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The first fullerene–heterofullerene dyad†

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The highly regioselective attack of a C_{60} malonate containing a terminal acetyl function to the heterofullerene cage $C_{59}N$ leads to the formation of the first fullerene–heterofullerene dyad, representing a new scaffold for directional energy transduction.

During the last few years fullerene scaffolding has been established as an important tool for the construction of functional nanostructures.[1] Fullerene dimers and dyads are one prototype of such organized architectures. So far three major routes for the formation of covalently linked fullerenes have been developed (Fig. 1): a) direct dimerization of the parent fullerene or of a fullerene derivative like $C_{60}O$, b) homocoupling of a functionalized fullerene derivative bearing, for example, an alkyne group and c) connection of two fullerene molecules with a bisfunctional bridging addend.[2] In most cases covalently linked fullerenes with two identical fullerene moieties are obtained with these methods. For the construction of specific molecular devices such as quantum computers or directional energy transducers it is important to design difunctional systems with distinguishable and addressable subunits. In the case of fullerene dyads, this prerequisite would be fulfilled if two different fullerene cages, for example, those of C_{60} and $C_{59}N$, were employed.

For the synthesis of such mixed fullerene dyads none of the reaction sequences mentioned above is feasible since the $C_{59}N$ cage exhibits C_s symmetry only. As a consequence, in contrast to I_h-C_{60} mono-additions to the [6,6]-bonds are much less regioselective. For example, for malonate addition to a $C_{59}N$ moiety under Bingel[3] conditions 16 difficult to separate regioisomers can be expected. We have shown recently that monomeric $C_{59}N$ derivatives with a saturating addend attached to the sp^3 carbon atom α to N are easily available by treatment of the $(C_{59}N)_2$ dimer with electron rich aromatics or enolizable carbonyl compounds in the presence of oxygen and *p*-TsOH.[4]

These reactions represent highly selective derivatisations of $(C_{59}N)_2$ and are now used for the directional synthesis of the first fullerene–heterofullerene dyad (Fig. 2).

For this purpose we developed a suitable bridging addend **1** which exhibits orthogonal reactivity with respect to the coupling with the C_{60} and $C_{59}N$ core, respectively. Malonate **1** was obtained by the reaction of 1-(3-hydroxyphenyl)ethanone with methyl 3-chloro-3-oxopropanoate in toluene. The two orthogonal binding sites are the malonate functionality which can undergo a Bingel[3] cyclopropanation of a [6,6]-bond of the C_{60} core and the acetyl group which can easily be connected to $C_{59}N$ in high regioselectivity.[4b,c]

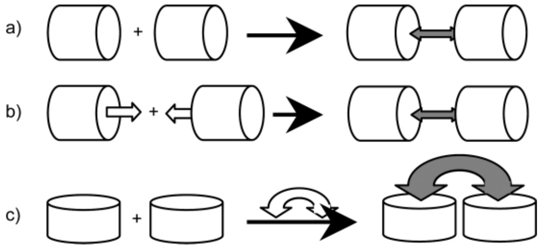
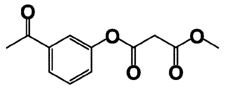


Fig. 1 Schematic representation of general routes for the connection of two fullerenes.



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As expected, the reaction of **1** with C_{60} in the presence of DBU and CBr_4 leads to the formation of the C_s symmetrical monoadduct **2**‡ (Scheme 1).

Subsequent treatment of $(C_{59}N)_2$ with 1 equiv. of **2** and 30 equiv. of *p*-TsOH at 150 °C in *o*-dichlorobenzene (ODCB) in a constant stream of air leads to the formation of the C_s symmetrical C_{60}–$C_{59}N$ dyad **3** in 27% yield (Scheme 2).

The complete structural characterisation of **3** was carried out by ^1H NMR, ^{13}C NMR, UV/Vis and FT-IR spectroscopy as well as by mass spectrometry.§ As can be seen from the comparison of the UV/Vis spectra depicted in Fig. 3 the spectrum of the mixed dyad **3** is, in first approximation, the superposition of the spectra of the fullerene monoadduct and $(C_{59}N)_2$.

In the region between $\delta = 8.5$ and $\delta = 7.7$ the ^1H NMR spectrum of **3** shows the expected signals of the phenyl protons and at $\delta = 4.23$ the absorption of the methyl group as a singlet. The characteristic singlet of the two protons of the methylene group which is attached directly to the sp^3 carbon atom of the heterofullerene cage can be found at $\delta = 5.48$.

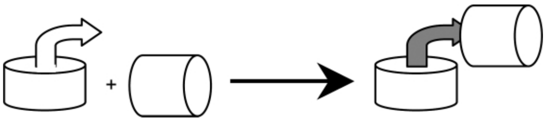
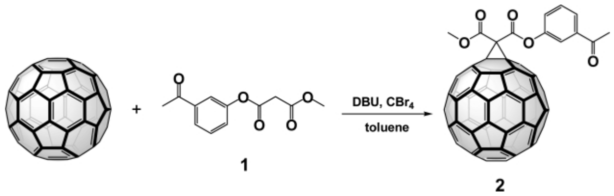
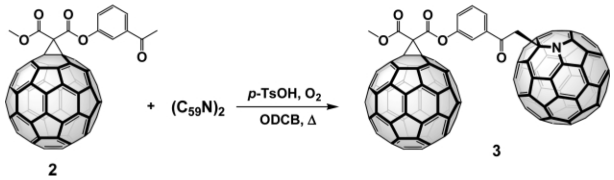


Fig. 2 Directional connection of two fullerene moieties.



Scheme 1



Scheme 2

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† Electronic supplementary information (ESI) available: fluorescence and transient absorption spectroscopy studies. See http://www.rsc.org/suppdata/cc/b3/b315006b/

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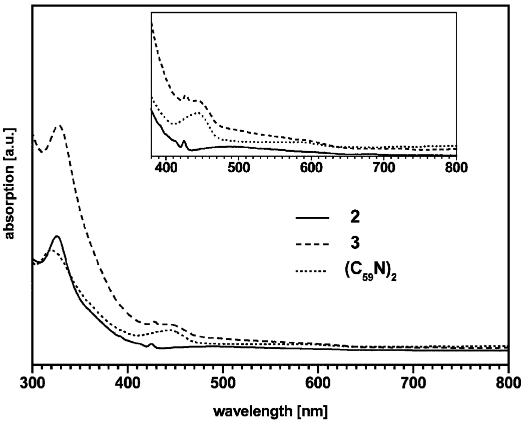

Fig. 3 Comparison of the UV/Vis spectra of $(C_{59}N)_2$, C_{60} monoadduct **2** and the dyad **3**.

The determination of the symmetry of the C_{60}–$C_{59}N$ dyad **3** was done by the analysis of its ^{13}C NMR spectrum. In the region between $\delta = 155$ and $\delta = 125$ a total of 60 signals can be assigned to the cage carbon atoms of the two fullerene moieties. 56 signals have double intensity and 4 signals have single intensity as they are located on the mirror plane of the C_{60} and $C_{59}N$ core, respectively. The signals of the substituted benzene ring are also located in the fullerene sp^2 region. They can easily be identified by a comparison of the spectrum of the dyad **3** with the spectrum of the bridge **1**. By a comparison of the fullerene ^{13}C NMR signals of the dyad **3** with the signals of other carbonyl functionalized $C_{59}N$ derivatives[4c] it is possible to separate the C_{60} resonances from the $C_{59}N$ resonances.

The carbonyl group of the ketone functionality resonates at $\delta = 193.29$ and the two unequivalent carboxyl groups of the malonic ester can be found at $\delta = 162.94$ and $\delta = 161.30$, respectively. The methano C atom of the malonic ester shows up at $\delta = 50.98$ and the signals for the two different [60]fullerene sp^3 C atoms fall together at $\delta = 70.85$. The very characteristic resonance of the sp^3-carbon atom of the $C_{59}N$ cage can be identified at $\delta = 78.58$ and the C atom of the methylene group which is attached to this cage atom resonates at $\delta = 49.97$.

Semiempirical calculations (PC Spartan Pro,[5] PM3) of the mixed dyad show that the two fullerene moieties are separated by a spatial distance of only 5.1 Å (Fig. 4). Directional electronic interaction should be facilitated by the fact that the low lying unoccupied orbitals are $C_{59}N$ based (LUMO (PM3): −2.954 eV). This is corroborated by the cyclic voltammetry of **3** where the reduction due of the $C_{59}N$-moiety was found at a peak potential of −941 mV and the subsequent reduction of the C_{60} cage at a peak potential of −1138 mV (*vs.* ferrocene in THF). A third reduction was observed at −1457 mV.

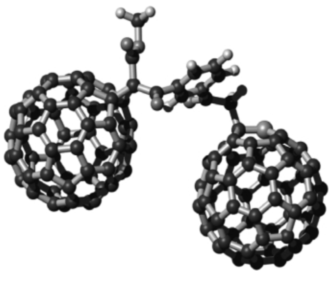

Fig. 4 Calculated (PM3) structure of the C_{60}–$C_{59}N$ dyad **3**.

Experimental proof for the directional electronic character of **3** was obtained from fluorescence and transient absorption spectroscopy (see also ESI†). After excitation at 350 nm rapid transduction of singlet excited state energy from the C_{60} core (1.76 eV) to the $C_{59}N$ core (1.50 eV) was observed. This energy transfer is exothermic by 0.26 eV and proceeds at $3.1 \pm 0.5 \times 10^9$ s^{-1}. The quantum yield of the overall energy transfer is close to 100%. Once formed, the $C_{59}N$ singlet is metastable and decays with a rate of 9.1×10^9 s^{-1} to the triplet manifold.

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Notes and references

‡ Selected data for **2**: ν(KBr)/cm^{-1} 3001, 2948, 2923, 2852, 1753, 1685, 1596, 1540, 1499, 1429, 1355, 1298, 1264, 1234, 1204, 1162, 1094, 1064, 1014, 956, 859, 806, 757, 742, 703, 670, 583, 553, 526 and 495; λ_{max}(CH_2Cl_2)/nm 257, 326, 408, 425, 493 and 682; ^1H NMR δ(400 MHz, $CS_2/CDCl_3$) 7.87 ("d", 2 H), 7.53 ("d", 2 H), 4.20 (s, 3 H, –OCH_3), 2.65 (s, 3 H, –CH_3); ^{13}C NMR δ(100 MHz, $CS_2/CDCl_3$) 194.54 (1 C, C=O), 162.70/160.92 (each 1 C, C=O), 150.46 (1 C, Ar–C), 144.99 (4 C), 144.89 (2 C), 144.88 (2 C), 144.72 (2 C), 144.67 (2 C), 144.61 (4 C), 144.44 (2 C), 144.43 (2 C), 144.37 (4 C), 144.32 (1 C), 144.24 (1 C), 144.21 (2 C), 143.61 (2 C), 143.55 (2 C), 142.78 (4 C), 142.74 (4 C), 142.65 (2 C), 141.91 (4 C), 141.54 (2 C), 141.48 (2 C), 140.78 (2 C), 140.74 (2 C), 139.43 (2 C), 138.51 (1 C, Ar–C), 138.39 (2 C), 129.52 (1 C, Ar–C), 126.19 (1 C, Ar–C), 125.45 (1 C, Ar–C), 120.64 (1 C, Ar–C)), 70.84 (2 C, sp^3-C_{60}), 53.57 (1 C, –OCH_3), 50.98 (1 C, methano-C), 26.07 (1 C, –CH_3); *m/z* (FAB) 954 $[M]^+$ and 720 $[C_{60}]^+$.

§ Selected data for **3**: ν(KBr)/cm^{-1} 3012, 2921, 2851, 1694, 1580, 1549, 1480, 1454, 1425, 1342, 1315, 1265, 1251, 1217, 1183, 1169, 1091, 1045, 1033, 993, 941, 902, 843, 794, 766, 678, 645, 578, 567, 554, 493, 481 and 423; λ_{max}(1,2-dichlorobenzene)/nm 328, 427, 447, 596 and 726; ^1H NMR δ(400 MHz, $CS_2/CDCl_3$) 8.43 ("d", 1 H), 8.39 ("s", 1 H), 7.82 (t, 1 H), 7.71 ("d", 1 H), 5.48 (s, 1 H, –CH_2–), 4.23 (s, 3 H, –OCH_3); ^{13}C NMR δ(100 MHz, $CS_2/CDCl_3$) 193.29 (1 C, C=O), 162.94/161.30 (each 1 C, C=O), 155.00 (2 C, $C_{59}N$), 150.92 (1 C, Ar–C), 148.26 (2 C, $C_{59}N$), 147.43 (2 C, $C_{59}N$), 147.25 (2 C, $C_{59}N$), 146.99 (2 C, $C_{59}N$), 146.88 (2 C, $C_{59}N$), 146.51 (1 C, $C_{59}N$), 146.46 (2 C, $C_{59}N$), 146.39 (2 C, $C_{59}N$), 146.10 (2 C, $C_{59}N$), 145.81 (2 C, $C_{59}N$), 145.68 (1 C, $C_{59}N$), 145.58 (2 C, $C_{59}N$), 145.11 (2 C, C_{60}), 145.00 (2 C, $C_{59}N$), 144.97 (4 C, C_{60}), 144.83 (2 C, $C_{59}N$), 144.78 (2 C, C_{60}), 144.74 (2 C, C_{60}), 144.70 (4 C, C_{60}), 144.59 (2 C, C_{60}), 144.53 (2 C, C_{60}), 144.46 (4 C, C_{60}), 144.39 (1 C, C_{60}), 144.28 (1 C, C_{60}), 144.25 (2 C, C_{60}), 144.23 (2 C, C_{60}), 144.19 (2 C, $C_{59}N$), 143.87 (2 C, $C_{59}N$), 143.70 (2 C, C_{60}), 143.63 (2 C, C_{60}), 142.97 (2 C, $C_{59}N$), 142.89 (4 C, C_{60}), 142.85 (4 C, C_{60}), 142.83 (2 C, C_{60}), 142.72 (2 C, $C_{59}N$), 142.67 (2 C, $C_{59}N$), 141.99 (2 C, C_{60}), 141.98 (2 C, C_{60}), 141.95 (2 C, $C_{59}N$), 141.64 (2 C, C_{60}), 141.61 (2 C, $C_{59}N$), 141.57 (2 C, C_{60}), 141.31 (2 C, $C_{59}N$), 141.10 (2 C, $C_{59}N$), 140.94 (2 C, C_{60}), 140.91 (2 C, C_{60}), 140.87 (4 C, $C_{59}N$), 139.59 (2 C, C_{60}), 139.58 (2 C, $C_{59}N$), 138.39 (1 C, Ar–C), 138.34 (2 C, C_{60}), 137.51 (2 C, $C_{59}N$), 134.51 (2 C, $C_{59}N$), 128.78 (1 C, Ar–C), 128.03 (1 C, Ar–C), 125.13 (2 C, $C_{59}N$), 124.67 (1 C, Ar–C), 121.52 (1 C, Ar–C), 78.58 (1 C, sp^3-$C_{59}N$), 70.85 (2 C, sp^3-C_{60}), 53.82 (1 C, –OCH_3), 51,04 (1 C, methano-C), 49.97 (1 C, –CH_2–); *m/z* (FAB) 1677 $[M]^+$, 722 $[C_{59}N]^+$ and 720 $[C_{60}]^+$.

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