

Synthetic Methods | Hot Paper |

A Dipyrin Programmed for Covalent Loading with Fullerenes

Chengjie Li,^[a, b] Klaus Wurst,^[c] and Bernhard Kräutler*^[a]Dedicated to Professor Johann Gruber on the occasion of his 90th birthday

Abstract: We describe here a di-(β,β' -sulfoleno)pyrrole programmed for efficient and specific β,β' -functionalization via [4+2] cycloaddition reactions. At 120 °C and in the presence of an excess of C₆₀-fullerene the di-(β,β' -sulfoleno)pyrrole decomposed cleanly, furnishing a di-(β,β' -fullereno)pyrrole and the corresponding monofullereno-dipyrrole in an overall yield of 96%. Hence, relatively mild thermolysis of the di-(β,β' -sulfoleno)pyrrole induced stepwise extrusion of two equivalents of SO₂, producing highly reactive dipyrrole- β,β' -diene intermediates readily, providing a very effective path to [4+2]-cycloadducts. As presented here by the example of the covalent attachment of C₆₀-fullerene units, a convenient general methodology for the efficient synthesis of covalent dipyrrole β,β' -cycloadducts is made available.

2,2'-Dipyrroles contain two conjugated pyrrolic rings,^[1] and are useful building blocks for the synthesis of porphyrins and related tetrapyrrolic macrocycles.^[2] Dipyrroles have also attracted considerable attention, in their own right, due to their unique photo-physical and electrochemical properties, which are modified in interesting ways after coordination with transition metal ions, or with boron in BODIPYs.^[1,2b,3] Various methods have been developed, in order to introduce functional groups at the pyrrole units of 2,2'-dipyrroles to tune their properties for a variety of applications, for example, as photo- and redox-

active compounds,^[4] as probes in bio-imaging,^[5] in energy up-conversion materials,^[6] and as microstructure building blocks.^[7] The modification of 2,2'-dipyrroles occurs with ease at their pyrrole- α positions, and the selective introduction of substituents at the pyrrole- β position has also been worked out.^[8] In contrast, incorporation of ring-fused groups on the pyrrole units of dipyrroles is still a demanding task.^[9] However, the preparation of β,β' -sulfolenopyrroles has opened access to highly reactive pyrrole-2,3-dienes^[10] suitable for [4+2] cycloaddition of various dienophiles at the pyrrole β,β' -positions.^[11]

We have recently designed 'programmed' porphyrinoid compounds, such as the symmetric tetra-(β,β' -sulfoleno)porphyrins (see Scheme 1), for the purpose of the synthesis of novel porphyrinoid assemblies.^[10b,12] From tetra-(β,β' -sulfoleno)porphyrins four SO₂ units were readily extruded consecutively at 140 °C, generating an array of highly reactive porphyrin-dienes, which provided a unique basis for attaching various dienophiles.^[12b,c] In contrast, the corresponding, less symmetric tetra-(β,β' -sulfoleno)corrole^[13] liberated the diene units quickly at the directly linked ('western') pyrroles (9 min at 140 °C) and allowed the regioselective loading of a corrole with two C₆₀-fullerene units at the "western" pyrroles. Broadly functioning paths to porphyrinoid conjugates with C₆₀-fullerenes are very useful, as these furnish attractive components of photovoltaic and other materials.^[14]

As reported here, heating of the di-(β,β' -sulfoleno)-dipyrrole **1**^[15] liberated SO₂ very readily (in contrast to the analogous β,β' -sulfolenopyrroles^[11a,16]), providing a mild and efficient path for twofold [4+2]-cycloaddition of the dienophile C₆₀.

Single crystals of the diene-masked dipyrrole di-(β,β' -sulfoleno)pyrrole **1**^[15] (monoclinic space group *P*₂₁/*c*) were obtained by mixing of *n*-hexane into the solution of **1** in CH₂Cl₂. The unit-cell contained four molecules of **1**. In the conjugated π -system of **1** the individual bonds showed significant bond-length alteration (Figure 1), as found in other dipyrroles,^[17] and consistent with the formula shown in Scheme 2. The methine bridge of **1** exhibits *Z,cis*-geometry and an H-bond is observed in the crystal between H₂N to N₁. The *Z,cis*-geometry is a common structural feature of 2,2'-dipyrroles, when not doubly protonated or attached to metal-ions with specific binding modes.^[18] The best planes through the two pyrrolic rings in the conjugated system were roughly co-planar (3.5° dihedral angle). The mean planes of the aryl group (at the dipyrrole *meso*-position) and of the dipyrrole core were at a dihedral angle of 74.1°, similar to the situation in other *meso*-phenyl substituted dipyrroles.^[17,18b,19] The angle C₄-C₅-C₆ (124.2°, see Figure S1) of the di-(β,β' -sulfoleno)pyrrole **1** is only slightly

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Scheme 1. Structural formulae of the β,β' -sulfenopyrrole based dipyrin **1**,^[15] of a tetrasulfenocorrole^[13] and a symmetrical tetrasulfenoporphyrin.^[12a,b]

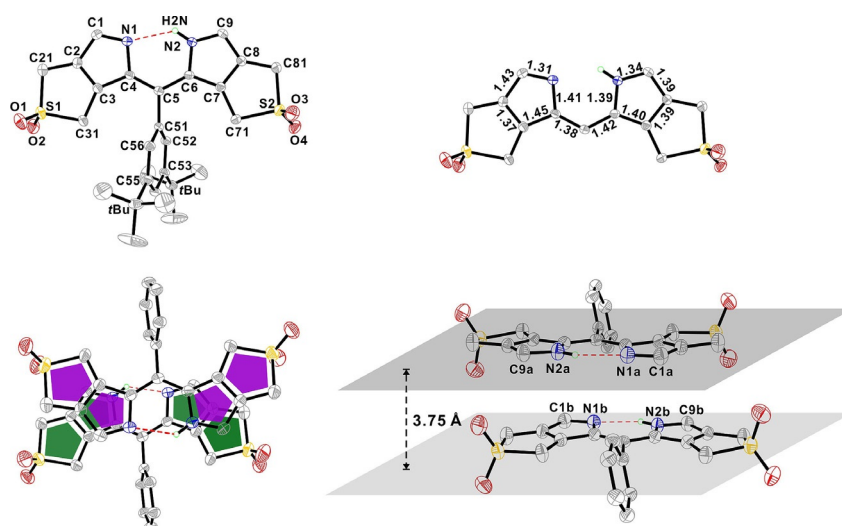
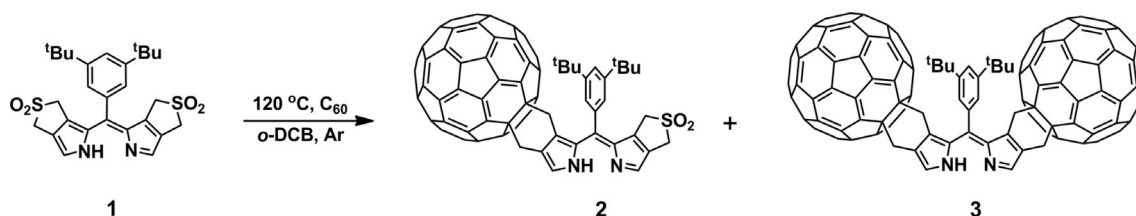


Figure 1. ORTEP plot of the crystal structure of the di-(β,β' -sulfenopyrrole) **1**. Top left: front view with numbering system; H-atoms at carbons were omitted for the sake of clarity. Top right: front view and bond lengths of the dipyrin core of **1**; H-atoms at carbons and the 3,5-di-*tert*-butyl-phenyl group were omitted for sake of clarity. Bottom left: top view of π -stacked dimer, highlighting the dipyrin cores. Bottom right: side view of two π -stacked dipyrins **1**, highlighting the distance between the two dipyrin planes. In both figures at the bottom H-atoms at carbons and the *tert*-butyl groups were again omitted.



Scheme 2. Thermolysis of dipyrin **1** in the presence of C₆₀ resulted in the loss of SO₂ and the covalent attachment of C₆₀-fullerene units to the β - and β' -positions of the pyrrole moieties.

smaller than that (127.2°) in the (2:1)-complex of Zn^{II}-ions with **1**,^[15] and similar to that of a related dipyrin with an aromatic *meso*-substituent.^[20] The two S atoms are positioned on opposite sides with respect to the plane of the dipyrin core, with out of plane distances of 0.16 and 0.28 Å for S1 and S2, respectively. In addition, the crystal structure revealed a remarkable π -stacking arrangement of the 2,2'-dipyrin **1**. In neighbors, tight π - π packing of the dipyrin cores of two molecules of **1** oriented the planes of the conjugated π -system in parallel, and at a mutual distance of 3.75 Å. However, the two molecules of **1** are related by a center of inversion in a dimer, so that their dipyrins-units are pointing into opposite directions (see Figure 1).

Heating of a deoxygenated solution of 2.33 mg (4.55 μ mol) of di-(β,β' -sulfenopyrrole) **1** and 23.45 mg (32.6 μ mol) of C₆₀ in 2 mL of 1,2-dichlorobenzene (*o*-DCB) at 120 °C for 20 min resulted in the complete decomposition of **1** (Scheme 2). From the reaction mixture 1.3 mg (or 24% yield) of the monofullerene-dipyrin **2** and 6.0 mg (or 72% yield) of bisfullerene-dipyrin **3** were isolated after column chromatography and crystallization from CS₂/EtOH.

The UV/Vis spectrum of the yellow 2,2'-dipyrin **1** exhibits the typical absorption maximum at 435 nm,^[15] as is shown in Figure 2. Upon attachment of C₆₀-fullerene units, the absorption maximum shifted by 18 nm to longer wavelength for the monoadduct **2**, and by 20 nm in the spectrum of the bisadduct

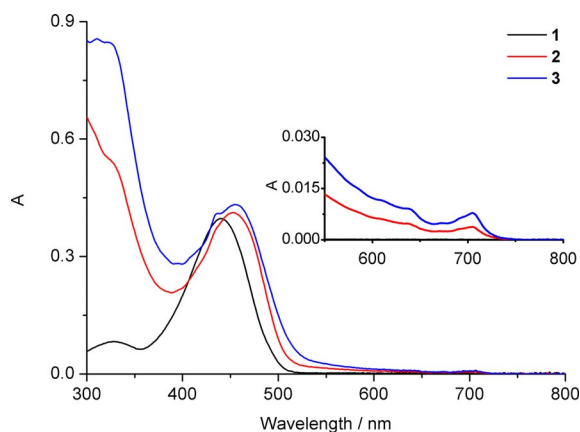


Figure 2. UV/Vis spectra of 2,2'-dipyrrin **1** (black trace) and of its mono-fullereno and bisfullereno-derivatives **2** (red trace) and **3** (blue trace), dissolved in toluene ($c = 1.53 \times 10^{-5}$ M).

3. The dihydrofullerene addends cause additional absorptions, with very characteristic weak maxima at 702 nm^[21] and broad bands with increasing intensity at shorter wavelengths, consistent with one or two C₆₀-addends in **2** and **3**, respectively. Similar effects on the UV/Vis-spectral characteristics were found in covalent porphyrin β,β'-conjugates of C₆₀, which were obtained by thermolysis of tetrasulfoleno-porphyrin.^[12b,13] Fluorescence, as reported for **1** and its Zn-complex,^[15] is absent in the fullerene adducts **2** and **3**, where the dipyrin luminescence is quenched effectively by the closely positioned C₆₀-addends.

The molecular formulas of fullereno-dipyrrins **2** and **3** were deduced from MALDI-TOF mass spectra. The spectrum of **2** featured a pseudo-molecular ion at m/z 1169.0 [M+H]⁺, corresponding to C₈₇H₃₂N₂O₂S. A strong fragment at m/z 1105.2 [M-SO₂+H]⁺ indicated the loss of a SO₂ group. The mass spec-

trum of **3** confirmed its molecular formula as C₁₄₇H₃₂N₂ by showing a molecular ion at $m/z = 1824.6$ [M]⁺ and a strong fragment at m/z 1105.2, from loss of one fullerene unit.

The structures of the fullereno-dipyrrins were established by detailed analysis with one and two-dimensional NMR spectra (¹H,¹H-COSY and ROESY, ¹H,¹³C-HSQC and HMBC spectra). The monoadduct **2** is less symmetric than its precursor **1**, and its NMR spectra showed, correspondingly, more signals (see Figures 3 and 4). In the ¹H NMR spectrum of **2**, for example, four singlets of methylene groups were seen at intermediate field, and two singlets for α-pyrrolic protons at low field (see Figure 4). In the spectrum of **2**, the two methylene singlets at 3.14 ppm and 4.10 ppm were present at a position quite similar to that in the ¹H NMR spectrum of **1**. Two further methylene singlets in the spectrum of **2** appeared at 3.60 ppm (broad singlet) and 4.46 ppm, shifted to lower field by de-shielding by the close-by fullerene unit. Each of these latter methylene signals coupled to C-atoms with chemical shift values of 39.2 ppm and 38.3 ppm (as seen in HSQC-spectra), as is typical for pyrrole β-methylene groups linked to a fullerene (Table S1 and Figure S5).^[13] In contrast, the other two methylene signals (3.14 ppm and 4.10 ppm) correlated to carbons at 55.5 ppm and 53.4 ppm in the HSQC spectra of **2**, indicating their attachment to the remaining sulfolene unit (Figure S5). The deduced location of methylene groups was confirmed in a ¹H,¹H-ROESY spectrum. There, the signals at 3.60 and 3.14 ppm showed correlations with H-atoms at the *ortho*-position of the *meso*-phenyl group and were assigned to H₂C³ and H₂C⁷, respectively (Figure 3). Such NOE correlations were not seen for the two signals at 4.46 and 4.10 ppm, consistent with assignment as H₂C² and H₂C⁸, respectively. The methylene groups exhibited a single resonance, each, in the ¹H NMR spectrum of **2** at room temperature, due to rapid conformational inversion of

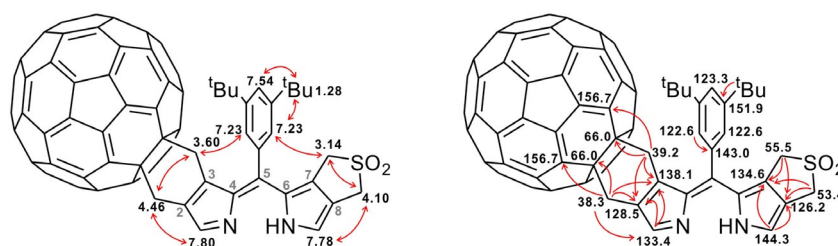


Figure 3. ¹H-¹H correlations observed in ¹H,¹H-ROESY (left, atom numbering is given in gray) and ¹H-¹³C correlations from ¹H,¹³C-HSQC and HMBC spectra (right) of a solution of **2** in CDCl₃/CS₂ (500 MHz, 25 °C).

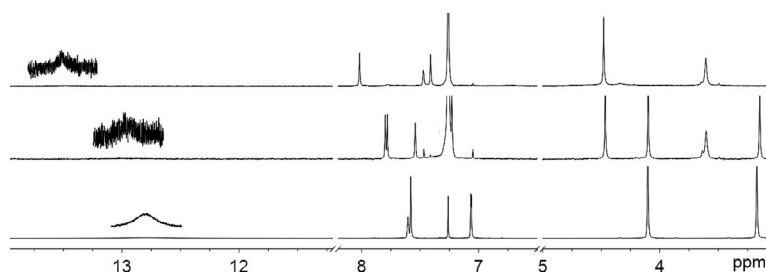


Figure 4. Relevant sections of ¹H NMR spectra of the fullerene bis-adduct **3** (top, CDCl₃/CS₂, 500 MHz), of the fullerene mono-adduct **2** (center, CDCl₃/CS₂, 500 MHz) and of the dipyrin **1** (bottom, in CDCl₃, 300 MHz).

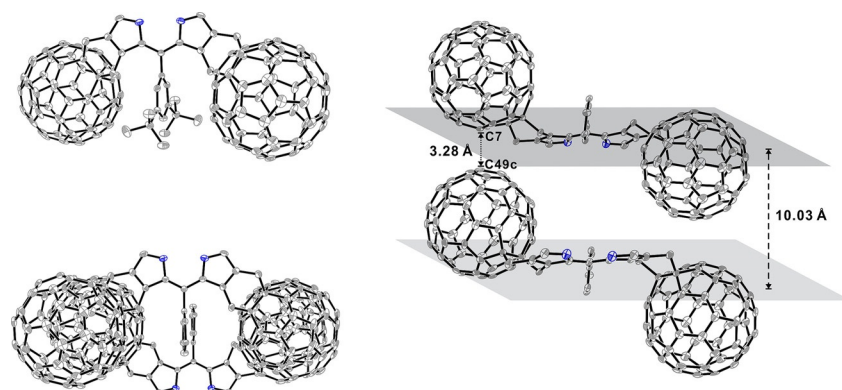


Figure 5. ORTEP plot of the crystal structure of the di-(β,β' -fullereno)pyrriin **3**. Top left: front view, in which H-atoms were omitted for the sake of clarity; bottom left: top view of π -stacked neighbors that relate by a center of inversion (with H-atoms and *tert*-butyl groups omitted). Right: side view of π -stacked neighbors, highlighting crucial distances between the planes of the two dipyrriin cores and between next neighbor carbon atoms of fullerene moieties.

the six-membered ring connecting the fullerene and pyrrole units of **2**, as has been observed in analogous fullereno-porphyrins.^[12b]

A singlet at 7.80 ppm was assigned to HC1, as it correlated with the fullerene-linked methylene group at 4.46 ppm in the ROESY spectrum of **2** (Figure 3). The other low field singlet (at 7.78 ppm) was assigned to HC9, as it correlated with the methylene group at 4.10 ppm (Figure 3). The attachment of a C_{60} -fullerene was further secured by a $^1H,^{13}C$ -HMBC spectrum, in which the methylene signals at 4.46 ppm and 3.60 ppm correlated with ^{13}C -signals at $\delta = 133.4$ ppm (pyrrole C1), as well as at $\delta = 66.0$ ppm (sp^3 -C of the fullerene unit) and at 156.7 ppm (adjacent sp^2 -C of the fullerene), that is, the typical chemical shift values of C-atoms at the fullerene C[6,6]-bond that has undergone [4+2] cycloaddition (Figure S6).^[12b,13,21,22] The pyrrole NH gave a broad weak signal at slightly lower field, when compared to the spectrum of its precursor **1**.

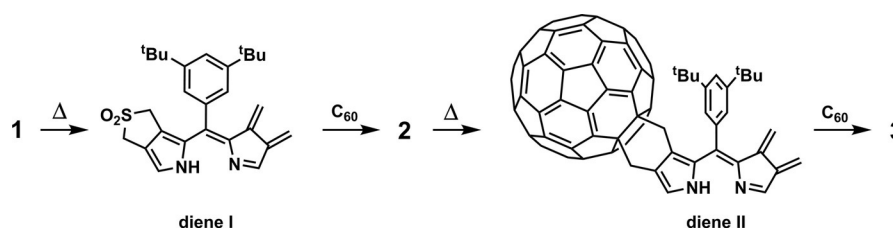
The di-(β,β' -fullereno)pyrriin **3** exhibited a simpler pattern of the signals in its 1H NMR spectrum than the monoadduct **2**, due to its more symmetric effective structure. Only two (broad) singlets of the eight diastereotopic methylene protons appeared at 4.48 ppm and 3.60 ppm as a consequence of fast conformational equilibration. The pyrrole α -H was shifted to 8.02 ppm (Figure 3 and Table S1 in the Supporting Information). In the $^1H,^{13}C$ -HSQC spectrum of **3**, the two methylene group singlets at 3.60 ppm and 4.48 ppm of the correlated to carbon resonances at 38.6 and 40.0 ppm of the neighboring fullerene addend (Figure S7), and, in a $^1H,^{13}C$ -HMBC spectrum, to the typical quaternary carbon of the fullerene moiety at 66.4 ppm (Figure S8). These correlations secured the attachment of the two fullerene units in **3**. The shielding effect of the phenyl group at the dipyrriin *meso*-position assisted the assignment of the signal at 3.60 ppm to H_2C3^1 and H_2C7^1 . When the 1H NMR data of **1**, **2** and **3** are compared, the signals of the pyrrole NH and α -H's, of the protons of the methylene group next to fullerene and at the *ortho*-position of the *meso*-phenyl substituent shift to lower field, upon consecutive loading with the C_{60} -fullerene, whereas the signal of the proton in the *para*-position of the *meso*-phenyl group shifts to higher field (Figure 3 and Figure S2).

Single crystals of the di-(β,β' -fullereno)pyrriin **3** grew from a solution of **3** in CS_2 when EtOH was mixed in slowly at 23 °C. Bis-adduct **3** crystallized in the monoclinic space group $C2/c$. The unit-cell contained four molecules of **3** and half a molecule in the asymmetric unit, which was completed by a crystallographic twofold rotation axis. The NH in the dipyrriin unit was disordered due to the effective symmetry of the structure of the dipyrriin core.

In **3** the two fullerene units are positioned on opposite faces with respect to the reference plane of the dipyrriin core (see Figure 5). The two pyrrolic rings in the dipyrriin core are twisted with a dihedral angle of 9.5° in the bisadduct **3** (increased from 3.5° in **1**). The angle between the mean planes of the aryl group and of the dipyrriin core has increased to 82.8°, a consequence of the steric bulk of the C_{60} substituent. In the crystal, the mean planes of the dipyrriin cores of neighboring molecules are positioned in parallel and at a distance of 10.03 Å. Two neighbor molecules relate to each other by a center of inversion, so that their dipyrriin cores are oriented in opposite directions. The fullerene units of **3** prevent intermolecular π - π stacking interactions of the dipyrriin core. They make remarkably short intermolecular contacts with closest distances between C7–C49c of 3.28 Å and C27–C36b of 3.36 Å (edge-to-edge interactions in the same row or column) (see Figure 5 and Figure S3).

In conclusion, the SO_2 groups of the di-(β,β' -sulfoleno)pyrriin **1** are rapidly extruded consecutively at 120 °C. This furnishes reactive diene intermediates that can be trapped by the C_{60} -fullerene via rapid [4+2] cycloaddition, attaching C_{60} units at the pyrrole β,β' -positions of the dipyrriin core and furnishing the bisadduct **3** as final product (Scheme 3). The intermediate mono(β,β' -fullereno)-adduct **2** still harbors one sulfolene function, which is available for further thermal diene formation and subsequent [4+2] cycloaddition reaction with alternative dienophiles. Conjugates of fullerenes with dipyrriins represent attractive photo- and redox-active components,^[1,4b] as has also been established for various of their porphyrinoid analogues.^[14,23]

The di-(β,β' -sulfoleno)pyrriin **1** serves as a masked form of a highly reactive bis-diene, undergoing [4+2]-cycloaddition



Scheme 3. Thermolysis of di-(β,β' -sulfoleno)pyrrole **1** in the presence of C_{60} -fullerene generates the reactive diene intermediates I and II, which undergo covalent attachment of C_{60} -units by sequential [4+2]-cycloaddition, furnishing the di-(β,β' -fullereno)pyrrole **3**.

reactions readily with typical dienophiles. In earlier work, symmetric tetra-(β,β' -sulfoleno)porphyrins and a tetra-(β,β' -sulfoleno)corrole were used as reactive precursors ‘programmed’ for loading with C_{60} -fullerene^[12b,d,13] and benzoquinone^[12c] by [4+2] cycloaddition. However, the three β,β' -sulfolenopyrrole derivatives with extended conjugated systems differ strongly by the ease and regio-selectivity of the loss of their SO_2 moieties. Unlike the situation found here with the dipyrrole **1** (rapid conversion at 120 °C), the detachment of two SO_2 moieties from the tetra-(β,β' -sulfoleno)porphyrin required longer heating at 140 °C,^[12b] and the corresponding conversion of analogous β,β' -sulfolenopyrroles even needed prolonged heating at 210 °C.^[11a,c]

In the present study, the representative di-(β,β' -sulfoleno)pyrrole **1** was shown to undergo a thermally induced process readily that set the stage for [4+2]-cycloaddition of the C_{60} -fullerene (or, presumably, of other fullerenes^[24]). Use of still other dienophiles, such as quinones,^[12c] will provide the opportunity for producing dipyrroles with further extended chromophoric systems. Indeed, the di-(β,β' -sulfoleno)pyrrole **1** is ‘programmed’ for heat-induced loss of SO_2 and subsequent introduction of a variety of covalent modifications at the pyrrole β -positions by [4+2]-cycloaddition chemistry. As was similarly explored with tetra-(β,β' -sulfoleno)porphyrins^[12b-e] and a tetra-(β,β' -sulfoleno)corrole,^[13] the reactive dipyrrole **1** proved to be a convenient 2,2'-dipyrrole building block. 2,2'-Dipyrroles are versatile bidentate ligands for coordination of metal ions^[1,15] and for higher order supramolecular architectures,^[1] useful in imaging and energy conversion. Indeed, the di-(β,β' -sulfoleno)dipyrrole **1** was first studied as a model component in zinc chelates,^[15] as models of the structurally more complex transition metal complexes of natural yellow bilins, such as phylloxanthobilins^[25] and bilirubin.^[26] The ‘programmed’ di-(β,β' -sulfoleno)pyrrole **1** is a novel member of semi-rigid pyrrole-based compounds, helping to expand the recently developed ‘porphyrin LEGO’ methodology^[12d] to the assembly of corresponding covalent molecular constructs in the fields of 2,2'-dipyrroles and BODIPYS.^[1-3]

Experimental Section

General: Dichloromethane (CH_2Cl_2) was from Sigma–Aldrich (Steinheim, Germany), and was distilled and filtered over basic Al₂O₃ before use. Toluene, *o*-dichlorobenzene (*o*-DCB), carbon disulfide (CS_2), ethanol (EtOH), ethyl acetate (EtOAc) and *n*-hexane (*n*- C_6H_{14}) were from VMR (Leuven, Belgium); C_{60} was purchased from Merck Corporation (USA). Column chromatography (CC): Fluka silica gel

60 (230 \approx 400 mesh). Thin layer chromatography (TLC): Merck 0.25 mm silica gel 60 plates without GF254. Equipment: UV/Vis: Agilent Cary 60 UV/Visible, λ_{max} in nm (log ϵ). Fluorescence (FL): Varian Cary Eclipse, λ in nm (rel. intensity); Nuclear magnetic resonance (NMR) spectra: Bruker 300 or Varian 500 Unity plus at 298 K, chemical shifts (δ) in ppm, with ¹H NMR: δ ($CHCl_3$) = 7.26 ppm, ¹³C-NMR: δ ($CDCl_3$) = 77.16 ppm. atom numbering as for X-ray data (see Figures 1 & 5). MALDI-TOF: Bruker Daltonics Ultraflex with *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malononitrile as matrix.

Synthesis: A solution of di-(β,β' -sulfoleno)pyrrole (**1**)^[15] (2.33 mg, 4.55 μ mol) and C_{60} (23.45 mg, 32.57 μ mol, 7.2 moleq) in 2 mL *o*-dichlorobenzene (*o*-DCB) was purged with Ar for 5 minutes and heated at 120 °C for 20 minutes under Ar in the dark. The reaction mixture was diluted with 1 mL *n*- C_6H_{14} and loaded on silica gel column (2 cm \times 15 cm). Bisadduct **3** was washed down with toluene and monoadduct **2** was eluted with toluene with 5% of EtOAc. After drying under reduced pressure, 1.3 mg of brown solid **2** were obtained (24% yield) after precipitation in CS_2 /EtOH, and 6.0 mg of **3** were obtained as brown single crystals (72% yield) by crystallization in CS_2 /EtOH (2:3, v/v). Monoadduct **2** UV/Vis (toluene): λ_{max} (log ϵ): 330 (4.54), 434.5sh (4.38), 453.5 (4.43), 702 (2.50). Monoadduct **2** showed no fluorescence emission. ¹H NMR (500 MHz, 25 °C, 1.7×10^{-3} M in $CDCl_3/CS_2 = 0.4$ mL/0.1 mL): 1.28 (s, *t*Bu), 3.14 (s, H_2C-7^1), 3.60 (s, H_2C-3^1), 4.10 (s, H_2C-8^1), 4.46 (s, H_2C-2^1), 7.23 (d, $J = 1.3$ Hz, HC-5⁶ and HC-5⁶), 7.54 (t, $J = 1.3$ Hz, HC-5⁴), 7.78 (s, HC-9), 7.80 (s, HC-1), 12.96 (brs, HN-2). MALDI-TOF MS: 1171.0 (10), 1170.0 (19), 1169.0 (23, $[M+H]^+$ Calcd. for $[M+H]^+ C_{87}H_{33}N_2O_2S$ $m/z = 1169.2$); 1107.1 (24), 1106.1 (71), 1105.2 (100, $[M-SO_2+H]^+$). Bisadduct **3** UV/Vis (toluene): λ_{max} (log ϵ): 327 (4.74), 435 (4.43), 455 (4.45), 702 (2.70). Bisadduct **3** showed no fluorescence emission. ¹H NMR (500 MHz, 25 °C, 1.0×10^{-3} M in $CDCl_3/CS_2 = 3.5/1.5$): 1.18 (s, *t*Bu), 3.60 (s, H_2C-3^1 and H_2C-7^1), 4.48 (s, H_2C-2^1 and H_2C-8^1), 7.41 (d, $J = 1.4$ Hz, HC-5² and HC-5⁶), 7.47 (t, $J = 1.4$ Hz, HC-5⁴), 8.02 (s, HC-9 and HC-1), 13.56 (br. s, HN-2). MALDI-TOF MS: 1828.5 (2), 1827.6 (7), 1826.6 (14), 1825.6 (22), 1824.6 (10, $[M]^+$ Calcd. for $[M]^+ C_{147}H_{32}N_2$ $m/z = 1824.3$); 1107.2 (30), 1106.2 (79), 1105.2 (100, $[M-C_{60}+H]^+$).

Crystallographic data: X-ray analyses: data collection on a Nonius Kappa CCD (for **1**) and on a Bruker D8 QUEST (for **3**), both equipped with graphite mono-chromatized Mo-K α -radiation ($\lambda = 0.71073$ Å). CCDC 1837889 (**1**) and 1837890 (**3**) (excluding structure factors) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: C₆₀-fullerene · cheletropic reaction · cycloaddition · Diels–Alder reactions · porphyrins

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