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Synthesis and characterization of a ferrocene-linked bis-fullerene[60] dumbbell[†]

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A new [60]fullerene dumbbell consisting of two fulleropyrrolidines connected to a central ferrocene unit by amide linkages has been prepared and fully characterized by elemental analysis, ¹H NMR, UV/Vis, fluorescence and mass spectrometry. The electrochemical properties as determined by cyclic voltammetry show ground state electronic communication between the ferrocene and the fullerene units. In addition, the preparaton of a ferrocene building block for an alternative linking approach is presented.

Introduction

Fullerenes are frequently employed as electron acceptor moieties in donor–acceptor systems, with C_{60} standing out as the most studied and well characterized member of the family. In the ground state, C_{60} can accept up to six electrons in a reversible manner,¹ and numerous studies of donor–acceptor dyad systems have shown that a large variety of C_{60} derivatives are acceptors for photoinduced electron transfer.²

Molecular derivatives consisting of more than one fullerene unit, such as the group of dimers resembling dumbbells, are less common. A C60-piperazine-C60 dumbbell was reported by Martín et al. already in 1996.³ Electrochemical characterization showed that the compound behaved as two independent donor-acceptor units with no observable interactions between the two fullerenes in the ground state. Further examples of dumbbell systems with donor fragments such as porphyrins, oligo(phenyleneethynylenes) and tetrathiafulvalenes have been reported and studied in the literature. While most of the reported C₆₀-donor-C₆₀ triads have shown a lack of electronic interactions between the moieties in the ground state, some have shown improved photophysical properties in the excited state as compared to the corresponding dyads (i.e. stabilization of charge separated states upon electron transfer) and photovoltaic devices based on some of these C₆₀ dumbbells have shown improved energy conversion efficiencies.4

It has been shown that C_{60} has an affinity for noble metals and hybridizes efficiently with gold surfaces, and recent singlemolecular conductivity measurements have employed C_{60} as a highly efficient anchoring group to metal electrodes.⁵ These types of dumbbells may hence find great use in molecular electronics, with C_{60} end groups increasing the still limited set of anchoring groups, and moreover rendering possible studies of conductivity

by direct methods.6 In a previous study, we found evidence for ground state electronic communication between C60 and an appended arene tricarbonyl chromium unit, with the possiblility of determining the redox state of the C₆₀ by IR spectroscopy.⁷ This property would, in a dumbbell or larger structure, be useful as i.e. a molecular memory. Unfortunately, the stability of the tricarbonylchromiumarene decreases in the presence of C60 and although it was possible to isolate and fully characterize the dyad, the corresponding dumbbell was not stable enough.8 In contrast, the isoelectronic ferrocene is stable under a large range of conditions, and organometallic dyads with C60 as acceptor and ferrocene as donor have been thorougly characterized.9 Dumbbells and higher C₆₀ oligomers with ferrocenyl links could thus be a class of compounds with interesting properties and potential application in molecular devices.

In the present paper, we report synthetic studies towards two new C_{60} -donor- C_{60} dumbbells 1 and 2 (Fig. 1), as well as characterization of 1 by NMR, UV/Vis and fluorescence spectroscopy, elemental analysis and mass spectrometry. The electrochemical properties of 1 have further been investigated by cyclic voltammetry. The route towards 2, with several new ferrocene derivatives, is also described.

Results and discussion

Both dumbbells have a central 1,1'-functionalized ferrocene unit linked to *N*-substituted fulleropyrrolidine units. In **1**, the link is *via* amides formed between a ferrocene acid chloride and fulleropyrrolidines in the final step of the synthesis, whereas the tertiary amine link in **2** is set up already in the ferrocenecontaining dipole precursor **12**. The reason for this general design is twofold: (i) It has been shown that there is good

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Fig. 1 Target structures 1 and 2.

electronic communication between the pyrrolidine nitrogen and the fullerene core in fulleropyrrolidines¹⁰ and (ii) the possibility to efficiently functionalize the fulleropyrrolidine nitrogens by organometallic groups could allow for controlled preparation of trimers, tetramers, pentamers and polymers by the use of fulleropyrrolidine bis-adducts as building blocks, accessible *via* established tether-based approaches.¹¹

Synthesis

In the convergent synthesis of 1 (Scheme 1), the fulleropyrrolidine component is prepared in a 1,3-dipolar cycloadditon of an in situ formed azomethine ylide from 3,4-bis(octadecyloxy)benzaldehyde and glycine to one of the double bonds of C₆₀. In order to facilitate purification and characterization, an aldehyde with long-chain aliphatic groups was employed. Fulleropyrrolidine 5 was isolated in 39% yield, and in contrast to most N-unsubstituted analogues, it was readily purified by (repeated) column chromatography on silica. The 1,1'-ferrocenedicarboxylic acid 3 was synthesized according to literature procedures¹² and converted to its di-acid chloride 4 by oxalyl chloride. Fulleropyrrolidine 5 and compound 4 were then reacted in stochiometric amounts in the presence of pyridine. Purification by precipitation in toluene/EtOH followed by column chromatography gave the target compound in 69% isolated yield. Elemental analysis as well as mass spectrometry (Maldi-TOF) and ¹H NMR are consistent with a pure compound. As expected, 1 is soluble in solvents such as CH₂Cl₂, CHCl₃, toluene and benzene. In addition to 1, reference compounds 6 and 7 (Fig. 2) were prepared.

A route towards the related dumbbell 2 is shown in Scheme 2. This target consists of two fulleropyrrolidines connected to a central ferrocene moiety by ethynylbenzene bridges and thus constitutes a more linear dumbbell, although the ferrocene unit is farther away from the fullerenes than in 1.

The initial steps, involving construction of the modified ferrocene building block were successful. The dipole precursor end **10** was obtained in three steps, starting with alkylation of *p*iodoaniline with ethyl-bromoacetate in the presence of sodium acetate to produce compound **8** in a purified yield of 48%.¹³ This compound was then reacted with ethynyltrimethylsilane under microwave-assisted Sonogashira coupling conditions¹⁴ to give



Fig. 2 Reference compounds used in this study *N*-acyl-2-(3,4-bis-(octadecyloxy)benzene)-3,4-fulleropyrrolidine 6 and 1,1-bis(pyrrolidinyl-carbonyl)ferrocene 7.

compound **9** in a purified yield of 86%. Deprotection using K_2CO_3 gave alkyne **10** in 74% yield. The ferrocene component **11** for the second Sonogashira coupling was prepared in three steps. Ferrocene was treated with *n*-butyl lithium and TMEDA followed by reaction with tributyltin chloride to yield 1,1'-bis(tributyl)stannyl ferrocene,¹⁵ which was subsequently reacted with iodine to give 1,1'-diiodoferrocene **11** in 70% purified yield.¹⁶ The assembly of **12** was achieved by a second Sonogashira coupling between an excess of **10** and compound **11** to give compound **12** as an orange solid in a purified yield of 39%. Hydrolysis of **12** gave compound **13** in 55% isolated yield.

The final step to the target dumbbell 2 would be a dual Prato reaction between compound 13, 4-methoxybenzaldehyde and C₆₀.

The reaction was attempted several times, in refluxing *o*-dichlorobenzene for up to two days without any indication of pyrrolidine formation. Inspection of molecular models indicated that, for a conformation of **13** with parallel substituents, intersubstituent hydrogen bonding may deactivate the secondary amine towards the initial imine condensation required for dipole formation. This interaction is not present in diester **12**. Although pyrrolidination of C₆₀ has been reported for *i.e.* ester derivatives of sarcosine,¹⁷ no traces of any pyrrolidinated product could be detected from our attempts using **12**, 4-methoxybenzaldehyde and C₆₀.

Characterization of 1

The IR spectrum of compound 1 (Fig. 3) shows signals similar to fulleropyrrolidine 5 together with a typical amide signal at 1634 cm⁻¹. A strong signal originating from C_{60} can be observed at 526 cm⁻¹ in both compounds. The signals from the ferrocene unit should appear in the region between 1100–800 cm⁻¹, but these are probably buried beneath the strong signals from the fulleropyrrolidines.

More distinct support that we have indeed obtained 1 was obtained from Maldi-TOF analysis. Several matrices were tried in both positive and negative detection mode. For α -cyano-4-hydroxycinnamic acid, no molecular ion peak was observed in either of the modes. In the positive mode, neither 9-nitroanthracene nor dithranol gave any molecular ion peak, instead a major, non-identified peak at m/z = 2902 together with some fragment ions was obtained. However, in negative mode, both 9-nitroanthracene and dithranol gave abundant molecular ion peaks



Scheme 1 Synthesis of dumbbell 1. Conditions: *i*) a) TMEDA, *n*-butyl lithium, *n*-pentane, RT, stirring, 12 h, b) THF, CO₂(g), purified yield 41%. *ii*) Oxalyl chloride, CH₂Cl₂, DMF, stirring, 1.5 h. *iii*) glycine, *o*-dichlorobenzene, reflux, 12 h, purified yield: 39%. *iv*) CH₂Cl₂, pyridine, stirring, 12 h, purified yield: 69%.



Fig. 3 IR spectrum (neat) of compound 5 (upper) and compound 1 (lower).

at m/z = 2989 (M⁻) as well as strong signals at m/z = 1468 and 1404 corresponding to different fragment ions of compound 1, generated by the strong laser required to ionize the compound.

The ¹H NMR spectrum of the compound in CDCl₃ at 25 °C (ESI†) has several signals for the octadecyl chains at 4.02, 1.80,

1.25 and 0.88 ppm. In addition, there are several unresolved broad signals in the region between 6.5 and 4.5 ppm (Fig. 4) as well as in the aromatic region, indicating that some dynamic process is taking place on the NMR timescale. This is not too surprising, since both the rotation around the central ferrocene unit as well as the rotation around the two amide bonds can be slow on the NMR timescale and lead to such broadening of signals.¹⁸ It is also important to consider that since the dumbbell 1 has two stereogenic centers and is prepared from a racemic mixture of fulleropyrrolidine 5 as the starting material, a mixture of four diasteromeric products is expected. Based on this we attempted some low temperature ¹H NMR measurements to determine whether we could observe individual signals for the different diastereomers. Unfortunately, precipitation of the compound at temperatures below -20 °C (CD₂Cl₂) prohibited us from slowing down the dynamics sufficiently to get any resolution of the signals and consequently to carry out this study.

However, by changing the solvent to benzene-d₆ and increasing the temperature to 70 °C we managed to get a ¹H NMR spectrum of improved quality with significantly sharper signals (Fig. 4 and ESI†). At this temperature the spectrum shows signals for a single product only, with two sets of aromatic signals (6H), four pyrrolidine doublets at 6.64, 6.37, 5.80, 5.78 ppm (4H), four resolved multiplets (J = 1.2 Hz) at 5.39, 5.31, 5.18, 5.12 ppm and four unresolved, partly overlapping multiplets at 4.41, 4.38 and



Scheme 2 Synthesis of precursors for dumbbell **2**. Conditions: *i*) NaOAc, ethanol, reflux 12 h (purified yield: 48%). *ii*) Ethynyltrimethylsilane (1.15 eq.), Pd(PPh₃)₂Cl₂, CuI, diethylamine, DMF, MW heating 120 °C, 45 min. (purified yield: 69%). *iii*) K₂CO₃, CH₂Cl₂, ethanol, RT, 12 h (purified yield: 74%). *iv*) a) Et₂O, *n*-BuLi (2.5 M), TMEDA, 0 °C, stirring 12 h, tributyltin chloride, RT, 12 h. b) CH₂Cl₂, -79 °C, I₂, stirring 12 h (purified yield: 70%). *vi*) Pd(PPh₃)₂Cl₂, CuI, DIPA, 90 °C, 2 days (purified yield: 39%). *vi*) NaOH, ethanol, reflux, 5 h (yield: 55%). *vii*) C₆₀ (3 eq.), 4-methoxybenzaldehyde (excess), *o*-dichlorobenzene, reflux, 2 days (yield: 0%).

4.29 ppm. The latter eight multiplets correspond to the ferrocene protons in the dumbbell which are all non-equivalent. The methine protons situated at the stereogenic centers in dumbbell **1** appear as a multiplet at 5.47 ppm. Also, there are two multiplets at 4.17 and 3.89 ppm originating from the eight methylene protons closest to the oxygen atoms in the octadecyl chains. The other signals from the octadecyl chains (140H) appear at 1.81, 1.75, 1.34 and 0.92 ppm.

Diffusion measurements carried out on the aliphatic signals (by the LED-PGSE pulse sequence) showed a significantly slower diffusion $(9.9 \times 10^{-11} \text{ m}^2 \text{ s}^{-1} \text{ in CDCl}_3)$ for **1** as compared to fulleropyrrolidine **5** ($1.2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ in CDCl₃) as expected based on the larger size of the dumbbell.

The UV/Vis spectra for toluene solutions of **1**, fulleropyrrolidine **5** and reference compound **6** are shown in Fig. 5. The UV/Vis spectrum of the dumbbell is relatively similar to the spectra of compound **5** and **6** with major absorption bands around 284 nm, ~312 nm and weak absorptions at 430 and around 700 nm characteristic for fulleropyrrolidines.¹⁹ Some differences in the area between 430–750 nm are however present that may indicate some ground-state interactions between the fullerenes and the ferrocene unit in compound **1**.

The fluorescence spectra of 1, fulleropyrrolidine 5 and fulleropyrrolidine 6 (Fig. 6) show the weak fullerene fluorescence in the region between 650-850 nm. Interestingly, the emission maxima for the dumbbell situated at 726 nm is red shifted as compared to



Fig. 4 Expansion of the 3.8–6.6 ppm region in the ¹H NMR spectra of compound 1. (Upper): In CDCl₃, at 25 °C. (Lower): In C₆D₆, at 70 °C.



Fig. 5 UV/Vis spectra of compound 1 (solid), compound 5 (dashed) and compound 6 (dotted). Spectra are normalized and recorded in toluene.

both compound **5** and **6** which have emission maximas at 715 nm and 712 nm respectively. Also, at the same concentrations one could expect the fluorescence yield to be twice as high in compound **1** relative to the two reference compounds since it contains two fulleropyrrolidines.

However, there is significant quenching of the fullerene fluorescence in the dumbbell relative to the reference compounds under identical experimental conditions and sample concentrations. Similar results were also obtained in 1,2-dichloroethane in which the quenching of the fluorescence for dumbbell **1** was slightly more pronounced.

Due to the high rotational flexibility around the central ferrocene unit, compound 1 can adopt a conformation in which the two fullerenes are in close proximity. It is therefore possible that the red shifted emission maxima and lower fluorescence yield



Fig. 6 Fluorescence spectra of compound 1 (solid), compound 5 (dashed) and compound 6 (dotted) in degassed toluene at 25 °C. The concentrations of the analytes were 0.10 mM, and the excitation wavelength was 470 nm.

are the result of an intramolecular excimer, formed by the two fullerenes in the dumbbell. However, based on the short life time of the fullerene singlet excited state, self-quenching *via* the formation of an intramolecular singlet excimer is not likely. Besides, no selfquenching has been found in C₆₀ solutions in *o*-dichlorobenzene at nearly saturated concentrations, and is also absent in a reported fullerene dimer in which the two covalently bonded fullerene cages are very close to each other.²⁰ Hence, the quenching of the fullerene emission is due to intramolecular energy or electron transfer between the fullerene and the ferrocene parts, which also has been observed in several related C₆₀-ferrocene systems.⁹

Cyclic voltammetry of the dumbbell 1 (Fig. 7 and Table 1) shows one quasi-reversible oxidation wave at +0.32 V (vs. Fc/Fc⁺) corresponding to the one electron oxidation of the central ferrocene unit in the dumbbell. This oxidation peak is shifted to higher potential as compared to the reference compound 1,1'bis(pyrrolidinylcarbonyl)ferrocene 7 by +60 mV. On the reduction side, four (quasi) reversible waves corresponding to the reduction of the C₆₀ part of the dumbbell can be observed. The intensity of these reduction waves are 2.0 ± 0.1 as large as the single oxidation wave at +0.32 V and correspond to two electrons each. These observations are consistent with the expected behaviour of the dumbbell 1, and are further evidence for its structure. Moreover, the four C₆₀ reductions indicate a lack of electronic interactions between the two fullerene cores in the ground state, which is consistent with previous studies of other C₆₀ dumbbells.⁴ The somewhat irregular shape of the two first reduction waves for dumbbell 1 is most likely due to some adsorption phenomenon taking place on the working electrode as similar results were obtained with fulleropyrrolidine 5.

A comparison of the reduction potentials of dumbbell 1 with those of fulleropyrrolidine **5** shows an anodic shift of between 80–170 mV for the four reversible or quasi-reversible reductions in dumbbell 1. Also, the difference in E^{0}_{red} increases by each reduction step. For a better comparison, the voltammogram of compound **6** which is a more appropriate reference compound was also recorded (Fig. 7), and its electrochemical data can be found in Table 1. For this compound, the reduction potentials are anodically shifted by 70–160 mV as compared to compound **1**.

Table 1 Electrochemical data for compounds 1, 5, 6 and 7 ^a										
Compound	E^{0}_{ox} [V]	$\Delta E_{\rm p} [{ m mV}]$	$E^{0}_{\mathrm{red},1}$ [V]	$\Delta E_{\rm p} [{ m mV}]$	$E^{0}_{\mathrm{red},2}$ [V]	$\Delta E_{\rm p} [{ m mV}]$	$E^{0}_{\mathrm{red},3}$ [V]	$\Delta E_{\rm p} [{ m mV}]$	$E^{0}_{\mathrm{red},4}$ [V]	$\Delta E_{\rm p} [{ m mV}]$
1	+0.32	114	-1.19	200	-1.60	170	-2.20	190	-2.70	210
5			-1.27	280	-1./2	290	-2.34	260	-2.87	320
7	+0.26	146	-1.09	120	-1,55	110	-2.10	120	-2.94	100

^{*a*} Potentials are reported against the ferrocene/ferrocenium couple. Working electrode: Glassy carbon electrode (3 mm); counter electrode: Pt; quasireference electrode: Pt. Toluene/acetonitrile (4:1) was used as solvent together with 0.1 M TBAPF₆. Concentrations of the analytes were 1 mM. All measurements were carried out at 25 °C under nitrogen atmosphere in degassed solvents. $E^0 = (E_{pc} + E_{pa})/2$, in which E_{pc} and E_{pa} correspond to cathodic and anodic peak potentials respectively. $\Delta E_p = (E_{pc} - E_{pa})$. Scan rate: 25 mVs⁻¹.



Fig. 7 (Left): Cyclic voltammograms of dumbbell 1 (upper) and fulleropyrrolidine 6 (lower). (Right): oxidation waves of ferrocene (dashed), 1,1-bis(pyrrolidinylcarbonyl)ferrocene 7 (dotted) and dumbbell 1 (solid).

Prato *et al.* have previously reported the electrochemical characterization of some ferrocenyl fulleropyrrolidines by cyclic voltammetry.²¹ In that study the authors found no apparent ground-state electronic interation between the fullerene and the ferrocene parts in a dyad in which the ferrocene was connected to the fulleropyrrolidine nitrogen by an amide group (as it is also in compound 1). The small differences in redox potentials observed for compound 1 as compared to the two reference compounds 6 and 7 indicate however some ground-state electronic interaction between the ferrocene unit and the fullerenes in the dumbbell.

Thus, a reasonable rationale for this is that the introduction of a secondary fulleropyrrolidine to the ferrocene unit leads to more pronounced interactions between the two electroactive moieties which become measureable by cyclic voltammetry.

Conclusion

We have successfully synthesized a highly soluble organometallic fullerene dumbbell in which two fulleropyrrolidines are connected to a central ferrocene unit. The dumbbell has been fully characterized by standard methods such as ¹H NMR, mass spectroscopy and elemental analysis.

Fluorescence spectroscopy showed a significant quenching of the fullerene emission that was red-shifted as compared to reference compounds **5** and **6**, indicating that energy or electron transfer occurs in the dumbbell in its excited state. Moreover, UV/Vis and in particular cyclic voltammetry studies revealed some degree of electronic communication between the central ferrocene unit and the fullerenes in the ground state. In contrast, no evidence for interactions between the two individual fullerenes in the dumbbell were observed, and the compound thus behaves as two independent donor-acceptor systems.

Experimental

General

Thin-layer chromatography analyses were performed on precoated Merck silica gel plates (60 F254) and visualized with UV light. Melting points were recorded on a Stuart scientific SMP10 melting point apparatus and are uncorrected. ¹H and ¹³C NMR spectra were recorded on a Varian 500 MHz spectrometer and chemical shifts are given in ppm (δ) using the residual CHCl₃ or C_6D_6 peak as internal standard. Diffusion measurements were made using the LED-PGSE pulse sequence. z-gradients were employed and 16 scans were acquired. A relaxation delay of 0 s. 10 ms gradient pulse duration, 100 ms diffusion delay, 5 ms storage delay were used and the gradient pulse strength was arrayed between 0 and 20 gauss cm⁻¹ (30 steps). The diffusion coefficients were calculated based on the diffusion coefficient of CHCl₃ (5.2×10^{-6} cm² s⁻¹). Solid state IR spectra were recorded on a Perkin-Elmer Spectrum-100 FT-IR spectrometer with an ATR accessory. The samples were analyzed by placing neat samples directly on the ATR crystal. UV spectra were recorded on a Varian Cary 3 Bio UV/Vis spectrometer. Fluorescence spectra were recorded on a Varian Cary Eclipse fluorescence spectrometer using a 10 mm quartz cell. The slits were 10 nm. 0.1 mM solutions of the analytes were made in degassed toluene and kept under nitrogen atmosphere during the measurements. Mass spectrometry was carried out using a Voyager-DE PRO Maldi-TOF spectrometer in negative ion-mode. Dithranol or 9nitroanthracene was used as a matrix. Matrix solutions were prepared in toluene (dithranol) or acetone (9-nitroanthracene) by dissolving 10 mg of the matrix in 1 mL of the solvent. The analytes were then dissolved in toluene and mixed with a small amout of the corresponding matrix solution and placed on the target plate. Cyclic voltammetry was carried out using a Solartron Mobrey 1285 potentiostat. Sample solutions (5 mL) were prepared from toluene/acetonitrile (4:1) containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) (Fluka, electrochemical grade) as supporting electrolyte. The working electrode was a glassy carbon disc (3 mm) and platinum electrodes served as quasi-reference and counter electrodes. The ferrocene/ferrocenium couple was used as an internal reference in all experiments. All cyclic voltammograms shown were recorded at a scan rate of 25 mV s⁻¹. Before the measurements, oxygen was removed by bubbling nitrogen through the stirred solutions and samples were kept under nitrogen atmosphere during all measurements.

3,4-Bis(octadecyloxy)benzaldehyde

3,4-Dihydroxybenzaldehyde (1.0 g, 7.25 mmol), 1-octadecylbromide (4.84 g, 14.5 mmol) and anhydrous potassium carbonate (2.0 g, 14.5 mmol) was dispersed in acetone (60 mL) and the mixture was refluxed under nitrogen atmosphere overnight. The hot reaction mixture was filtrated and the solid material on the filter paper was collected and subjected to column chromatography (silica, dichloromethane). The first band was collected and dried *in vacuo* (purified yield: 1.9 g, 41%). Mp 85 °C. $\delta_{\rm H}$ (500 MHz, CDCl₃, 25 °C): 9.83 (1H, s), 7.41 (1H, dd, J = 8.1, 1.9 Hz), 7.39 (1H, d, J = 1.9 Hz), 6.95 (1H, d, J = 8.1 Hz), 4.08 (2H, t, J = 6.6 Hz), 4.05 (2H, t, J = 6.6 Hz), 1.85 (4H, m), 1.48 (4H, m), 1.41–1.20 (56H, m), 0.88 (6H, m) ppm. $\delta_{\rm C}$ (125 MHz, CDCl₃, 25 °C): 191.2, 154.8, 149.6, 130.0, 126.8, 111.9, 111.1, 69.29, 69.27, 32.1, 29.9, 29.8, 29.5, 29.2, 29.1, 26.15, 26.10, 22.8, 14.3 ppm.

2-(3,4-Bis(octadecyloxy)benzene)-3,4-fulleropyrrolidine (5)

C₆₀ (50 mg, 0.07 mmol), glycine (10 mg, 0.13 mmol), 3,4bis(octadecyloxy)benzaldehyde (80 mg, 0.12 mmol) was dissolved in o-dichlorobenzene (3 mL) in a 25 mL pear-shaped flask equipped with a reflux condenser and the mixture was stirred at 150 °C under nitrogen atmosphere overnight. Methanol (5 mL) was added to precipitate the crude product which was filtered off on a glass sinter funnel. The solid material was washed with methanol and was then subjected to two subsequent column chromatography purifications on silica. In the first column toluene was used to remove unreacted C₆₀, and the product was then eluted together with unreacted 3,4-bis(octadecyloxy)benzaldehyde using toluene:EtOAc (2:1). Final purification of the compound was accomplished by a subsequent column using pentane:EtOAc 10:1 to remove non-C₆₀ containing substances and then toluene: EtOAc 2:1 to elute compound 1 as a brown solid (purified yield: 37 mg, 39%). FT-IR (neat): $v_{\text{max}}/\text{cm}^{-1} = 2918$, 2850 (s, C–H stretch), 1604 (N-H bend), 1590, 1513, 1466, 1429, 1381, 1303, 1262, 1232, 1177, 1134, 1020, 942, 892, 842, 800, 764, 719, 693, 659, 623, 598, 574, 553, 525(s). $\delta_{\rm H}$ (500 MHz, CDCl₃, 25 °C): 7.36 (1H, d, J = 2.1 Hz),

7.28 (1H, dd, J = 8.3, 2.1 Hz), 6.91 (1H, d, J = 8.3 Hz), 5.72 (1H, s), 5.08 (1H, d, J = 10.3 Hz), 4.86 (1H, d, J = 10.3 Hz), 4.01 (2H, t, J = 6.8 Hz), 3.98 (2H, t, J = 6.8 Hz), 3.26 (1H, br s, NH) 1.80 (2H, m), 1.74 (2H, m), 1.43 (4H, m), 1.34–1.19 (56H, m), 0.88 (6H, m) ppm. $\delta_{\rm C}$ (125 MHz, CDCl₃, 25 °C): 156.4, 153.6, 149.5, 149.1, 147.4, 147.15, 147.35, 147.30, 147.1, 146.9, 146.7, 146.5, 146.40, 146.35, 146.30, 146.2, 146.1, 145.9, 145.63, 145.60, 145.55, 145.46, 145.44, 145.42, 145.40, 145.32, 144.8, 144.7, 144.50, 144.47, 144.3, 143.1, 142.86, 142.77, 142.72, 142.67, 142.46, 142.37, 142.31, 142.29, 142.19, 142.18, 142.07, 142.02, 141.9, 141.7, 140.32, 140.28, 140.0, 139.8, 136.4, 136.3, 136.1, 136.0, 130.1, 121.0, 114.4, 113.5, 69.7, 69.3, 32.1, 29.9, 29.6, 29.50, 29.46, 29.3, 26.2, 22.9 ppm. MS (Maldi-TOF, 9-nitroanthracene, negative mode) m/z: 1376 (M⁻).

1,1'-Ferrocenedicarboxylic acid¹²

Ferrocene (3.0 g, 16.1 mmol) was added to a flame-dried threenecked flask equipped with a septum. The flask was evacuated and flushed with nitrogen. Dry pentane (45 mL) and TMEDA (6 mL) was added to the flask via syringe. The resulting mixture was cooled to 0 °C and allowed to stir for 15 min. Butyl lithium (2.5 M in hexanes, 17 mL) was slowly added to the cooled solution using a syringe. The solution was then allowed to stir under nitrogen atmosphere overnight after which a precipitate had formed in the reaction flask. Dry THF (100 mL) was added to the flask, resulting in a red solution. CO_2 (g) was then bubbled though the solution during a 1.5 h period resulting in the formation of a yellow precipitate. Water (150 mL) was added to the reaction mixture and the organic solvents were then evaporated. The aqueous phase was washed with diethyl ether $(3 \times 100 \text{ mL})$ and the aqueous phase was then acidified using HCl (1 M) resulting in an orange/yellow precipitate. The precipitate was filtered off using a glass sinter funnel and the solid was then dried in vacuo (purified yield: 1.81 g, 41%). $\delta_{\rm H}$ (500 MHz, DMSO-d₆, 25 °C): 4.69 (4H, t, *J* = 1.8 Hz), 4.45 (4H, t, J = 1.8 Hz) ppm.

1,1'-*N*,*N*'-(2-(3,4-Bis(octadecyloxy)benzene)-3,4fulleropyrrolidinyl)ferrocenedicarboxamide (1)

1,1'-Ferrocenedicarboxylic acid (10.0 mg, 0.0365 mmol) was added to a flame-dried flask equipped with a septum. Dry dichloromethane (1.5 mL), DMF (100 µL) and oxalyl chloride (0.1 mL) was added via syringe and the mixture was allowed to stir under nitrogen atmosphere for 1.5 h. The solvents were evaporated and the residue was redissolved in dry dichloromethane (4 mL). The resulting solution of 1,1'-ferrocenedicarboxylic acid chloride was added to a solution containing compound 1 (100 mg, 0.073 mmol) in dry dichloromethane (10 mL) and dry pyridine (0.9 mL). The mixture was stirred under nitrogen atmosphere at room temperature overnight. The solvent was evaporated and the crude product was redissolved in toluene. Ethanol was then added and the resulting precipitate was filtered off. The solid material was washed with pentane and ethanol and was then subjected to column chromatography (pentane:EtOAc 10:1-toluene/EtOAc 5:1) to afford compound 2 as a brown solid. (Purified yield: 75 mg, 69%) C₂₂₀H₁₆₈FeN₂O₆ (2989.23): calcd. C 88.33 H 5.66 N 0.94; found C 88.34 H 5.72 N 1.25. FT-IR (neat): $v_{\text{max}}/\text{cm}^{-1}$ = 2920, 2850 (C-H), 1635, 1589, 1513, 1462, 1456, 1429, 1392, 1258, 1238, 1189, 1137, 1090, 1023, 854, 802, 770, 759, 743, 720, 699,

576, 563, 552, 525. $\delta_{\rm H}$ (500 MHz, C₆D₆, 70 °C): 7.80 (1H, d, J = 2.2 Hz), 7.78 (1H, d, J = 2.2 Hz), 7.68 (2H, m), 7.07 (1H, d, J = 8.2 Hz), 7.05 (1H, d, J = 8.2 Hz), 6.64 (1H, d, J = 12 Hz), 6.37 (1H, d, J = 12 Hz), 5.80 (1H, d, J = 12 Hz), 5.78 (1H, d, J = 12 Hz), 5.47 (2H, m), 5.39 (1H, m), 5.31 (1H, m), 5.18 (1H, m), 5.12 (1H, m), 4.41 (2H, m), 4.38 (1H, m), 4.29 (1H, m), 4.17 (4H, m), 3.89 (2H, t, J = 6.5 Hz), 3.87 (2H, t, J = 6.5 Hz), 1.81 (4H, m), 1.75 (4H, m), 1.34 (120H, m), 0.92 (12H, m) ppm. MS (MALDI-TOF, dithranol, negative mode) m/z: 2989 (M⁻).

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