



Metal-chelating capacities attached to fullerenes

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Dedicated to Professor Dr Dick Stufkens on the occasion of his retirement and in admiration of his nice physico-chemical studies of metal-diimine compounds, and to our long friendship.

Contents

Abstract	141
1. Introduction	142
2. Fullerene–porphyrin dyads	142
2.1 First examples	142
2.2 Linker effects in C ₆₀ -porphyrin dyads	143
2.3 Changing the fullerene moiety	145
2.4 Ionophoric linkers	146
2.5 C ₆₀ -Phytochlorin dyads	147
2.6 Parachute C ₆₀ -porphyrin dyads	148
2.7 Axial bound dyads	148
2.8 Other C ₆₀ -porphyrin dyads	149
3. Fullerene–porphyrin triad structures	150
4. Multi-C ₆₀ porphyrins	151
5. Self assembled monolayers of C ₆₀ -porphyrins	153
6. Ruthenium, copper and platinum complexes	153
6.1 Ruthenium complexes	153
6.2 Copper and platinum complexes	155
7. Fullerenes with ionophoric groups	156
7.1 Fullerene crown ethers	157
7.2 Parachute-type fullerene crown ethers	158
7.3 Other fullerene ionophores	159
8. C ₆₀ -Ferrocenyl complexes	160
9. Organometallic C ₆₀ -based catalysts	160
10. Concluding remarks	161
References	161

Abstract

This review describes the synthesis, properties and application of fullerenes covalently attached to metal-chelating groups. The application of these structures in artificial photosynthetic systems and their reaction on external stimuli, such as light or electrons is described. Furthermore, the use of fullerene organometallic building blocks in macromolecular synthesis and catalysis has been highlighted. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the last decade, numerous new compounds comprising C_{60} and (organo)metallic entities have been prepared and studied. An arbitrary classification based on the interaction between the fullerene unit and the (organo)metallic moiety can be made, namely (i) endohedral fullerenes, (ii) charge-transfer compounds and cocrystallites, (iii) (transition) metal coordination complexes, and (iv) metalated bucky-ligands. Endohedral fullerenes, or fullerenes with a metal inside, were simultaneously discovered with the fullerenes themselves [1]. In most cases, lanthanide metal ions have been caged during the arc plasm synthesis of fullerenes [2]. Inclosure of metal atoms or other guests inside the C_{60} molecule via organic synthesis is still a great challenge to chemists [3]. In charge-transfer compounds, the fullerene moiety can act as a electron acceptor, and a large variety of organic and (organo)metallic molecules as donor [4,5]. Best known in this class are the alkali-metal fullerides which are already superconducting at relatively high temperatures [6]. In metal-complex fullerene cocrystallites, the interaction between the fullerene and the metal complexes is fundamentally van der Waals, such as observed in $C_{60}(\text{ferrocene})_2$ [7] and cocrystallates of tetraarylporphyrins with C_{60} [8]. Furthermore, C_{60} is often described as an electron deficient polyolefin, capable of forming coordination bonds to transition metals. Various of these metal- C_{60} complexes have been synthesized and structurally characterized. An excellent review concerning this subject was recently published by Balch and Olmstead [9]. The last class comprising C_{60} and (organo)metallic entities are the so-called metalated bucky-ligands, comprising a (metalated) ligand covalently attached to C_{60} , and it is this class that is the subject of this review.

A large variety of ligands with different binding modes have been attached to C_{60} , as schematically depicted in Fig. 1. The most commonly reported compounds in this field are the porphyrin- C_{60} dyads, which have been synthesized for application in artificial photosynthesis [10]. Moreover, nitrogen containing donor ligands, such as pyridine, bipyridine (bpy), terpyridine (terpy) and *ortho*-phenanthroline (phen), and anionic arene ligands, such as the terdentate coordinating

bisaminoaryl (pincer) ligand $[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6]^-$ (NCN), and its bidentate analog $[\text{C}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2]^-$ (C,N), have been attached to C_{60} and subsequently applied in ruthenium, copper and platinum chemistry. Furthermore, cation-complexating fragments (for example, crown ether groups) have been attached to C_{60} and studied for their properties, such as the formation of Langmuir monolayers. Finally, a number of studies have been reported considering the synthesis of ferrocenyl containing fullerene complexes as donor-acceptor dyads and triads and the application of metalated bucky-ligands in catalysis. This review gives a short survey on the reported metallated bucky-ligands from the past decade. The aim will be on the synthesis and characterization of these systems, however, properties and specific physical measurements will be briefly mentioned.

2. Fullerene-porphyrin dyads

In 1994, the first example of [60]fullerene anchored to zinc porphyrin was presented by Gust and coworkers [11]. Nowadays, it is established that the combination of a porphyrin unit and C_{60} leads to a photoactive compound, capable of electron or energy transfer upon photoexcitation. In particular, the structure and chemical properties of the linker between these dyads has a large influence on the excited state processes. Therefore, the structural aspects in these systems were studied in the last years, leading to a large variety of C_{60} -porphyrin dyads. Moreover, the addition of more chromophores, leading to triads and multi-chromophoric compounds, and the application of these systems in solar cells have been points of interest.

2.1. First examples

C_{60} -porphyrin **1** was prepared by a Diels-Alder reaction of diene-substituted porphyrin to C_{60} (Fig. 2) [11]. The influence of the C_{60} moiety upon the photophysical behavior of the porphyrin unit was studied in more detail. Steady-state luminescence spectroscopy revealed that the porphyrin excited state was significantly quenched as compared with parent zinc porphyrin.

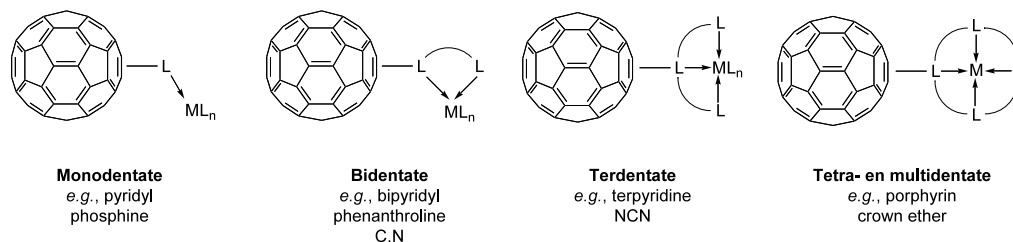
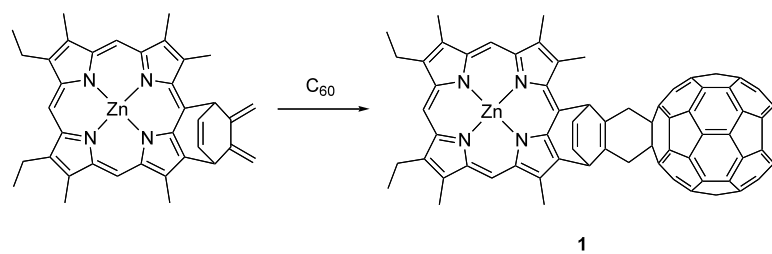
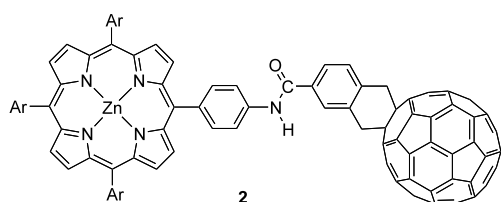


Fig. 1. Binding modes of metalated bucky-ligands.

Fig. 2. The first reported C_{60} -porphyrin by Gust [11].

Time-resolved fluorescence measurements showed that the charge-separated state $C_{60}^{\bullet-}-ZnP^{*+}$ was produced by electron transfer from the porphyrin photoexcited state to the fullerene moiety in toluene or benzonitrile. For the free base of **1**, this was only observed in benzonitrile. In toluene, however, intersystem crossing occurred producing the fullerene singlet excited state.

Soon hereafter, Sakata et al. reported the synthesis of dyad **2** [12]. Similarly to **1**, quenching of the excited porphyrin singlet state was observed, due to electron transfer from the excited porphyrin singlet state to the fullerene singlet state. The accepting properties of C_{60} were compared with benzoquinone [13]. Accelerated charge separation and decelerated charge recombination were observed in **2** compared with the analogous C_{60} -benzoquinone compound. This was explained by a smaller reorganization energy for the C_{60} molecule with respect to the benzoquinone acceptor (Eq. (1)).



(1)

2.2. Linker effects in C_{60} -porphyrin dyads

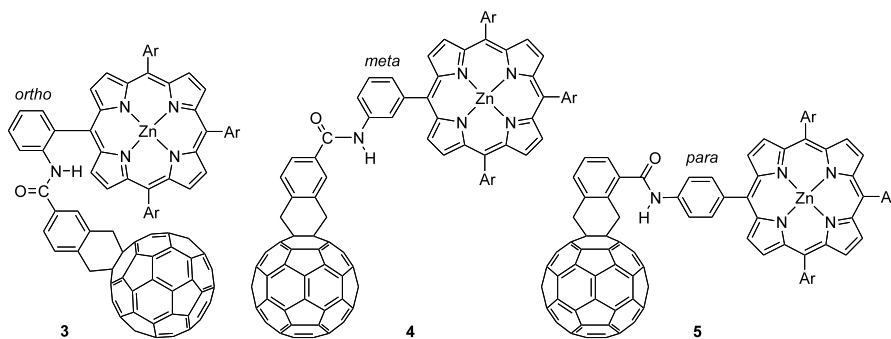
The effects on charge separation and -recombination

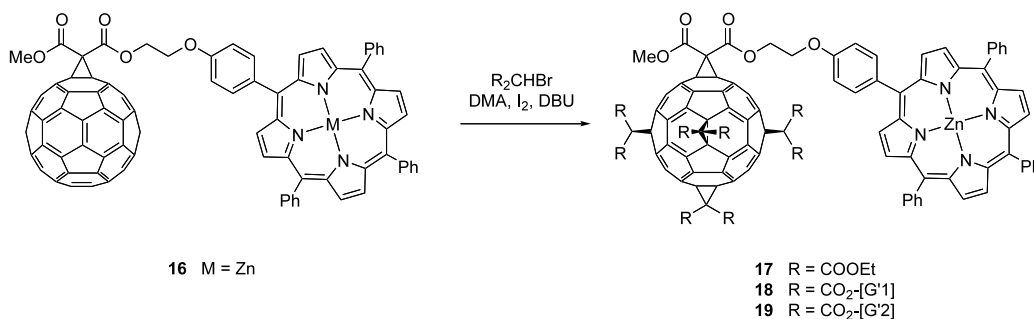
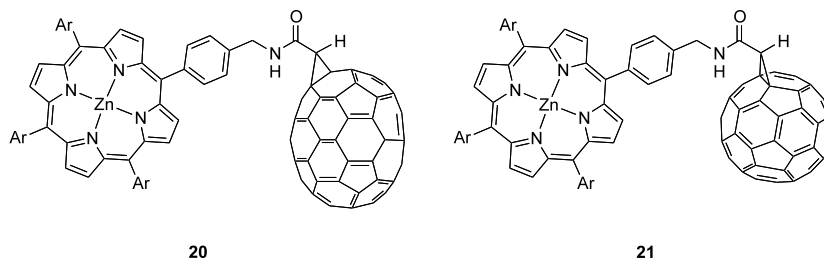
processes in fullerene–porphyrin dyads upon changing the linker between the two chromophores were intensively studied. The structure of the linker in **2** was varied systematically (Fig. 3). The covalent bond between the porphyrin phenyl group and the linker was varied from *ortho* (**3**), *meta* (**4**) to *para* (**2** and **5**) [14]. In addition, the cyclohexene ring fused to C_{60} was also attached to the 2,3-position (**5**) on the aromatic spacer (3,4-position for **3** and **4**).

Analogous to **2**, the charge-separated state was formed for **3–5** upon photoexcitation of the porphyrin entity. Dyad **4** showed the slowest rates of charge separation and charge recombination. This was attributed to the stronger electronic interaction between the donor and acceptor moieties in case of *ortho* and *para* (**3** and **5**, respectively) linkage as compared with the *meta* structure in **4**.

Upon changing the linker between C_{60} and porphyrin from amide to acetylene (Figs. 4, 6 and 7), an acceleration of the formation of the $C_{60}^{\bullet-}-P^{*+}$ state by a factor 3 was found [15,16]. Furthermore, upon removing the carbon=carbon double bonds in the steroid linker in **8**, quenching of the porphyrin excited states decreased significantly [17].

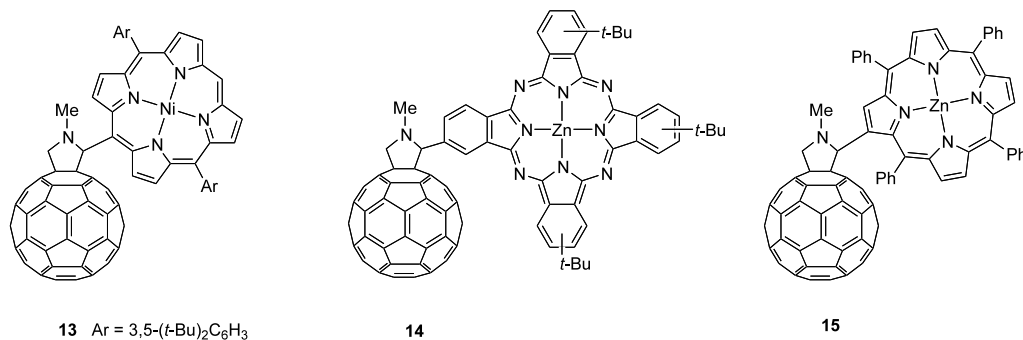
In the ‘ball and chain’ dyad **9**, the two chromophores are in relative fixed position with a distance of 9 and 13 Å for the folded and the stretched conformation, respectively [18,19]. A relative long-lived charge separated state ($C_{60}^{\bullet-}-ZnP^{*+}$, lifetime of 420 ns) was formed upon photoexcitation of **9** (Eq. (2)).

Fig. 3. Geometric isomers of dyad **2** (Ar = 3,5-(*t*-Bu) $_2$ C $_6$ H $_3$).

Fig. 6. Fullerene-porphyrin dyad **16** and selective penta-substituted isomers (**17–19**).Fig. 7. C₇₀-porphyrin **20** and C₆₀ analog **21** (Ar = 3,5-(*t*-Bu)₂C₆H₃).

two porphyrin β-protons were observed, attributed to the deshielding effect of the C₆₀ moiety (Eq. (3)).

tween the chromophores, and the rigidity of the linker all play an important role in this respect.



(3)

The Soret- and the Q-band in the electronic absorption spectra were red shifted by 16–17, 2–4, and 6–7 nm for **13**, **14**, and **15**, respectively. Furthermore, changes in the oxidation/reduction behavior were observed for **13** and **14**. Photoexcited state measurements were performed for **15** only. The porphyrin photoexcited state was quenched by energy transfer to the singlet state of the fullerene entity [26]. In more polar solvents such as benzonitrile, photoinduced electron transfer occurred instead, yielding the charge-separated states with lifetimes of 50 and 290 ps for **15** and its free base, respectively.

The results reported for **2–15** and various other dyads (see below) demonstrate that the dialog between C₆₀ and porphyrin in both the ground and excited state is influenced by the connector between the two chromophores. Through-bond interactions, the distance be-

2.3. Changing the fullerene moiety

The effect of extra substitution of the fullerene core in fullerene–porphyrin dyads was studied using dyad **16** [28]. Modified Fréchet type dendrimers were introduced by a selective five-fold Bingel reaction giving the octahedral-substituted fullerodendrimer compounds **17–19** (Fig. 6) [29].

Bathochromic shifts for the porphyrin Soret and Q-bands (UV–vis spectroscopy) and shifts to more negative reduction potentials (cyclovoltammetry) were observed going to higher generation dendrimer substituents. For **16**, quenching of the porphyrin excited state was observed due to electron transfer to the fullerene entity. However, this process was absent for the hexa-adducts **17–19**; the photoinduced porphyrin

excited state decayed similarly to parent porphyrin compounds. This indicated that the fullerene unit had become inactive as chromophore after the attachment of extra groups to its surface.

Not only C_{60} was incorporated in dyad compounds. For C_{70} derivative **20**, the photoinduced charge separated state was formed twice as fast in comparison with the corresponding C_{60} derivative **21** (Fig. 7) [30]. This demonstrated that higher fullerenes may also be suitable molecules for incorporation in dyad systems.

2.4. Ionophoric linkers

The extent of the electronic interaction between two chromophores in dyad structures depends in large amount on the spacial arrangement of the chromophores with respect to each other. A small variety of fullerene–porphyrin dyads has been constructed in which the conformation of the two chromophores can be altered upon addition of metal ions, forcing the linker in a certain conformation upon coordination (Fig. 8).

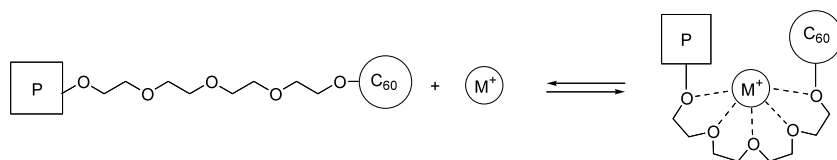


Fig. 8. Changes in the linker structure, induced by cation complexation.

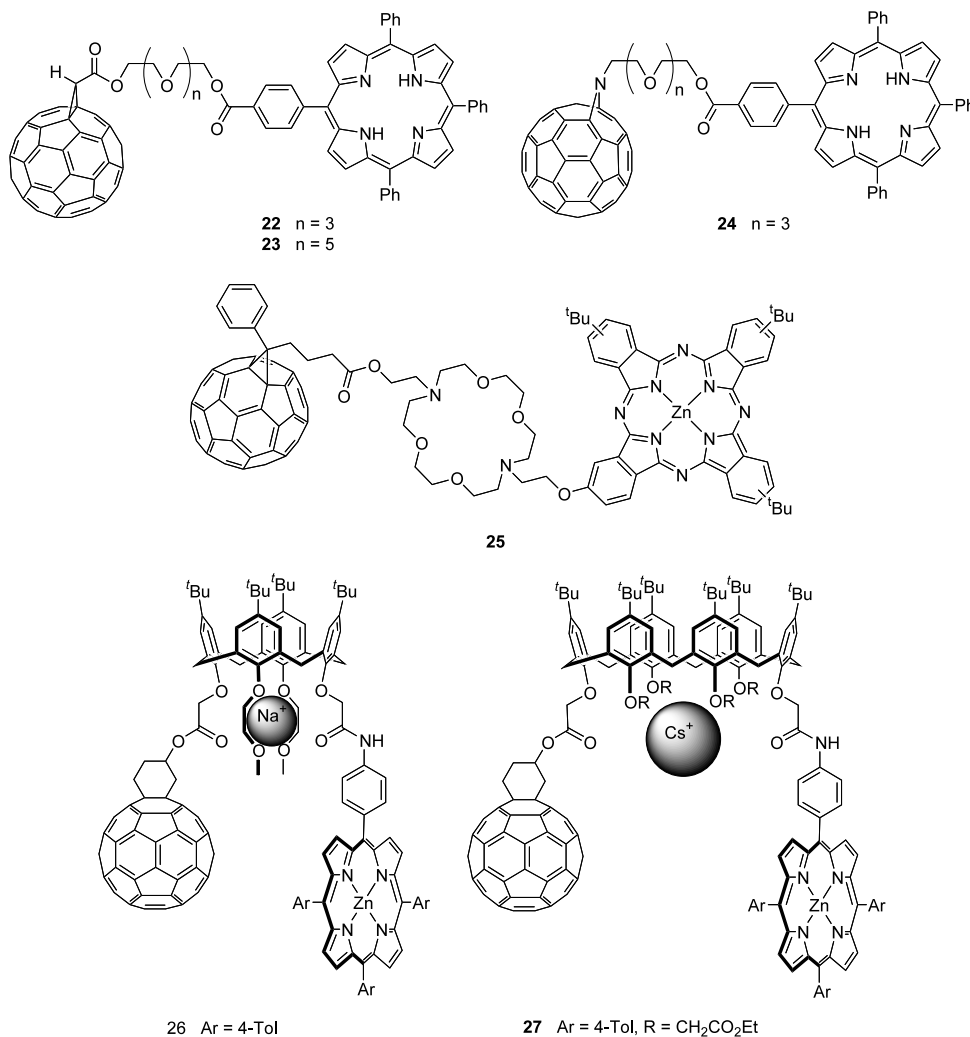
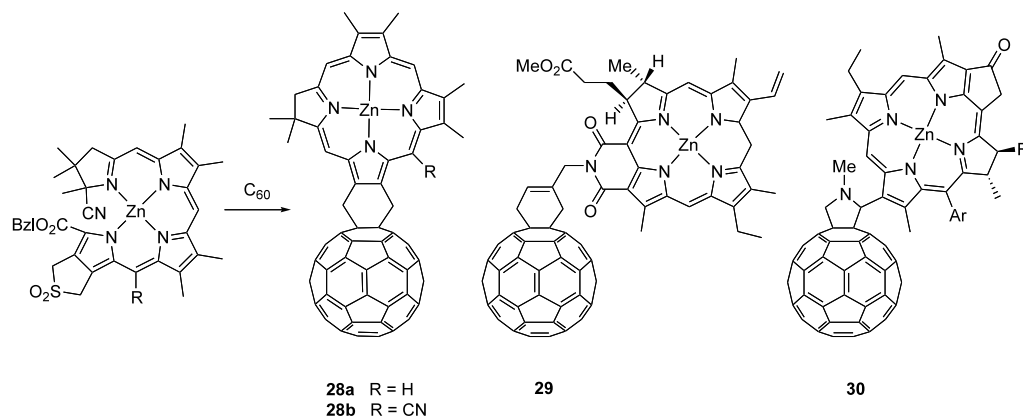
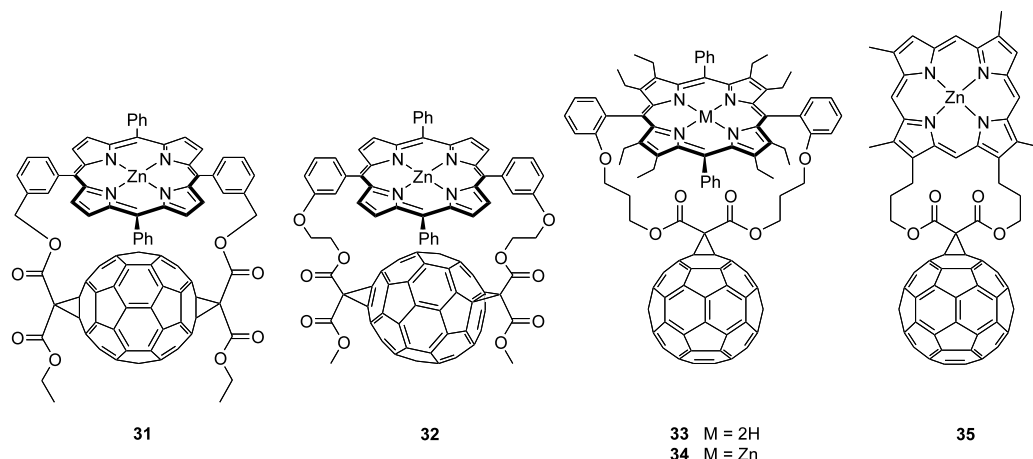


Fig. 9. C_{60} -porphyrin dyads, attached together using ionophoric linkers.

Fig. 10. C_{60} -Phytochlorin dyads **28–30**.Fig. 11. Parachute type C_{60} -porphyrin dyads.

Suitable linkers, capable of binding metal ions, were introduced in C_{60} -porphyrin dyads, such as polyether chains (**22–24**) [31,32], azacrown ether groups (**25**) [33], or a calix[*n*]arene moiety (**26** and **27**, Fig. 9) [34]. Upon addition of metal ions to **22** and **24**, the porphyrin UV–vis absorptions became red shifted. Furthermore, the porphyrin excited state luminescence in **22** decreased with increasing amount of potassium ions in solution. This was explained by a potassium induced conformational change of the polyether chain leading to a closer proximity of the two chromophores (Fig. 8), which led to more effective quenching of the porphyrin excited state by the C_{60} group.

Although the photoinduced porphyrin excited state in dyad **25** was already quenched analogous to other C_{60} -porphyrin dyads, no additional effects were observed upon addition of metal ions [33]. The addition of metal ions to calix[*n*]arene **26** did not lead to changes in the absorption and fluorescence properties either. For **27**, however, the addition of KBPh_4 or CsBPh_4 led to a decrease in the fluorescence intensity of the porphyrin excited singlet state, due to a conformational change in the calixarene linker upon metal coordination, resulting

in a closer distance between the porphyrin and C_{60} moieties.

2.5. C_{60} -Phytochlorin dyads

A small number of complexes based on C_{60} and phytochlorin have been reported. Chlorin- C_{60} dyads **28a** and **28b** were prepared by a cascade of steps in an unusual one-pot synthesis (Fig. 10) [35,36]. This reaction gave **28b** as minor side-product, but **28a** and **28b** could be separated with chromatography. No physical properties have been reported for these compounds. For dyads **29** and **30**, synthesized by Diels Alder and

Table 1
Lifetimes (ns) of charge separated states for **33–36**.

Compound	Toluene	THF	Benzonitrile
31	0.730	^a	^a
32	0.619	0.385	0.038
33	3.5	0.314	0.155
34	1.015	0.099	0.099

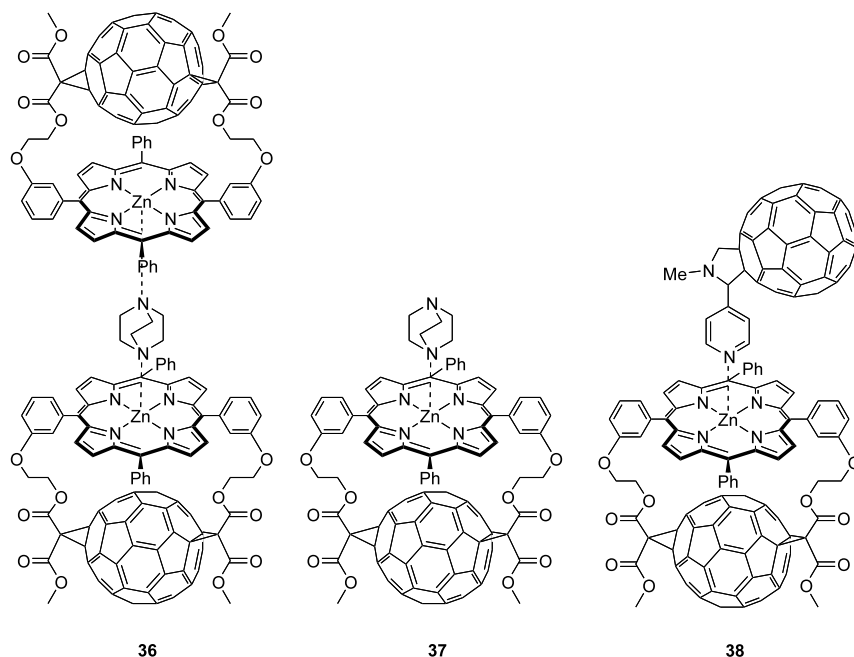
^a Not reported.

Prato reaction, quenching of the photoinduced chlorine excited states was observed [37,38].

Time-resolved fluorescence and absorption spectroscopy revealed that an intramolecular exciplex was formed upon photoexcitation of the chlorine moiety of **30** [39]. Such an exciplex was not detected for analogous C₆₀-porphyrin dyads. This exciplex relaxed in toluene directly to the ground state, while in benzonitrile, the charge-separated state C₆₀^{•-}-Chl^{•+} was formed.

2.6. Parachute C₆₀-porphyrin dyads

Parachute-shaped porphyrin-C₆₀ dyads with a close face-to-face arrangement of the two chromophores were prepared via double Bingel cyclopropanation affording the *trans*-1 (**31**) [40,41] or *trans*-2 (**32**) [42] bisadducts, or using single Bingel addition, yielding **33–35** (Fig. 11) [43,44]. As commonly observed for porphyrin-C₆₀ dyads, the luminescence of the porphyrin photoinduced excited state was almost completely quenched in **31–35** due to energy or electron transfer from the porphyrin singlet excited state to the fullerene.



(4)

Detailed photophysical measurements of **31–34** showed that these parachute-type dyads exhibit comparable photophysical properties [45,46]. In both polar and non-polar solvents, the charge-separated state C₆₀^{•-}-ZnP^{•+} was formed upon photoexcitation of the porphyrin moiety, in contrast to other (non-parachute) porphyrin-C₆₀ dyads, which only showed charge separation in polar solvents. The lifetimes of the charge-separated state decreased considerably in more polar solvents (Table 1).

The effect of the addition of a third photoactive component on the photophysical properties of **32** was studied in more detail [47]. Upon addition of 0.5 equivalents of DABCO (diazabicyclooctane) to **32**, complex **36** was formed initially. When more DABCO was added, **36** was converted to the triad **37**. The photophysical properties of **36** resembled that of dyad **32** itself (see above). For **37**, however, the charge-separated state C₆₀^{•-}-ZnP-DABCO^{•+} with a lifetime of 1980 ps was formed upon photoexcitation of the porphyrin moiety.

Addition of a pyridine substituted fullerene as electron accepting moiety to **32** afforded **38**. Excitation of the porphyrin unit in **38** did not lead to changes in the luminescence spectra with respect to **32**, since charge transfer to the covalently bound fullerene unit was found to be significantly faster than to the coordinately bound fullerene unit. Upon excitation of the fullerene units in **38**, a new mechanism was observed for the formation of the charge separated state, which was explained by interference of the solvent (benzonitrile) with the coordination of the pyridine fullerene to the zinc porphyrin moiety (Eq. (4)).

2.7. Axial bound dyads

Fullerene-porphyrin dyads have commonly been constructed using covalent linkers, but a number of noncovalently bound dyads have also been reported. Fullerene substituted pyridines, were coordinated in an axial way to metalated porphyrins and porphycenes, giving **38** (vide supra) and **39–43** (Figs. 12 and 13) [48–52].

In these systems, electron transfer upon photoexcita-

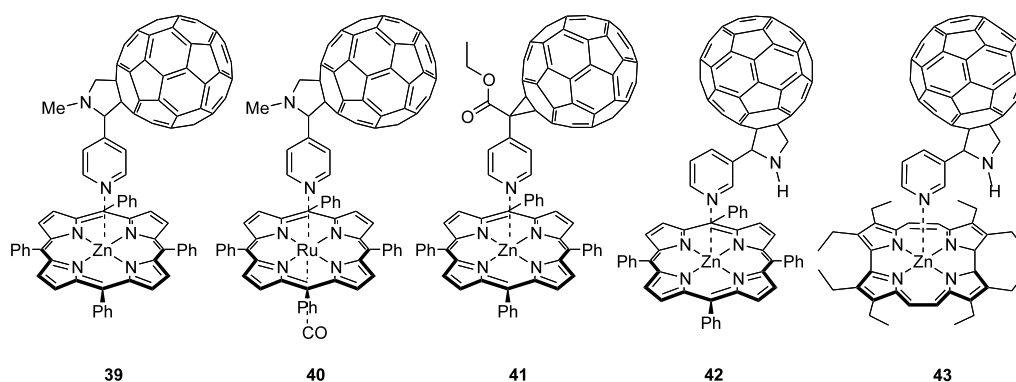
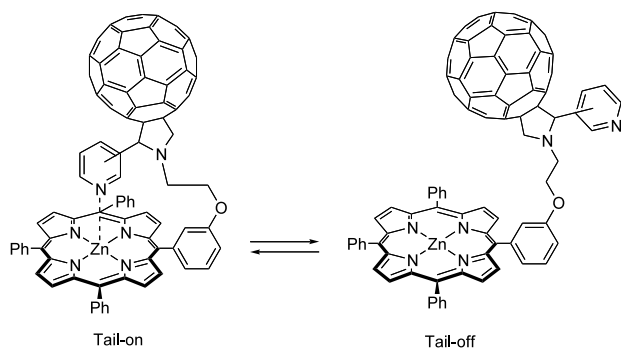


Fig. 12. Axial bound fullerene porphyrin dyads.

Fig. 13. ‘Tail-on’ and ‘tail-off’ coordination modes of dyad **44**.

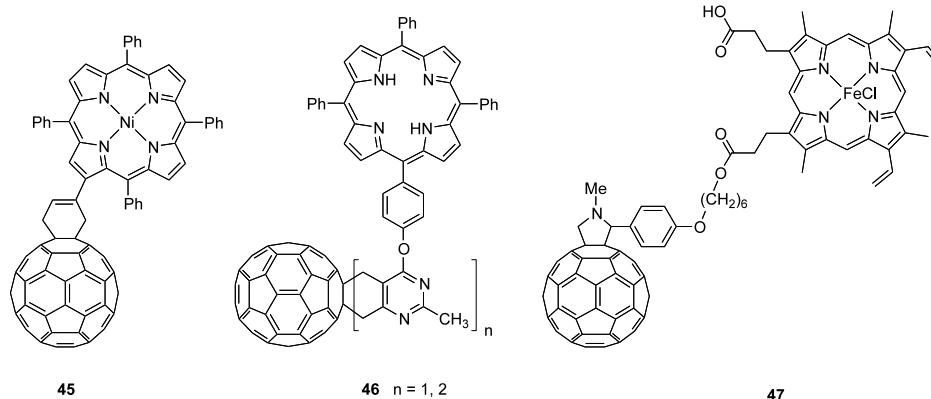
tion should be followed by splitting of the radical pair, mimicking a key step in natural photosynthesis. The formation of 1:1 complexes **39**–**43**, after mixing C_{60} bearing a pyridyl group with metal porphyrin/porphycene complexes, was confirmed by NMR and UV–vis spectroscopy, and by a single crystal structure determination for **39** [50]. For all complexes, the fluorescence of the porphyrin/porphycene moiety was quenched by electron transfer from the porphyrin to the axial coordinated fullerene. For **40**, radical-ion pairs were generated by both inter- and intramolecular electron transfer. These charge-separated state had a

lifetime of 10 μ s in THF, and several hundred of microseconds in benzonitrile.

Detailed studies on the proximity of the coordinated fullerene unit in axial bound fullerene porphyrin dyads were performed with **44** [53]. The ‘tail-on’ and ‘tail-off’ binding mode of the pyridyl-fulleropyrroldine to the zinc porphyrin unit was found to be temperature- and chemical-controlled. However, the photoinduced charge-separated state was formed independently of the coordination of the fullerene. Long-lived ion pairs with a lifetime of about 1000 ns were observed in this system.

2.8. Other C_{60} -porphyrin dyads

By Diels–Alder reaction of buta-1,3-dien-2-yl- and pyrimidine-substituted porphyrin moieties with C_{60} , **45** [54] and **46** [55] were prepared, respectively, but not further studied. The effect of C_{60} in a protein environment was studied with **47**, which was introduced in a myoglobin protein via exchange with the heme unit. In the modified protein, the autoxidation rate upon C_{60} -incorporation was found to be six times faster than for untreated myoglobin (Eq. (5)).



(5)

3. Fullerene–porphyrin triad structures

In triad systems, not only charge separation/recombination processes play an important role, but also charge shifts between photoactive centers. A small range of triads were prepared, comprising C_{60} ,

porphyrin and a third chromophore, such as pyromellitimide (**48**) [56,57], ferrocene (**49**) [57,58], a second porphyrin unit (**50**) [59,60], and a carotene tail (**51–54**) [61–65], which are depicted in Figs. 14 and 15. After photoexcitation of the porphyrin moiety in **48–50**, charge separation and charge shift processes were ob-

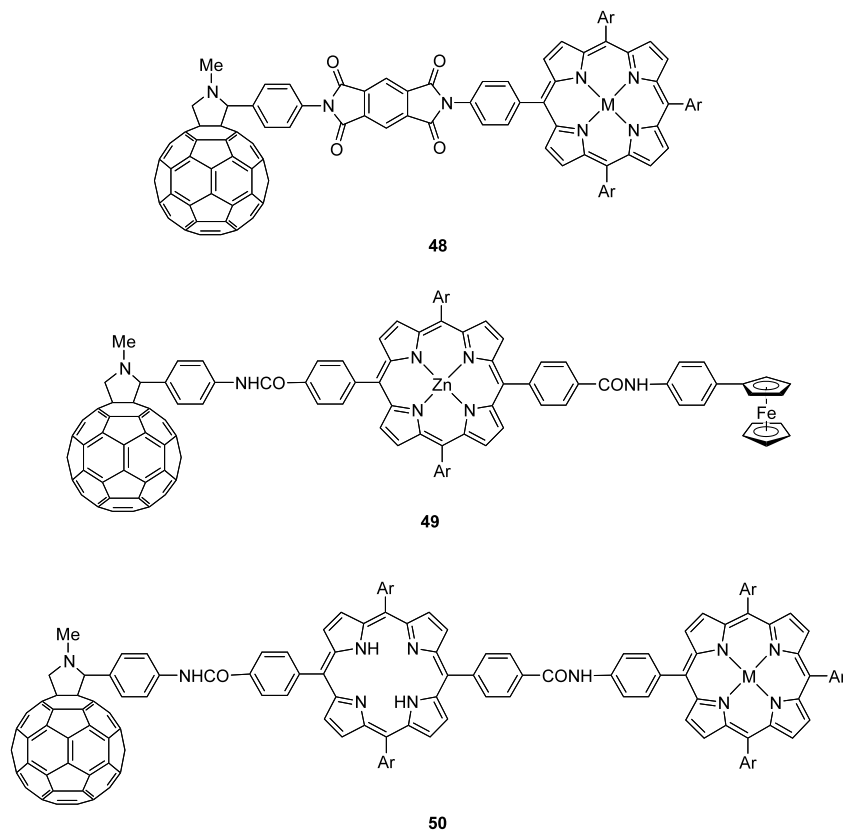


Fig. 14. Triad systems based on C_{60} , porphyrin and a third chromophore (Ar = 3,5-(*t*-Bu) $_2$ C $_6$ H $_3$).

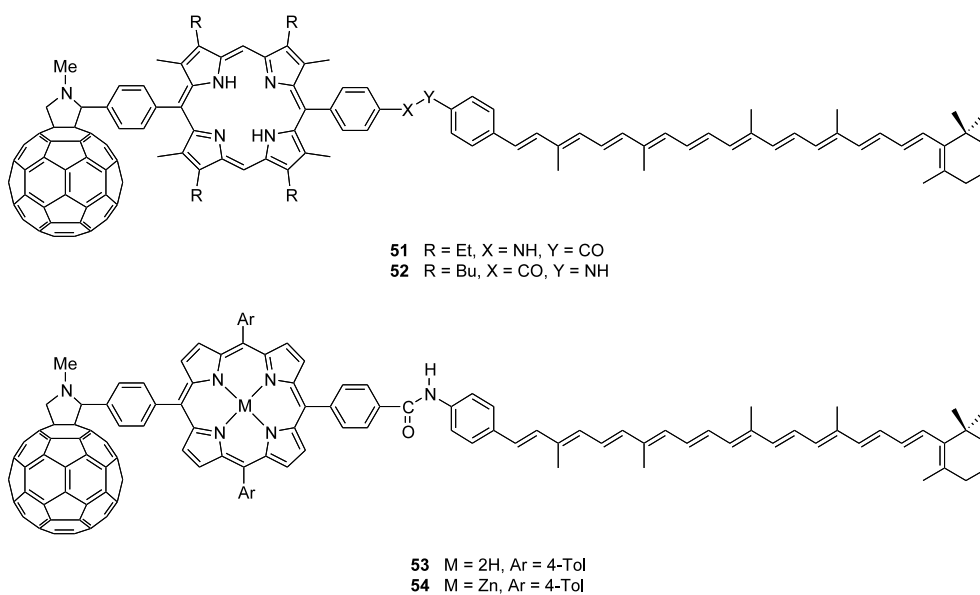
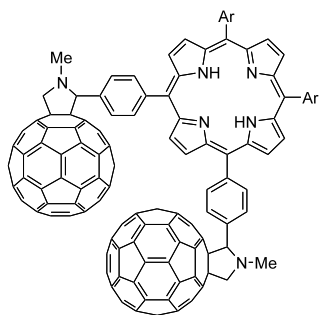


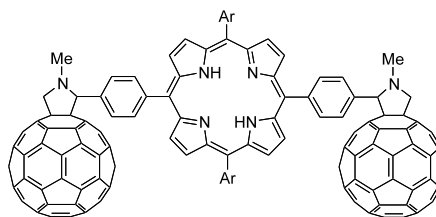
Fig. 15. C_{60} -porphyrine-carotene triad systems.

served, affording the final (desired) charge separated states $C_{60}^{\bullet-}-Im-ZnP^{\bullet+}$ (**48**), $C_{60}^{\bullet-}-ZnP-Fc^{\bullet+}$ (**49**), and $C_{60}^{\bullet-}-H_2P-ZnP^{\bullet+}$ (**50**), respectively.

For **49** and **50**, remarkable long lifetimes of these states were observed, namely 15.6 μ s (DMF) and 21 μ s (benzonitrile), respectively. The back electron transfer in the fullerene radical anion zinc porphyrin radical cation pairs was found to be promoted by O_2 , forming reactive oxygen species, such as singlet oxygen or the superoxide anion [66]. Upon exciting carotene derivatives **51–54**, the charge-separated state $C_{60}^{\bullet-}-H_2P-C^{\bullet+}$ was produced. For **51**, the excited state decayed in 2-methyltetrahydrofuran solution at room temperature (r.t.) in 170 ns via charge recombination into the triplet carotene state $C_{60}-H_2P-{}^3C$. The formation and decay of the $C_{60}^{\bullet-}-H_2P-C^{\bullet+}$ state was also investigated by EPR studies, which were in agreement with the optical measurements [62]. At 77 K, the lifetime for the charge-separated state increased to the μ s-scale, but more interestingly, it could be increased by 50% by application of a small (20 mT) magnetic field [63]. Interestingly, upon inducing small structural changes in **51**, significant changes in the photophysical properties were observed. For example, upon reversing the amide bond



57



58

(6)

in **51**, the quantum yield (ϕ) and lifetime of the charge-separated state increased from 0.22 and 170 ns (**51**) to 0.88 and 340 ns (**52**) [64].

Additional fine-tuning of **52** was accomplished by changing the octaalkyl groups in **52** to *meso*-phenyl groups in **53** and **54** [65]. For **53**, the $C_{60}^{\bullet-}-H_2P-C^{\bullet+}$ state was formed with a ϕ close to unity, although back electron transfer from the charge-separated state accelerated. Photoexcitation of the zinc analogs of **51** and **52** did not lead to the formation of the $C_{60}^{\bullet-}-ZnP-C^{\bullet+}$ state. However, for **54** this excited state was formed with a ϕ of 0.40. This was attributed to the applied structural changes leading to a more favorable oxidation potential of the zinc-porphyrin moieties.

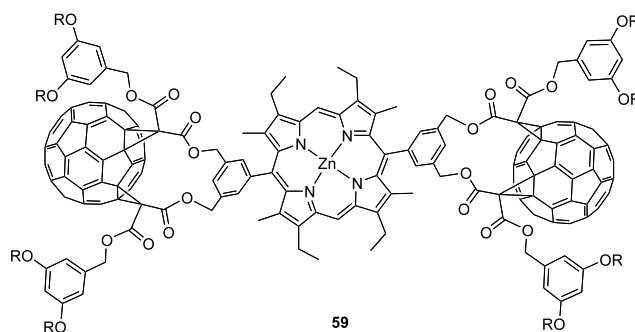
4. Multi- C_{60} porphyrins

The attachment of more than one C_{60} moiety to a

porphyrin unit was reported by a number of groups. Bisfullerene compound **55** was formed as a side-product during the synthesis of parachute-shaped dyad **31** [40,41]. NMR spectroscopic analysis of **55** and the corresponding zinc analog **56** showed that these compounds prefer the conformation in which one C_{60} sphere is located below the plane of the porphyrin (Fig. 16). Most remarkable is the fact that the photophysical properties of **55** and **56** are similar to that for the corresponding parachute shaped dyad **31**, which suggests that the porphyrin and one of the fullerene units stay in close proximity, even in the excited state.

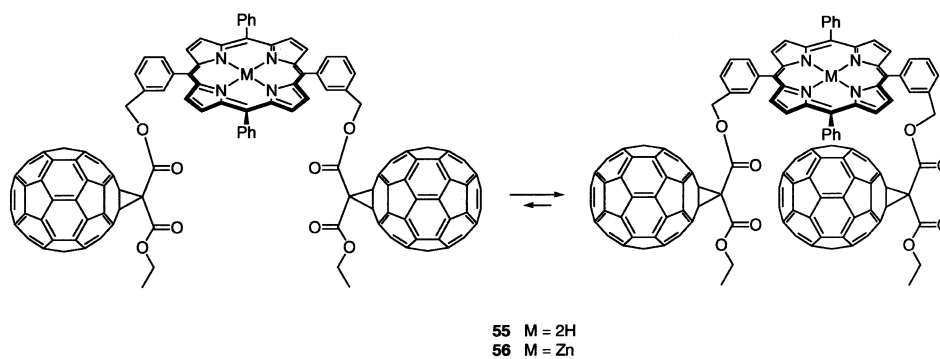
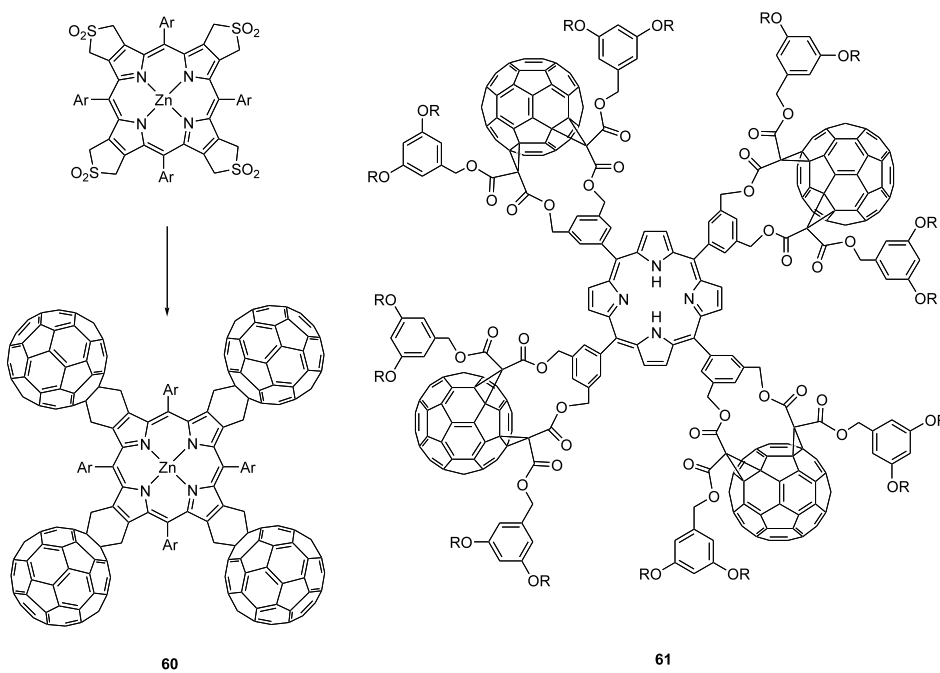
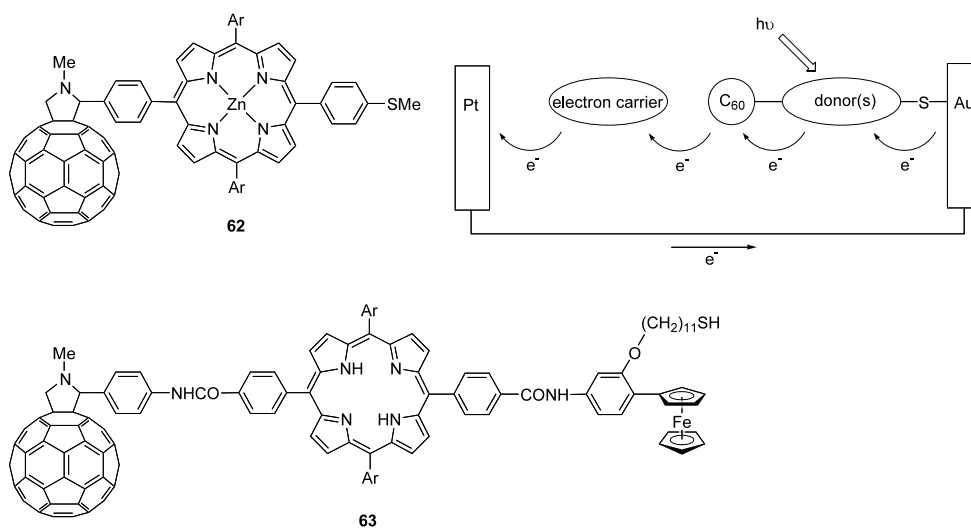
Rotational isomerism was also observed for **57**, in which two fullerene moieties are substituted in a 1,2-manner to tetraphenyl porphyrin [67]. Molecular mechanics calculations showed that the C_{60} U in **57** are within van der Waals contact in the most stable isomer. UV-vis spectroscopy and fluorescence spectra of **57** indicated that there is an interaction between the chromophores in the ground state, which could be an effect of the close proximity of the fullerene units, since this behavior was not observed for the corresponding 1,3-substituted compound **58** (Eq. (6)).

Bisfullerene porphyrin **59** was synthesized by Nierengarten and coworkers [68,69]. 1H -NMR analysis of **59** showed that in solution two conformers were present in which the C_{60} groups are in a relative *cis* or *trans* orientation. The free energy barrier for this conformational equilibrium ($\Delta G^\ddagger = 85 \text{ kJ mol}^{-1}$) was measured using variable temperature NMR spectroscopy (Eq. (7)).



59

(7)

Fig. 16. An example of rotational isomerism in **55** and **56**.Fig. 17. Tetrafullerene porphyrin structures, synthesis of **60** and structure of **61**.Fig. 18. Thio containing fullerene-porphyrin dyad **62** and triad **63**, and a schematic representation of a photoelectrochemical cell (Ar = 3,5-(*t*-Bu)₂C₆H₃).

The number of attached fullerenes around a central porphyrin unit could be increased to four via thermolysis of a tetrasulfoleno porphyrin in the presence of C_{60} , affording **60** (Figs. 17 and 18) [70]. Macrostructure **61** was prepared analogous to **59** [71]. The oxidation potential of the porphyrin unit in **61** was shifted by 175 mV anodically with respect to the parent porphyrin ligand, while the fullerene moieties were not influenced by the porphyrin unit. No further (photo)physical measurements were performed for these tetrafullerene porphyrins.

5. Self assembled monolayers of C_{60} -porphyrins

This functionalities were introduced in fullerene–porphyrin dyads **62** [72] and triad **63** [73,74] to enable the formation of self-assembled monolayer (SAM) on a gold electrode. Cathodic photocurrents under illumination were observed in the presence of electron carriers in solution, such as oxygen or methyl viologen, with high quantum efficiencies of 20–25% [75]. Moreover, in analogous systems without C_{60} , the observed photocurrent was five times smaller than those measured for **62** and **63**. These results demonstrated the potential of these systems and the important role C_{60} may play in light conversion systems.

6. Ruthenium, copper and platinum complexes

Several (oligo)pyridine ligands, such as 2,2'-bipyridine (bpy), 2,2':6',2''-terpyridine (terpy), 1,10-*ortho*-phenanthroline (phen), and di(2-pyridyl)pyridazine, have been attached to C_{60} . Furthermore, C,N-chelating aminoarene ligands were prepared and characterized. Ruthenium, copper or platinum complexes derived from these ligands were studied for their photoactivity, and used as building sites in the formation of new fullerene containing organometallic assemblies [76].

6.1. Ruthenium complexes

Fulleropyrrolidine-bpy ligands were synthesized starting from several aldehyde-bpy precursors, and subsequently metalated by $Ru(bpy)_2Cl_2 \cdot H_2O$ in refluxing 1,2-dichloroethane in the presence of NH_4PF_6 . Using this methodology, complexes **64–66** with different spacers between the ruthenium center and C_{60} were obtained and characterized (Fig. 19). In **64**, the $[Ru(bpy)_3]^{2+}$ moiety is linked to C_{60} -pyrrolidine via a flexible triethylene glycol spacer [77]. In **65**, the spacer is a rigid androstane skeleton, which suppresses conformational freedom in the dyad [78]. The hexapeptide spacer in **66** was incorporated to alter the dimensional structure of the dyad upon temperature and/or solvent

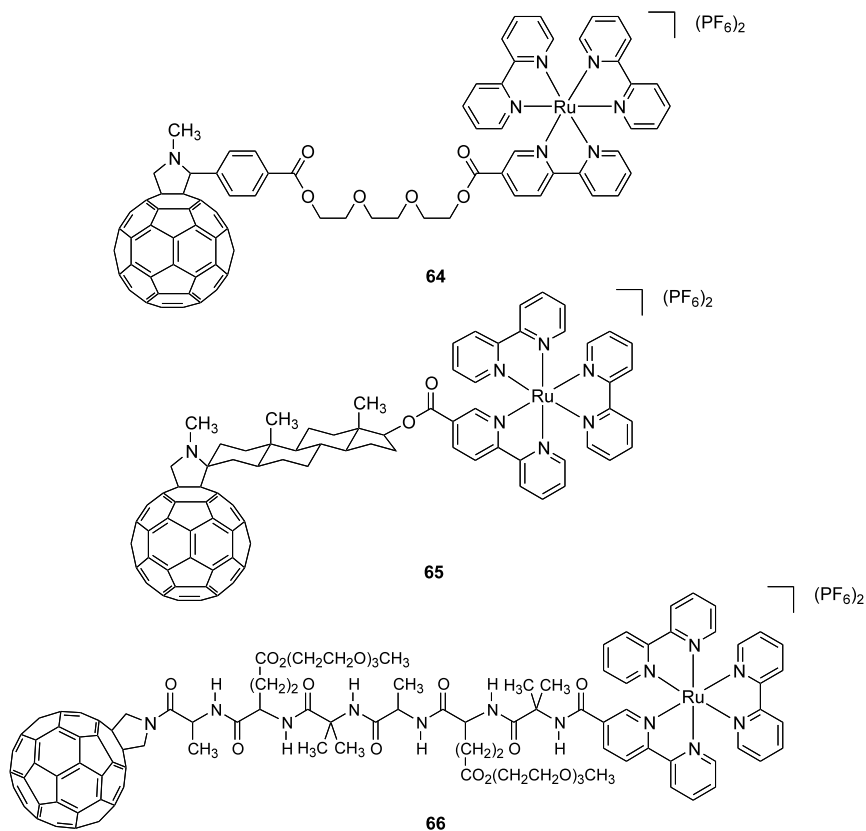


Fig. 19. Ruthenium bipyridine complexes **64–66**.

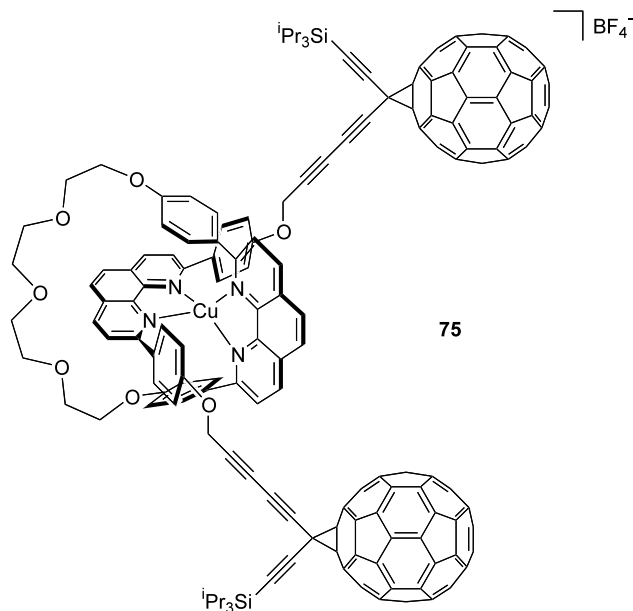


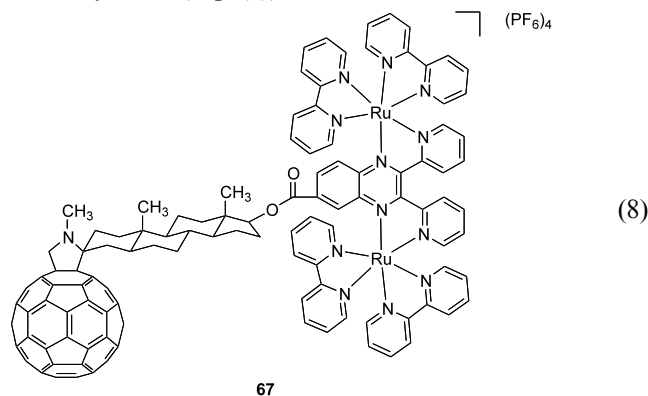
Fig. 20. Rotaxane structure **75** by Sauvage and coworkers [86].

variations, thereby affecting interactions between the donor and acceptor unit [79].

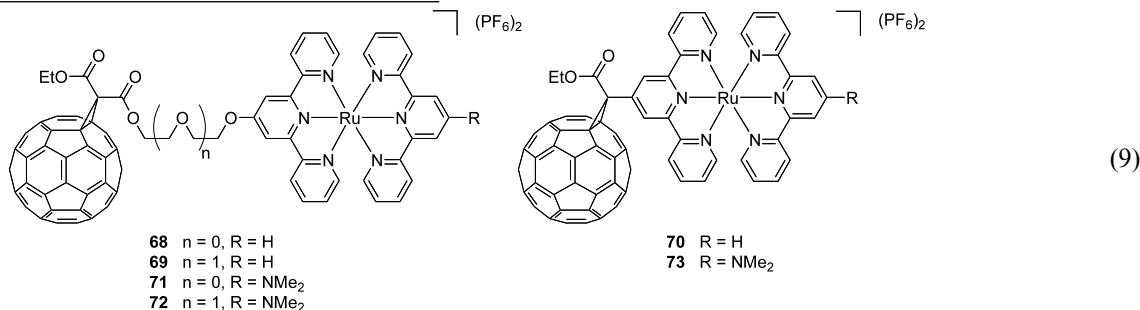
UV–vis absorption spectroscopy and cyclic voltammetry revealed that no electron/energy transfer processes take place in the ground states of **64–66**. The photoexcited $[\text{Ru}(\text{bpy})_3]^{2+}$ MLCT state was quenched in all dyads by electron transfer from the ruthenium complex to the fullerene moiety [77,78,80]. An absorption band, assigned to $[\text{Ru}(\text{bpy})_3]^{3+}$ (688 nm) was observed for **64**. Moreover, light induced electron spin resonance (LESR) measurements confirmed the formation of radicals after photoexcitation of **64**. For **65**, additional evidence of a charge separated state was found by the detection of the fullerene radical-anion absorption band at 1040 nm. The lifetime for the charge-separated state in **65** was found to be solvent dependent, namely 210 ns (CH_2Cl_2) and 100 ns (acetonitrile), respectively. In **66**, the peptide spacer between C_{60} and the ruthenium acted as a molecular switch. In chlorobutane, the ruthenium MLCT excited state is quenched by the fullerene moiety, giving the $\text{Ru}^{3+} - \text{C}_{60}^{\bullet-}$ charge-separated state. When a strong protic solvent (1,1,1,3,3,3-hexafluoro-2-propanol, HFIP) was added, the helical structure of the peptide was disrupted

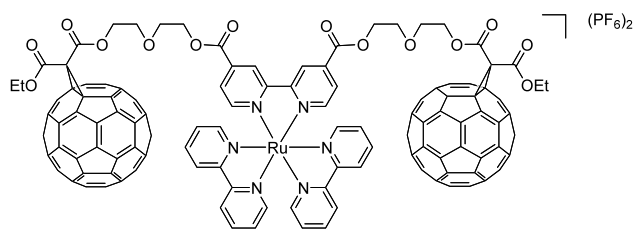
leading to an increase in the distance between the photocenters. In this situation, the electron transfer process did not proceed. Removal of HFIP restored the original structure of the peptide spacer and reactivated the electron transfer process. This ‘switching’ behavior could be repeated for ten times.

While intermolecular electron transfer was observed for **65**, the dinuclear complex **67** only displayed energy transfer from the photoexcited MLCT state to the C_{60} group [81]. Complexes **65** and **67** were applied in the preparation of remarkable stable photoactive films by well controlled layer-by-layer deposition [82]. The obtained photocurrent was found to increase linearly with the amount of deposited monolayers, demonstrating the potential of these complexes in artificial photosynthesis systems (Eq. (8)).



2,2':6',2''-Terpyridine (terpy) ligands were attached to C_{60} via Bingel cyclopropanation reaction, affording complexes **68–70** [83,84]. A Me_2N donor substituent was also introduced in the second terpy ligand giving triad complexes **71–73**. Moreover, **74**, consisting of $[\text{Ru}(\text{bpy})_3]^{2+}$ with two fullerene units attached, was synthesized and characterized. No differences in the UV–vis spectra of **68–73** were observed with respect to the free ligands. The Ru(II)/Ru(III) oxidation potentials for **71–73** were shifted 300 mV negatively with respect to complexes **68–70** due to the additional NMe_2 group. Additionally, the Ru(II)/Ru(III) oxidation potentials for **70** and **73** were found to be shifted somewhat to more positive values with respect to **68**, **69**, **71** and **72**, which was explained by the closer distance between the ruthenium metal complex and the fullerene moiety (Eqs. (9) and (10)).





74

(10)

6.2. Copper and platinum complexes

The application of C_{60} moieties as stoppers in a copper(I) bis(phenanthroline) [85] rotaxane structure (**75**, Fig. 20) has been shown by Sauvage and coworkers [86]. The redox potential of the Cu(I)/Cu(II) couple appeared to be shifted anodically to 0.865 V versus SCE in CH_2Cl_2 with respect to the mono-nuclear com-

plexes by the electron withdrawing character of the C_{60} U. However, the fullerene reduction potential was not influenced.

Detailed photophysical studies of **75** showed that the fullerene excited state was quenched via energy transfer to the copper(I) center, in competition with intersystem crossing to triplet fullerene [87]. The copper-terpy MLTC excited state was quenched via electron transfer to the fullerene moieties, leading to the $C_{60}^{\bullet-} - [Cu(phen)_2]^{2+}$ charge-separated state.

The effect of an increasing amount of fullerene groups around a photoactive copper complex was studied by Armaroli and coworkers [69,88]. A range of structures based on a bis(1,10-phenanthroline) copper(I) core surrounded by 4, 8 and 16 fullerene units was prepared (**76–78**, Fig. 21) and their electrochemical and photophysical properties analyzed. Absorption and luminescence measurements showed that due to the increasing number of fullerenes around the copper(I)

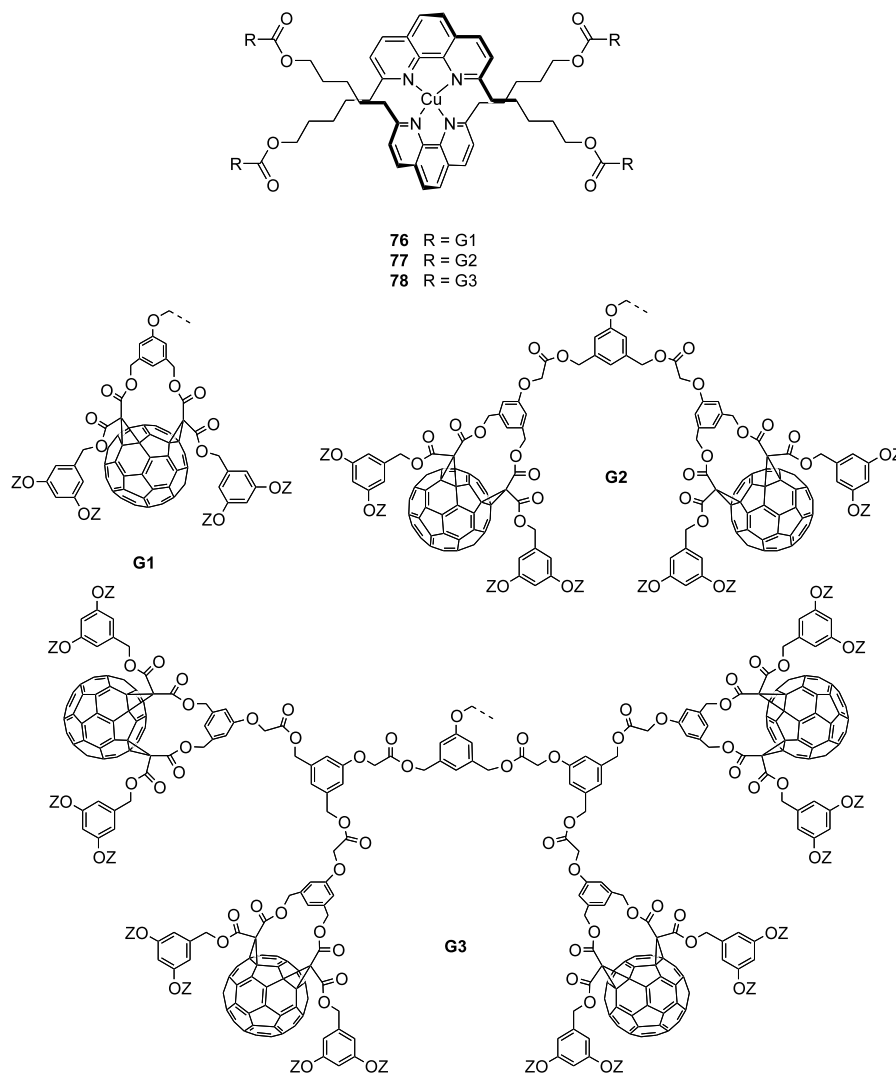
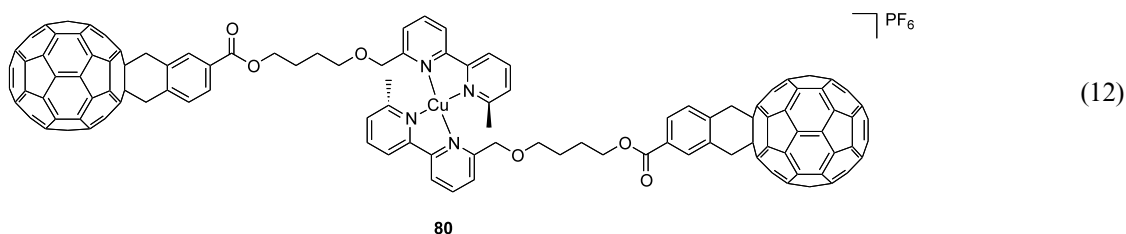


Fig. 21. Bis(1,10-phenanthroline) copper(I) core, and the fullerene containing dendritic substituents.

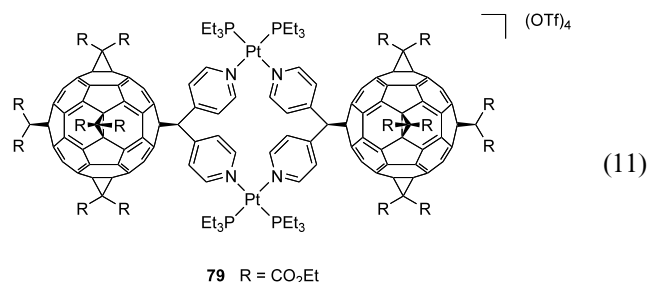
phenanthroline core, the copper center has become shielded from stimuli, such as light or electrons. In this respect, the copper(I) center has been buried in a ‘dendritic black box’.

Copper(I) and platinum(II) complexes were also applied as a building site in supramolecular assemblies. Diederich and coworkers reported the synthesis of a diplatinum cyclophane containing two fullerenes (**79**) [89], formed by mixing *cis*-Pt(OTf)₂(PEt₃)₂ with free

A similar approach was used in the formation of the non-covalent dimeric structure **80** [90]. Successful (self) assembly of the dimer was demonstrated by FD mass spectrometry. Cyclovoltammetric studies in combination with in situ ESR experiments showed three reversible reduction potentials, which were ascribed to the metal center and the fullerene moiety (Eq. (12)).



fullerene bipyridine ligand. At first, insoluble compounds were formed with the corresponding monosubstituted-fullerene ligand. Hexasubstitution of the fullerene surface in an octahedral fashion yielded a soluble complex (**79**). The selective formation of **79** was confirmed by a single crystal structure determination (Eq. (11)).



The methanofullerene CN–platinum(II) complexes **81** and **82** (CN = [C₆H₄(CH₂NMe₂)₂][−]) were applied in the preparation of new fullerene containing macrostructures (Fig. 22) [91]. However, insoluble structures were formed, and, therefore, phosphine ligands containing fluorinated tails were introduced, affording complexes **83** and **84**. These complexes showed not only enhanced solubility in organic solvents, but also in fluorinated solvents such as perfluoro methylcyclohexane. Using **83**, a soluble bisfullerene CN–platinum(II) dimeric structure with a 4,4′-bipyridyl bridge (**85**) was obtained.

7. Fullerenes with ionophoric groups

The superconducting properties of alkali-metal fullerenes stimulated chemists to prepare fullerene deriva-

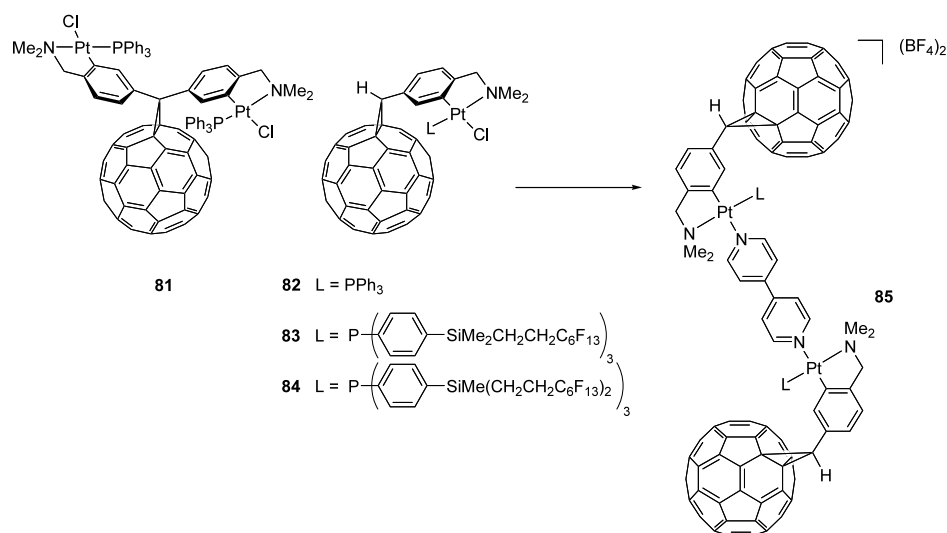
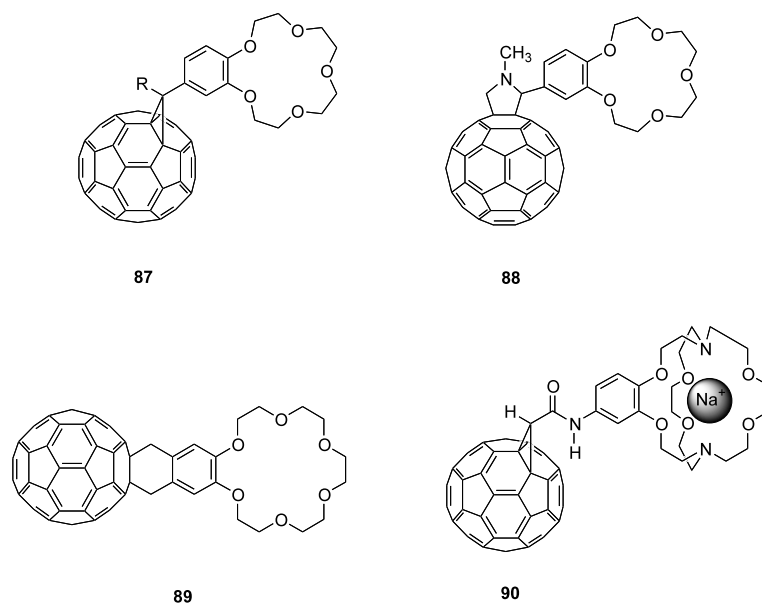


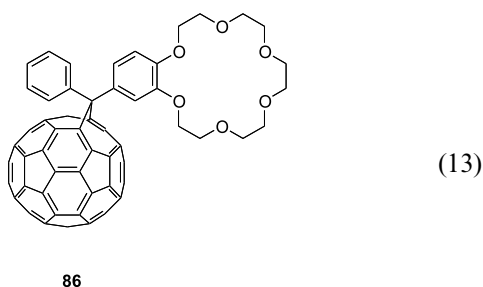
Fig. 22. Methanofullerene CN–platinum(II) complexes **81**–**85**.

Fig. 23. Crown ether moieties bound to C₆₀.

tives, in which a positive charge (of a metal cation) is located near the electron-rich fullerene surface. This would allow to tune the chemical and physical properties of the fullerene moiety. Moreover, the attachment of an ionophoric group, such as a crown ether group, affords amphiphilic structures, able to form Langmuir monolayers at air–water boundaries.

7.1. Fullerene crown ethers

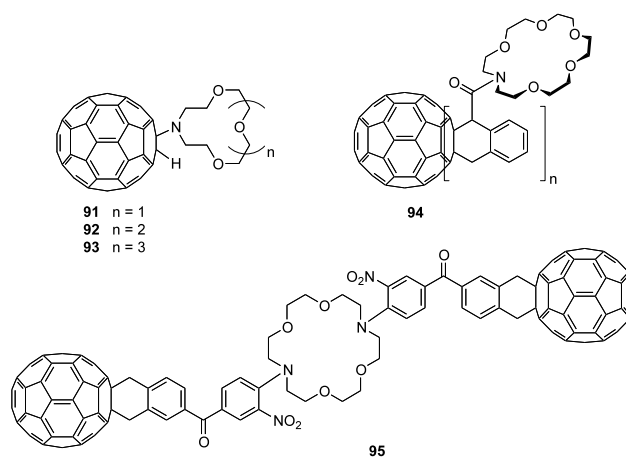
The first fullerene derivative containing a binding site for alkali-metals was reported by Wilson and coworkers. A benzo[18]crown-6-ether tag was attached to C₆₀, giving fulleroid **86**, in order to facilitate the detection of fullerene derivatives with electrospray ionization mass spectroscopy (ESI-MS) [92,93], and to study the electrochemistry of the fullerene derivatives [94,95] (Eq. (13)).



Host–guest complexes of **86** with potassium ions were observed with ESI-MS. The molecular cross-sectional area of **86** in Langmuir | Langmuir–Blodgett films was found to be 84 Å² per molecule on water [96]. Adding KCl not only stabilized this monolayer during compression/decompression cycles, but also increased

the limiting molecular cross-sectional area to 101 Å² per molecule due to changes in structure upon coordination of K⁺ in the crown ether moiety.

Other examples of ionophoric group containing fullerenes have been reported, such as crown ethers **87–89** (Fig. 23) [97–100], the sodium fullero cryptate **90** (Fig. 23) [101], and fullerene azacrown ethers **91–95** (Fig. 24) [102–104]. Upon complexation of metal cations, shifts were observed in the UV-vis spectra of **87** and **88**. Extraction experiments showed increased solubility (ca. 22 times) of **89** in protic solvents upon K⁺ complexation. The amphiphilic properties of **89** and **90** were studied among other amphiphilic fullerene derivatives using surface area versus pressure measurements and optical light microscopy. Compound **89** exhibits self-aggregation processes on the water surface, and showed to have an molecular cross-sectional area of 80

Fig. 24. C₆₀-azacrown ether compounds **91–95**.

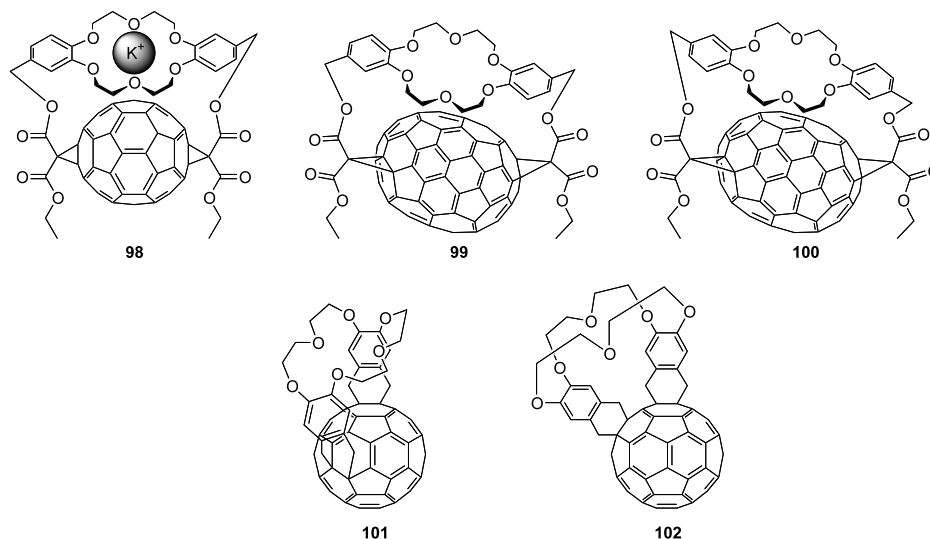
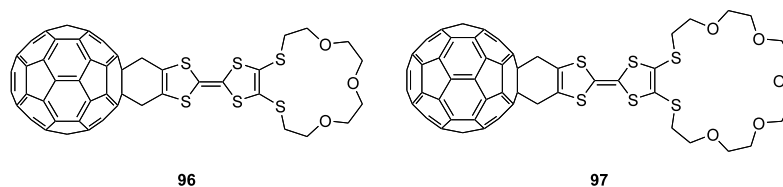


Fig. 25. Parachute-type fullerene crown ether compounds **98–102**.

\AA^2 per molecule were measured on pure water. Spread on a 1 M KCl subphase, the molecular cross-sectional area increased to 90 \AA^2 per molecule, due to the increased hydrophilic character of the crown ether moiety upon complexation of the potassium cations (analogous to **86**). Sodium containing cryptate **90** forms a monolayer with a molecular surface area of 95 \AA^2 per

trochemical measurements. Lithium cations did not influence the properties of **96** or **97**. For sodium and potassium ions, shifts in UV–vis and oxidation potential of the tetrathiafulvalene group were observed. The fullerene moiety was unaffected during these measurements as a result of the large distance between the crown ether and the fullerene moieties (Eq. (14)).



(14)

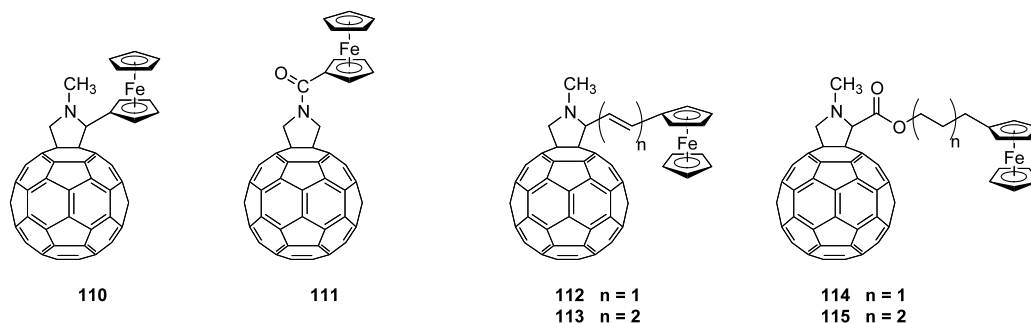
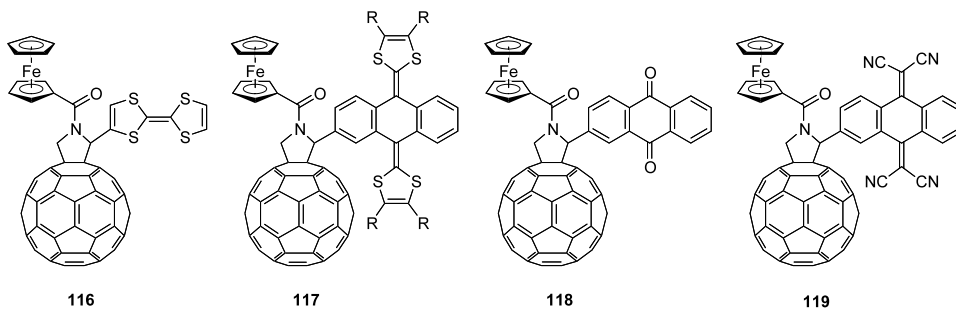
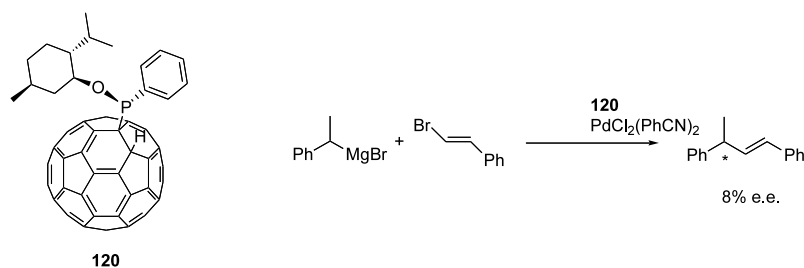
molecule, stabilized by the hydrophilic bulky crown ether groups, although some aggregation behavior was observed during compression and decompression cycles.

The C_{60} -azacrown ethers **91–93** were synthesized by hydroamination of C_{60} with the corresponding parent azacrown ether compounds. Computational calculations and optical spectroscopic measurements suggested the existence of two isomers arising from 1,2- and 1,4-additions. Addition of potassium ions in the subphase led to enlargement of the molecular cross-sectional area in Langmuir films with respect to ion-free subphases. Films of **91–93** transferred on hydrophilic glass, exhibited second-order nonlinear susceptibilities [105].

The synthesis and properties of the two fullerene tetrathiafulvalene crown ethers **96** and **97** were reported by Liu and Echegoyen [106]. The effects of complexation of cations (Li^+ , Na^+ , K^+) to the crown ether moiety was studied by UV–vis spectroscopy and elec-

7.2. Parachute-type fullerene crown ethers

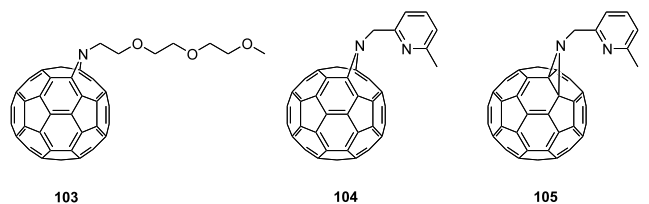
Parachute type C_{60} -crown ether **98** and the C_{70} analogs **99** and **100** were prepared by selective Bingel macrocyclization in order to obtain a relative fixed positioned crown ether moiety with respect to the fullerene surface (Fig. 25) [107,108]. The structures of the potassium adducts, **98** and **99** were confirmed by single crystal structure determinations. Potassium ions were found to bind to **98** with a small selectivity over other metal ions. More importantly, shifts in the fullerene-centered reduction potentials upon complexation with various cations were observed for both the C_{60} as the C_{70} analogs. This demonstrated that the properties of the fullerene moiety can be altered upon ion complexation near the fullerene surface. The addition of a bis-*o*-quinodimethane crown ether compound to C_{60} led to the formation of the parachute type bisadducts **101** (*trans*-4 bisadduct) with a small amount of **102** (*cis*-2 bisadduct) [109]. These compounds showed different

Fig. 26. C₆₀-ferrocenyl dyads **110**–**115**.Fig. 27. C₆₀-ferrocenyl triads **116**–**119**.Fig. 28. Application of the chiral ligand **120** in cross coupling.

ionophoric properties. For example, **101** exhibited a high complexing ability toward potassium ions, while **102** hardly complexes cations at all.

7.3. Other fullerene ionophores

The group of Shinkai studied the interaction of **103**–**105** with silver cations and alcohols by UV–vis spectroscopy [110–112]. They observed that Ag⁺ ions, coordinated to the 5,6-bridged nitrogen atom, directly interacted with the C₆₀ surface (Eq. (15)).



(15)

This work was extended to the synthesis of fullerocrown **106**, in which several carbon atoms of C₆₀ were included in the crown ether ring, and fullerencalixarenes **107**–**109** [113–115]. Complexation studies of **107**

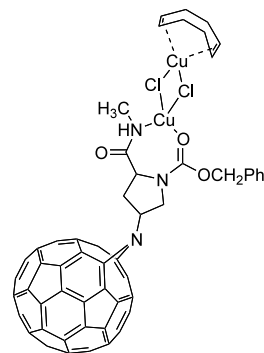


Fig. 29. Example of a dicopper complex applied as oxidation catalyst.

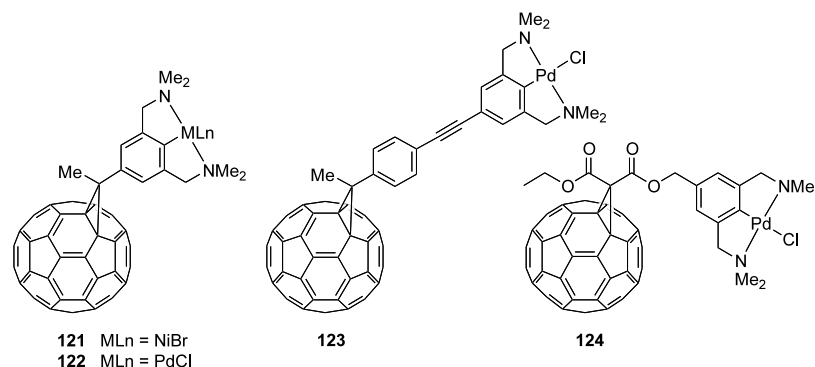
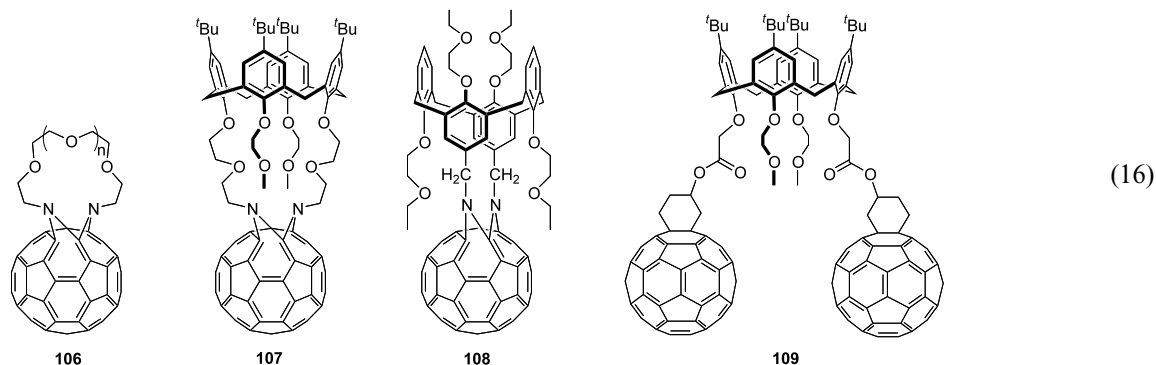


Fig. 30. Methanofullerene NCN–metal complexes.

and **108** with a large variety of alkali and earth-alkali cations showed that complexed ions direct positive charge to the fullerene surface, hereby changing the fullerene properties (Eq. (16)).

9. Organometallic C₆₀-based catalysts

A number of metallated C₆₀-ligand systems was used as catalytically active materials. For example, Naka-



8. C₆₀-Ferrocenyl complexes

A variety of ferrocenyl fulleropyrrolidines were prepared by 1,3-dipolar addition of ferrocene-substituted 1,3-azomethineylids to C₆₀, yielding dyads **110–115** (Fig. 26) [116–118] and triads **116–119** (Fig. 27) [119]. Photoexcitation of the fullerene moiety in **112–115** led to the formation of the charge-separated state C₆₀^{•-}–Fc^{•+}. For **112** and **113**, this state decayed directly by through-bond interactions to the ground state, while the aliphatic spacer in **114** and **115** stabilized this state, leading to lifetimes of 1.8 and 2.5 μs in benzonitrile, respectively.

The linkage of additional electroactive components in **116–119** did not lead to additional electron- or energy-transfer processes. Thus, for **116** and **117**, photoinduced electron transfer took place from the tetrathiafulvanyl moieties to C₆₀, leaving the ferrocene unit inactive. For **118** and **119**, only a reaction between the ferrocene donor and C₆₀ as acceptor occurred. Other C₆₀-ferrocene structures were obtained in studies concerning the reactivity of tetraferrocenyl[5]-cumulene [120] and in the preparation of thermotropic liquid crystals [121,122].

mura and coworkers have reported the synthesis of C₆₀ bearing phosphine and phosphinite substituents as new chiral ligands, using the steric bulk of the fullerene moiety [123]. A palladium complex of **120** was tested for its catalytic activity in asymmetric cross-coupling reactions (Fig. 28). The observed e.e. of 8% indicates that the palladium center remains only partially coordinated to **120** during the catalytic reaction, but this system has to be further tuned for successful application in enantioselective synthesis.

A number of azafullerene adducts of the chiral azide (2*S*,4*S*)-4-azido-1-benzyloxycarbonyl-2-(*t*-butylamino-carbonyl)pyrrolidine (Fig. 29) were used as ligand in copper and ruthenium catalyzed reactions [124,125]. These complexes were successfully applied as catalysts in the oxidation of alkylphenylsulfides and in asymmetric hydrogenation of olefins.

Nickel(II) and palladium(II) metal centers were introduced into methanofullerene NCN ligands affording **121–124** (Fig. 30). In these systems, the fullerene substituent was considered as an alternative in the preparation of catalysts bound to carbon supports, such as carbon nano-tubes and coal fibers. The increase in size

of the catalyst by anchoring it to C₆₀ could lead to application of these molecules in a nano-filtration reactor [126,127].

The palladium complexes **122**–**124** were tested in Lewis-acid catalysis. In the aldol condensation of benzaldehyde with methyl *iso*-cyano acetate, the fullerene-derivatized catalysts were as active as the unsubstituted NCN palladium complex. In the Michael reaction of methyl vinyl ketone and ethyl cyanoacetate, however, a deactivation/decomposition process of the catalyst revealed that the fullerene moiety cannot always be considered as an inert support material. Although attachment of the methanofullerene substituent led to an enlargement of the catalyst, this was not sufficient for application in a continuous flow reactor, as was shown by a 72% retention of **122** over a nanomembrane.

10. Concluding remarks

The development of organic chemistry directed to fullerenes has promoted the synthesis and characterization of a wide variety of fullerene (substituted) ligand systems. Especially, the properties of the fullerene moiety upon ligand attachment and subsequent metal introduction have been investigated in great detail. The electrochemical and photophysical properties of the fullerene moiety in these systems can be tuned in a controlled manner upon coordination of metal centers to binding domains, such as crown ethers or porphyrins near the fullerene surface. In particular, the studies performed by various authors have shown that systems comprising a fullerene and an organometallic moiety are promising components in artificial photosynthetic systems. In this respect, the nature of the linker between the chromophores, the solvent, and complexed metal ion(s) influence the mode of photoactive response of the complex on external stimuli, such as light or electrons. Remarkably, small changes in these systems often lead to big changes in properties such as efficiency (ϕ). The application of C₆₀ in organometallic macromolecular synthesis has also been investigated. In this area, the chemical properties of the fullerene, such as solubility and chemical reactivity, play an important role for application of C₆₀ as, for example, a catalyst scaffold.

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