

Metallo-Supramolecular Fullerene Architectures: Synthesis and Characterization of Bucky Ligands and a Non-Covalent Dimer

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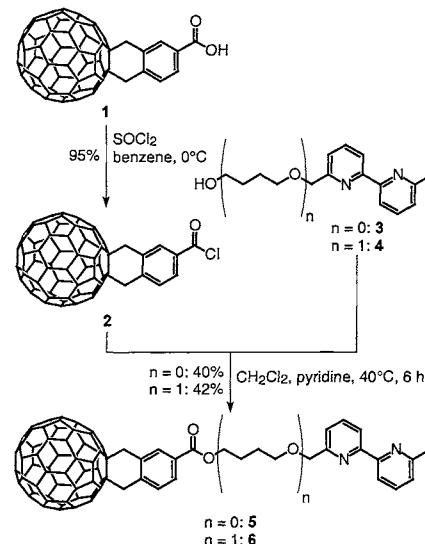
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Two novel bidentate 6,6'-disubstituted 2,2'-bipyridine ligands in which the heterocyclic system is attached to *o*-quinodimethane functionalized [60]fullerene units with variable spacers were obtained. A first supramolecular non-covalent dimer was prepared using copper(I) ions and characterized by FD mass spectrometry, cyclovoltammetry and ESR.

Due to the remarkable photo-¹ and electrochemical² properties, buckminsterfullerene (C_{60}) has attracted a large number of scientists since its discovery in 1985. Therefore, fullerene represents an interesting functional unit for applications such as molecular,³ optoelectronic⁴ or light-harvesting devices.⁵ Recent developments in the functionalization of fullerenes⁶ have opened the way for the combination of other electro- or photoactive units with fullerenes.⁷ Especially the use of metallo-supramolecular building blocks has found increasing interest in the last years.⁸ However, the potential of these supramolecular units to undergo self-organization processes in the presence of certain metal ions to non-covalently link different fullerenes has only been utilized in very recent examples.⁹ Furthermore, the described synthetic procedures cannot easily be transferred to other supramolecular units. Here, we describe a new variable synthetic procedure for fullerene derivatives connected to bipyridines (6-position) with special metal binding abilities as well as the reversible self-organization of one ligand to a non-covalently assembled fullerene dimer.

The combination of fullerene chemistry with self-assembling heterocyclic metallo-supramolecular systems requires an easy and flexible way of connecting the units with different spacers to modulate both the electro- and photochemical properties as well as the solubility behavior. Among the suitable ways of chemically modifying the electron deficient [60]fullerene, Diels-Alder cycloaddition reactions play an important role.¹⁰ We used the fullerene carboxylic acid chloride **2** as functionalized fullerene unit, which can be prepared from the corresponding acid **1** using thionyl chloride (Scheme 1).¹¹ The acid **1** ($C_{69}H_8O_2$) was synthesized by addition of an *ortho*-quinodimethane intermediate to C_{60} .¹² On the other hand, we chose mono-functionalized 6,6'-disubstituted 2,2'-bipyridines as heterocyclic building blocks due to their easy preparation as well as their model function for the use of other functionalized *oligo*(bipyridines).¹³

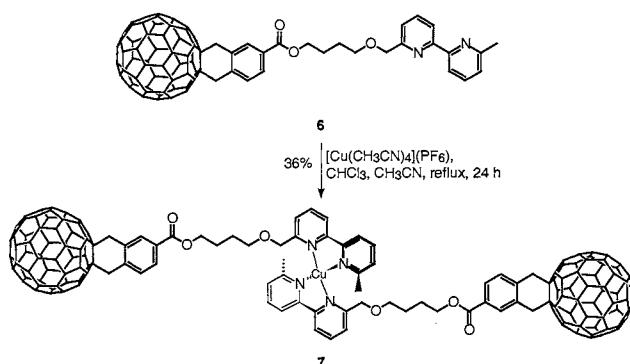
The 6-(hydroxymethyl)-6'-methyl-2,2'-bipyridine (**3**) was reacted in an ester condensation with **2** in $CHCl_3$ with pyridine as catalyst to obtain the fullerene-bipyridine unit **5** in 40% yield (Scheme 1).¹⁴ Compound **5** was isolated using size exclusion chromatography (preparative GPC). To increase the distance between the functional units and to improve the solubility, we also introduced a spacer unit. 6-(Hydroxytetramethyleneoxy-



Scheme 1. Synthesis of the bucky ligands **5** and **6**.

methyl)-6'-methyl-2,2'-bipyridine (**4**) (obtained from 6-bromomethyl-6'-methyl-2,2'-bipyridine after reaction with 4-*tert*-butyloxybutanol/NaH and removal of the *tert*butyl group¹³) was reacted with **2** using the above described condensation to yield 42% of the fullerene-bipyridine compound **6** with a C_4 -spacer.¹⁵ This method can easily be expanded to other spacer lengths as well as other functionalized bipyridine or *oligo*(bipyridine) moieties (see e.g.¹⁶).

The fullerene-bipyridine system **6** was used to synthesize a first non-covalent supramolecular dimer. Compound **6** was reacted with $[\text{Cu}(\text{CH}_3\text{CN})_4(\text{PF}_6)]$ in a $\text{CHCl}_3/\text{CH}_3\text{CN}$ mixture



Scheme 2. Self-assembly of dimer **7**.

(Scheme 2). After evaporation of the solvent and purification in CHCl_3 /diethylether mixtures, the bis(fullerene-bipyridine) copper(I) complex **7** with a molar mass of 2452 g/mol was isolated in 36% yield as a brown solid.¹⁷

The successful complex formation was clearly demonstrated by FD mass spectrometry (Figure 1). Together with the molar mass peak of the complete dimer with an intensity of 4% (M^+ , 2452.7 g/mol, calc. 2452.28), the mass peak of the complex after loss of the counter ion was detected with 100% intensity ($\text{M}^+ - \text{PF}_6 + \text{H}$, 2308.8 g/mol, calc. 2308.32). Further signals of the fragmented C_{60} -bipyridine/Cu(I) complex with 7% intensity (1184.9 g/mol, calc. 1185.12) and C_{60} -bipyridine (44%, 1122.5 g/mol, calc. 1122.19) were obtained.

First results of the electrochemical properties of **7** were obtained combining cyclovoltammetry and ESR (Figure 2).

In the reduction of **7** there are three nearly reversible reduction processes. Two are at about -0.6 and -0.7 V respectively. In this

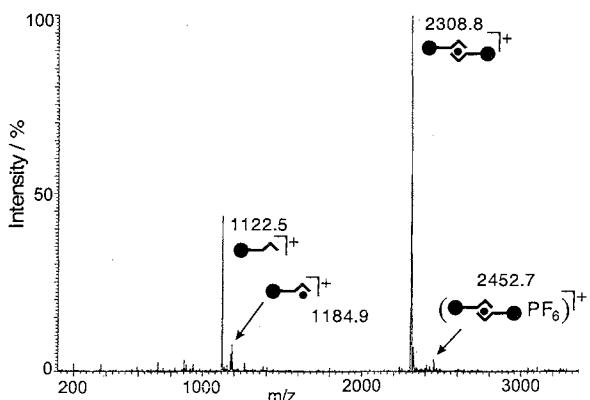


Figure 1. FD mass spectra of **7** with the calculated fragments.

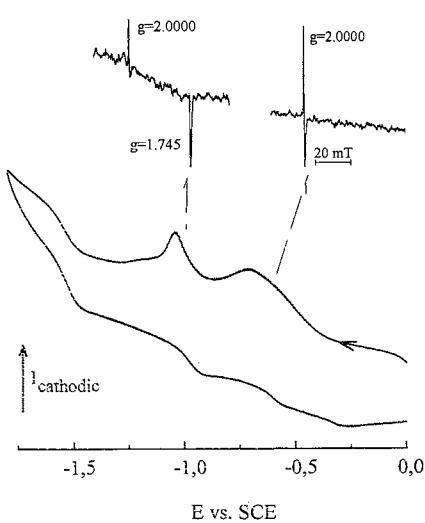


Figure 2. Cyclic voltammogram and ESR spectra.¹⁸ The insets represent the corresponding ESR spectra observed in the marked potential regions.

potential region the *in-situ* ESR-voltammetric experiment gave a typical ESR line of fullerene anion radicals (inset of Figure 2, right). At a more negative potential (-1.1 V) a wave was found combined with a new ESR line with $g = 1.745$ what points to a redox processes at the metal center.

Efforts in the direction of the construction of higher ordered architectures using more complex organic ligands and dendritic structures are under investigation as well as studies using *in-situ* UV/Vis and ESR-technique are currently in progress.

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- 14 Isolation using size exclusion chromatography (GPC, PSS, 100 Å, 10 µm, CHCl_3). $^1\text{H-NMR}$ (500 MHz, $\text{CS}_2/\text{THF}(\text{d}_8)$): δ 2.71 (s, 3 H, H_7), 4.49 (s, b, 2 H, H_{benzyl}), 4.82 (s, b, 2 H, H_{benzyl}), 5.65 (m, 2 H, H_7), 7.38 (d, $J = 7.5$, 2 H, H_5 , H_6), 7.68 (t, $J = 7.5$, 1 H, H_4), 7.78 (m, 1 H, H_4), 7.95 (m, 3 H, H_3 , 2 H_{arom}), 8.32 (m, 1 H, H_3), 8.4 (m, 1 H_{arom}); MS (FD) m/z (%): 1050.5 (100, M^+ , calc. 1050.14).
- 15 $^1\text{H-NMR}$ (500 MHz, $\text{CS}_2/\text{THF}(\text{d}_8)$): δ 1.73 (m, 4 H, $\text{H}_{2,3}$), 2.56 (s, 3 H, H_7), 3.60 (m, 4 H, $\text{H}_{1,4}$), 4.42 (s, b, 2 H, H_{benz}), 4.59 (s, b, 2 H, H_{benz}), 4.67 (s, 2 H, H_7), 7.13 (d, $J = 7.5$, 1 H, H_5), 7.45 (d, $J = 7.5$, 1 H, H_5), 7.65 (t, $J = 7.5$, 1 H, H_4), 7.78 (m, 1 H, H_{arom}), 7.83 (m, 1 H, H_4), 8.20 (m, 1 H, H_3), 8.22 (m, 1 H, H_{arom}), 8.34 (m, 1 H, H_3), 8.36 (m, 1 H, H_{arom}); MS (FD) m/z (%): 1122.1 (100, M^+ , calc. 1122.19); UV-VIS (λ_{max} /nm (ϵ), CHCl_3): 276 (45600), 329 (50700), 432 (2900).
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- 17 MS (FD) m/z (%): 2452.7 (4, M^+), 2308.8 (100, $\text{M}^+ - \text{PF}_6 + \text{H}$), 1184.9 (7, $\text{M}^+ - \text{C}_{60}\text{Bpy-PF}_6$), 1122.5 (44, $\text{M}^+ - \text{Cu-C}_{60}\text{Bpy-PF}_6$); UV-VIS (λ_{max} /nm (ϵ), CHCl_3): 274 (90600), 310 (36700), 432 (2900).
- 18 Cyclic voltammogram obtained in a saturated solution of **7**, 0.1 M TBAPF_6 in CH_3CN /toluene (1:1) solution.