100) [C$_{70}^+$]. − MS (HR FAB): *m/z* (± 0.008): 1077.099 [$^{12}C_{81}$ $^{13}CH_{14}NO_4^+$, calcd. 1077.096], 1076.088 [M$^+$ + H, calcd. 1076.092], 1075.085 [M$^+$, calcd. 1075.084], 841.006 [$^{12}C_{69}{}^{13}C^+$, calcd. 841.003], 839.998 [C$_{70}^+$, calcd. 840.000]. − CV (0.05 V s^{-1}): E_{red} [V]: E^1 = −0.54, E^2 = −0.90, E^3 = −1.28.

(1*E*)-3′-[2-(2,4,6-Trimethoxyphenyl)vinyl]isoxazolo[4′,5′:1,2][70]-fullerene (7d): IR (KBr): ṽ = 2924 cm^{-1}, 1604 (C=N), 1575 (C=C), 1534, 1452, 1428, 1415, 1345, 1282, 1263, 1202, 1156, 1119, 1066, 1035, 811, 798. − UV/Vis (CHCl$_3$): λ$_{max}$ (lg ε) = 222 nm (4.47), 233 (4.49), 308 (4.01), 388 (3.75), 459 (3.65), 486 (3.57). − ^{1}H NMR (300 MHz, CS$_2$/[D$_6$]acetone, 9:1): δ = 2.04 (quint., [D$_5$]acetone, solv.), 3.75 (s, 6 H, 2,6-OC*H*$_3$), 3.78 (s, 3 H, 4-OCH$_3$), 6.00 (s, 2 H, arom. 3,5-CH), 7.38 (d, ^3J = 16.9 Hz, 1 H, olef. CH), 7.99 (d, ^3J = 16.9 Hz, 1 H, olef. CH). − ^{13}C NMR (75 MHz, 1-chloronaphthalene/[D$_6$]acetone, 9:1, 26840 scans): δ = 54.50 (4-OCH$_3$), 55.03 (2 C, 2,6-OCH$_3$), 73.19 (*C*CN, aliph. C, C^1), 90.38 (2 C, arom. 3,5-CH), 106.51 (CON, aliph. C, C^2), 113.56 (arom. 1-C), 116.26 (olef. CH), 124.03 (1-chloronaphthalene, high-field signal, solv.), 130.93, 131.05, 131.08, 132.17, 132.21, 132.26, 137.28, 139.55, 140.19, 141.22, 142.69, 142.87, 142.99, 143.33, 145.33, 145.37, 146.32, 146.57, 146.84, 147.92, 147.96, 148.10, 148.33, 148.39, 148.70, 149.08, 149.45, 149.48, 150.11, 150.28, 150.52, 150.66, 154.10, 154.13, 154.46, 155.41 (each 2 C, fullerene or 1 C=N, C$^{3'}$), 160.40 (2 C, *C*OCH$_3$ and arom. 2,6-C), 162.07 (*C*OCH$_3$, arom. 4-C); for the assignment of the signals at δ = 130.93, 131.05, 131.08, 132.17, 132.21 and 132.26, a ^{13}C-NMR reference spectrum of the solvent (10000 scans) was used. − MS (MALDI-TOF): *m/z* (%): 1075 (100) [M$^-$], 840 (84) [C$_{70}^-$]. − MS (FAB): *m/z* (%): 1076 (1) [M$^+$ + H], 1075 (1) [M$^+$], 840 (100) [C$_{70}^+$]. − MS (HR FAB): *m/z* (± 0.008): 1077.104 [$^{12}C_{81}{}^{13}CH_{14}NO_4^+$, calcd. 1077.096], 1076.090 [M$^+$ + H, calcd. 1076.092], 841.000 [$^{12}C_{69}{}^{13}C^+$, calcd. 841.003], 839.994 [C$_{70}^+$, calcd. 840.000]. − CV (0.05 V s^{-1}): E_{red} [V]: E^1 = −0.54, E^2 = −0.90, E^3 = −1.26.

(1*E*)-3′-[2-(2,4,6-Trimethoxyphenyl)vinyl]isoxazolo[4′,5′:6,5][70]-fullerene (8d) and (1*E*)-3′-[2-(2,4,6-Trimethoxyphenyl)vinyl]isoxazolo[4′,5′:5,6][70]fullerene (*ent*-8d): IR (KBr): ṽ = 2958 cm^{-1}, 2923, 2853, 1605 (C=N), 1580 (C=C), 1533, 1463, 1430, 1345, 1283, 1262, 1205, 1156, 1118, 1068, 1034, 810. − UV/Vis (CHCl$_3$): λ$_{max}$ (lg ε) = 223 nm (5.10), 235 (5.12), 332 (4.61), 393 (4.23), 440 (4.12), 491 (3.78). − ^{1}H NMR (300 MHz, CS$_2$/[D$_6$]acetone, 9:1): δ = 2.04 (quint., [D$_5$]acetone, solv.), 3.79 (s, 3 H, 4-OCH$_3$), 3.80 (s, 6 H, 2,6-OCH$_3$), 6.03 (s, 2 H, arom. 3,5-CH), 7.28 (d, ^3J = 16.9 Hz, 1 H, olef. CH), 8.07 (d, ^3J = 16.9 Hz, 1 H, olef. CH). − ^{13}C NMR (75 MHz, 1-chloronaphthalene/[D$_6$]acetone, 9:1, 8160 scans): δ = 54.57 (4-OCH$_3$), 55.09 (2 C, 2,6-OCH$_3$), 72.85 (*C*CN, aliph. C, C^1), 90.48 (2 C, arom. 3,5-CH), 106.78 (CON, aliph. C, C^2), 113.76 (arom. 1-C), 115.61 (olef. CH), 124.03 (1-chloronaphthalene, high-field signal, solv.), 132.08, 132.17, 134.18, 137.38, 137.40, 139.64, 139.81, 139.83, 140.25, 142.26, 142.54, 142.62, 143.04, 143.31, 143.42, 143.57, 143.71, 143.82, 144.02, 144.17 (each 2 C, fullerene), 144.34 (4 C, fullerene), 144.40, 144.48, 144.91, 145.20, 145.21, 145.25, 145.27, 145.30, 145.39, 145.45, 145.87, 145.99, 146.08, 146.17, 146.25, 146.35, 146.47, 146.49, 146.62, 147.27, 147.30, 147.57, 147.81, 147.90 (each 2 C, fullerene), 148.08 (6 C, fullerene), 148.22, 148.27, 148.36, 148.40, 148.46, 148.48, 148.67, 148.76, 148.82 (each 2 C, fullerene), 148.86 (4 C, fullerene), 149.53, 150.13, 150.16, 150.93, 150.97, 153.91, 155.52, 156.18 (each 2 C, fullerene and 1 C=N, C$^{3'}$), 160.45 (2 C, *C*OCH$_3$, arom. 2,6-C), 162.15 (*C*OCH$_3$, arom. 4-C); for the assignment of the signals at δ = 132.08, 132.17 and 134.18, a ^{13}C-NMR reference spectrum of the solvent (10000 scans) was used. − MS (MALDI-TOF): *m/z* (%): 1075 (39) [M$^-$], 840 (100) [C$_{70}^-$]. − MS (FAB): *m/z* (%): 1076 (25) [M$^+$ + H], 1075 (11) [M$^+$], 840 (100) [C$_{70}^+$]. − MS (HR FAB): *m/z* (±0.008): 1076.095 [M$^+$ + H, calcd. 1076.092], 841.002 [$^{12}C_{69}{}^{13}C^+$, calcd. 841.003], 840.006 [C$_{70}^+$, calcd. 840.000]. − CV (0.05 V s^{-1}): E_{red} (V): E^1 = −0.53, E^2 = −0.89, E^3 = −1.25.

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Received May 17, 1999
[O99282]