DOI: 10.1002/cctc.201402262

Fullerene as a Platform for Recyclable TEMPO Organocatalysts for the Oxidation of Alcohols**

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[60]Fullerene has been employed successfully as a molecular platform to anchor 12 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) moieties. Such an octahedrally substituted C_{60}-derivative has been employed as an organocatalyst for the oxidation of primary and secondary alcohols using the Anelli protocol. The reaction showed a general applicability to various alcohols, and the catalyst was recovered easily and could be recycled for at least seven cycles with no loss in catalytic activity. EPR spectroscopy studies revealed that the amount of radicals decreases during the catalytic cycles, even if the recovered material still displays unchanged catalytic activity. This new approach paves the way to use fullerene as a molecular platform to support other kinds of organometallic and organocatalysts as well as for their use as model compounds to understand the behavior of other nanocarbon-supported catalysts.

Introduction

Oxidations of both primary and secondary alcohols to aldehydes and ketones, respectively, are processes of fundamental importance on academic and industrial scales because of their key role in organic synthesis.[1] 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO) derivatives represent one of the most employed classes of metal-free compounds for the selective oxidation of alcohols,[2] although their relatively high prices prevent large-scale use, and new methods and strategies devoted to its recovery have been explored.[3] Recently, we have been engaged in the synthesis and application of ionic-liquid-tagged TEMPO derivatives[4] as recyclable catalysts for the oxidation of alcohols through the “release and catch” approach.[5] With this background, we planned to employ the [60]fullerene sphere as a molecular platform to host several organocatalyst moieties for the first time to achieve a controlled, highly loaded, C_{60}-based recyclable catalyst in the oxidation of alcohols to their corresponding carbonyl compounds. As a result of the multigram production of fullerene,[6] this exotic allotrope of carbon has been studied intensively to find a suitable application. Some of the potential applications of C_{60} derivatives are in the fields of organic photovoltaics,[7] nanomedicine,[8] and smart materials.[9] Carbon nanoforms (CNF) such as nanotubes (CNT), nanodiamonds (nD), graphenes, and related materials have been employed widely as supports both for metal nanoparticles and organometallic complexes to be employed in catalysis.[10] However, just a few studies deal with the use of fullerenes in catalysis, which focus mainly on the preparation of heterogeneous C_{60}-metal mixtures,[11] and very recently, a fullerene-metformine multiadduct has been employed as ligand for Pd^{II} to form a recyclable nanocatalyst species for Suzuki couplings.[12] In the last two decades, several examples of C_{60}-TEMPO systems prepared through the Prato,[13] Bamford–Stevens,[14] and Bingel synthetic protocols[15] have been reported. As an example, nitroxide malonate methanofullerenes in combination with the anticancer drug cyclophosphamide showed a high antitumor activity against leukemia P-388,[15d] and a fulleropyrrolidine nitroxide has been employed as paramagnetic probe to explore the inner environment of single-walled carbon nanotubes by forming peapods.[13k] Nonetheless, to date, almost all other TEMPO-fullerene systems have been employed mainly for EPR spectroscopy and electrochemical investigations and there are no examples of their catalytic activity.

Results and Discussion

With the aim to explore whether fullerene can be employed successfully as a recyclable molecular support to host a controlled number of catalytic moieties, we prepared three C_{60}-TEMPO systems to be tested in the oxidation of alcohols: C_{60}-T_2 (**2**), C_{60}-T_4 (**3**), and C_{60}-T_{12} (**4**) that have two, four, and 12 TEMPO moieties, respectively (Scheme 1). The synthesis starts with the formation of TEMPO-bismalonate **1**[15d,16] from malonyl

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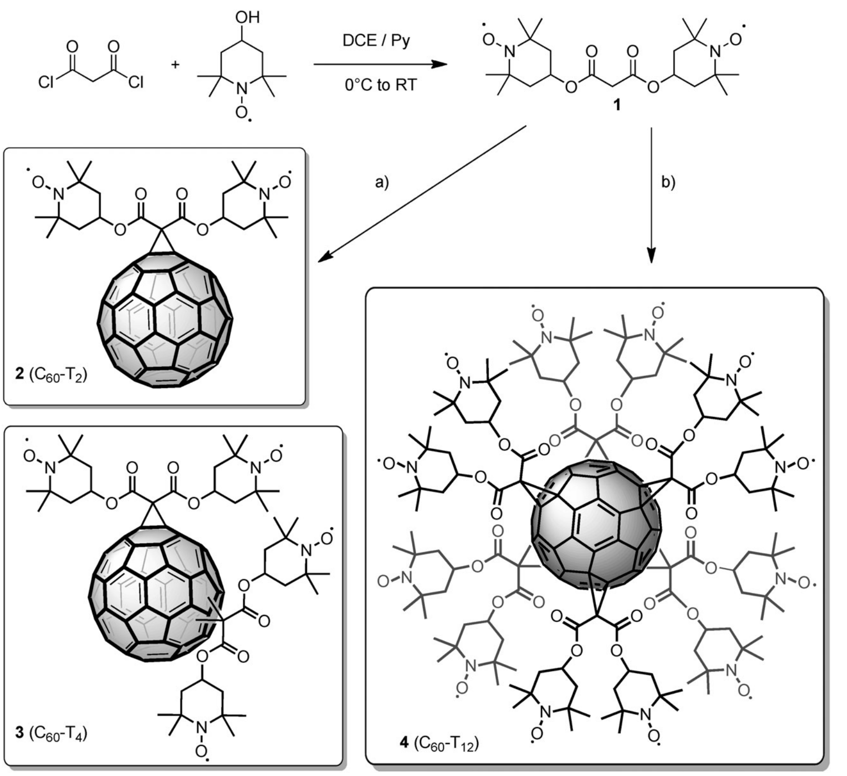
[**] TEMPO = 2,2,6,6-tetramethylpiperidine-1-oxyl

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201402262.



Scheme 1. Synthesis of C_{60}-TEMPO systems. Reaction conditions: a) C_{60}, CBr_4 (2 equiv.), **1** (1 equiv.), DBU (4 equiv.), PhCl, RT, 24 h. Yield: **2** (28%), **3** (10%); b) C_{60}, CBr_4 (50 equiv.), **1** (10 equiv.), DBU (20 equiv.), PhCl, RT, 72 h. Yield: **4** (54%).

chloride and 4-hydroxy-TEMPO. The Bingel reaction has been applied to prepare the TEMPO/fullerene conjugates: if a 1:1 stoichiometry was employed, **2**[15d,17] and **3** were isolated by column chromatography in 28 and 10% yield, respectively, whereas the use of 10:1 stoichiometry (**1**/C_{60}) led to **4** in 54% yield. As a result of the paramagnetic nature of the nitroxide moieties in these new systems, no valuable structural information can be gained by NMR spectroscopy. Indeed, as expected, the ^{1}H NMR spectrum of **4** has a very low resolution, which makes structural assignment rather difficult. To obtain some useful information from NMR spectroscopy, **4** was converted into the analogous *N*-hydroxylamine, an excess of phenylhydrazine was added directly into the NMR tube,[18] or it was reduced by $Na_2S_2O_4$. Nevertheless, the proton spectra so obtained are not well resolved, but show the presence of all the signals of TEMPOH (Figures S1 and S2). Better indications have been achieved from FTIR spectra of C_{60}-TEMPO systems, which show the presence of the carbonyl stretching vibration along with that of N–O· radicals at $\tilde{\nu} = 1465\ cm^{-1}$ and that of C_{60} at $\tilde{\nu} = 527\ cm^{-1}$ (Figure S3). Finally, ESI-MS confirmed the proposed hexakis adduct structure for **4**, and the relevant peaks at *m/z* 3206.1 ($[M+Na]^+$) and 1614.5 ($[M+2\,Na]^{2+}$) were present (Figure S4).

Figure 1 a shows the EPR spectrum of a THF solution of **4**. This spectrum mainly shows one broad signal, the integrated intensity of which corresponds to the initial amount of nitroxides expected for a hexakis adduct. The broadening (peak-to-peak line width of 15 G) of the signal is reminiscent of that obtained from very concentrated nitroxide solutions (>0.05 M).[19] As the shape of the signal is independent of the concentration of the radical in the range 0.01–1 mM, the signal broadening is ascribed to spin exchange caused by the proximity of the spin centers of **4** within the framework of the fullerene. This signal is indicative of the presence not only of triplet transitions between two nitroxide units connected to the same malonate unit but also of other multiplet transitions from higher spin states that arise from multiple interactions between the 12 radical units.[20] The spectrum also shows a signal characterized by three equally spaced sharp lines presumably caused by molecules of **4** that contain some tetramethylpiperidine units in the diamagnetic form. Theoretical simulation of the experimental spectrum, however, indicated that these correspond to less than 3% of the total amount of nitroxide (Figure S6).

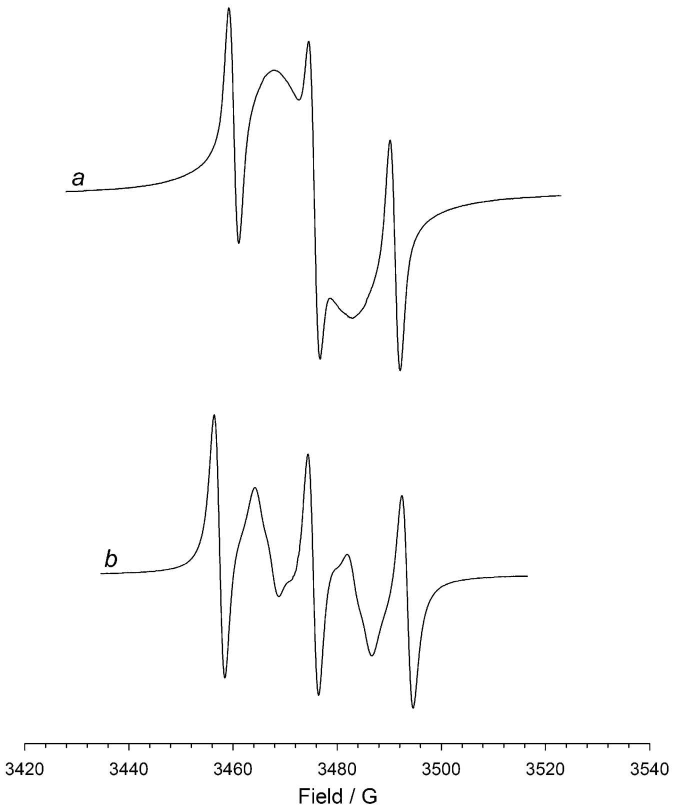


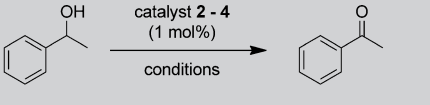
Figure 1. EPR spectra of a) **4** and b) **3** in THF at room temperature.

The spectrum of **3** shows a five-line pattern (Figure 1 b) in which the second and fourth lines are broader. This spectrum is very similar to that of a C_{60}-T_2 derivative described by Nuretdinov et al. in which spin exchange could be operative between only two nitroxide units.[15d] This suggests that spin exchange occurs in **3** mainly between the two nitroxide units linked to the same malonate fragment and not between radical centers that belong to different malonate units. This finding suggests that steric hindrance drives the formation of these bis adducts to keep the functionalized units quite far apart (mainly as equatorial and *trans* adducts).

With the fullerene-TEMPO systems in hand, we started to test their catalytic activity in the oxidation of 1-phenylethanol to acetophenone by applying three different conditions in which the co-oxidant was varied: hypervalent iodine(III) [bis-(acetoxy)iodo]benzene (BAIB),[21] oxygen in the presence of *tert*-butyl nitrite (TBN) as cocatalyst,[22] and sodium hypochlorite solution (commercial bleach) in the presence of KBr and $NaHCO_3$ to adjust the pH (Anelli's conditions).[2a–c] The results are collected in Table 1 and show that with BAIB as the terminal oxidant only **4** in 1 mol% is able to convert 1-phenylethanol fully (entry 3). The three catalysts gave almost the same promising results if oxygen was used (entries 4–6) even if the yields were not quantitative. Finally, complete conversions in a very short reaction time were obtained with all the C_{60}-TEMPO conjugates if bleach in dichloromethane (DCM) was used (entries 7–9). In all cases, control experiments performed with no catalysts afforded conversions < 5%.

Then, we focused on **4** to explore the substrate scope of the reaction because of its greater TEMPO/C_{60} ratio, which allowed us to use less catalyst with a fixed loading (e.g., 2.1 mg of **4** is needed for 0.8 mmol of alcohol versus 4.5 mg of **2**). Catalyst **4** was highly active in the oxidation of a wide range of substrates (Table 2). Primary benzylic alcohols, such as benzyl-, *p*-bromo-, and *p*-nitrobenzyl alcohols as well as 2-naphthalenemethanol were converted quantitatively between 0.5 and 1.5 h (entries 1–4). Secondary benzylic alcohols such as 1-indanol and benzoin were converted quantitatively (entries 5–6), whereas diphenylmethanol gave benzophenone in 87% yield (entry 7). Cyclic secondary alcohols such as cyclohexanol and 1-*tert*-butoxycarbonyl-4-hydroxypiperidine (entries 8–9) and acyclic secondary alcohols such as 2-decanol and 4-phenylbutan-2-ol (entries 10–11) were oxidized with complete conversions with longer reaction times in the latter cases. Finally, excellent yields were obtained with primary aliphatic alcohols within 0.5–2 h (entries 12–14). Interestingly, primary alcohols afforded the corresponding aldehydes selectively without undergoing easy autoxidation to the corresponding carboxylic acid[23] probably because TEMPO systems are free-radical scavengers and hence act as autoxidation inhibitors.[2g, 24]

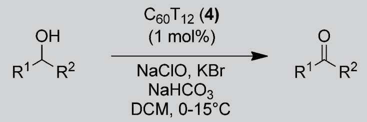
Table 1. Catalytic oxidation of 1-phenylethanol with **2**, **3**, and **4** under different reaction conditions.[a]

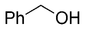
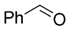
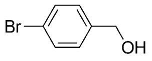
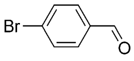
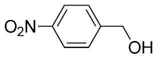
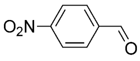
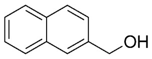
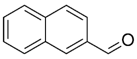
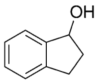
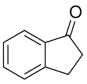
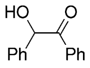
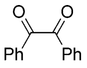
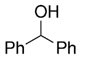
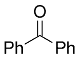
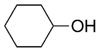
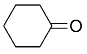
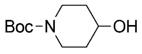
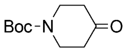
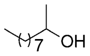
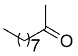
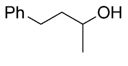
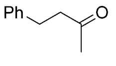


Entry	Catalyst	Conditions	*t* [h]	Yield [%]
1	**2**	BAIB[b]	16	70
2	**3**	BAIB[b]	16	trace
3	**4**	BAIB[b]	16	> 95
4	**2**	aerobic[c]	4	75
5	**3**	aerobic[c]	4	72
6	**4**	aerobic[c]	4	72
7	**2**	NaClO[d]	1	> 95
8	**3**	NaClO[d]	1	> 95
9	**4**	NaClO[d]	1	> 95

[a] In all the reactions 1 mol% (based on TEMPO) of catalyst was employed. [b] Reaction conditions: alcohol (0.8 mmol), BAIB (1.1 equiv.), DCM (2 mL), RT. [c] Reaction conditions: alcohol (0.8 mmol), TBN (15 mol%), O_2 (balloon), water (0.5 mL), 50 °C. [d] Reaction conditions: alcohol (0.8 mmol), NaClO (2.86 mL, 0.35 м), KBr (0.16 mL, 0.5 м), $NaHCO_3$ (1.28 mmol), DCM (2 mL), 0–15 °C.

Table 2. Catalytic oxidation of primary and secondary alcohols with **4** under Anelli's conditions.[a]



Entry	Substrate	Product	*t* [h]	Yield [%]
1			0.5	> 95
2			0.5	> 95
3			0.5	> 95
4			1.5	> 95
5			1.0	> 95
6			7.0	> 95
7			8.0	87
8			1.5	> 95
9			4.0	> 95
10			6.0	> 95
11			6.0	> 95
12	n-$C_6H_{12}OH$	n-$C_5H_{10}CHO$	0.5	> 95
13	n-$C_{10}H_{21}OH$	n-$C_9H_{19}CHO$	1.5	> 95
14	$Ph(CH_2)_5OH$	$Ph(CH_2)_4CHO$	2.0	> 95

[a] Reaction conditions: alcohol (0.8 mmol), NaClO (2.86 mL, 0.35 м), KBr (0.16 mL, 0.5 м), $NaHCO_3$ (1.28 mmol), DCM (2 mL), 0–15 °C.

Next, the different polarity between the oxidation products and **4** was exploited to recover the catalyst easily and to perform a complete recycling study. After the first reaction, the carbonyl compound can be isolated quickly by short chromatography by eluting with a mixture of low-polarity solvents (see Experimental Section and Figure S7). Then, the catalyst, which displays a greater affinity toward silica gel than the product and reactants, can be recovered easily by eluting with a more polar mixture and it can be recycled after evaporation of the solvent. A recycling study that used 1 mol% of **4** for the oxidation of 1-phenylethanol or 1-decanol on a 4 mmol scale is shown in Figure 2. In both cases, catalyst **4** can be recycled for at least five cycles with just a small decrease in catalytic activity (96–84% for acetophenone; 98–81% for decanal). The catalyst recovered from the five cycles with 1-phenylethanol was further employed in a sixth and seventh cycle with 1-decanol as the alcohol. Quantitative conversion to decanal was observed in these two additional cycles (data not shown). Finally, the possibility to decrease the catalyst loading was considered, and the complete conversion of 1-phenylethanol (4 mmol) was achieved by using 0.1 mol% of **4** (based on TEMPO) in a concentrated DCM solution (2 mL) with a longer reaction time (6 h).

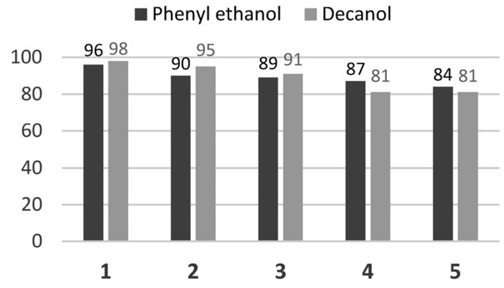


Figure 2. Recycling of **4** (1 mol%) in the formation of acetophenone or decanal.

We also recorded the EPR spectrum of **4** recovered after five cycles in THF. The EPR spectrum is significantly different from that recorded from the fresh sample and exhibits a three-line group as the main signal (Figure 3). This suggests that during the catalytic cycles nitroxide units are in part converted to diamagnetic units to lead to a dramatic decrease of the spin-exchange interaction between the 12 nitroxide units. Quantitative analysis, performed by comparison of a doubly integrated spectrum to a spectrum of a solution of 2,2-diphenyl-1-picrylhydrazyl (DPPH) of known concentration, indicated that after five cycles the total amount of nitroxide was reduced to 24%. As the catalyst still shows good activity after five cycles, it is plausible that the nitroxide is converted to the diamagnetic oxoammonium form during the different catalytic cycles.

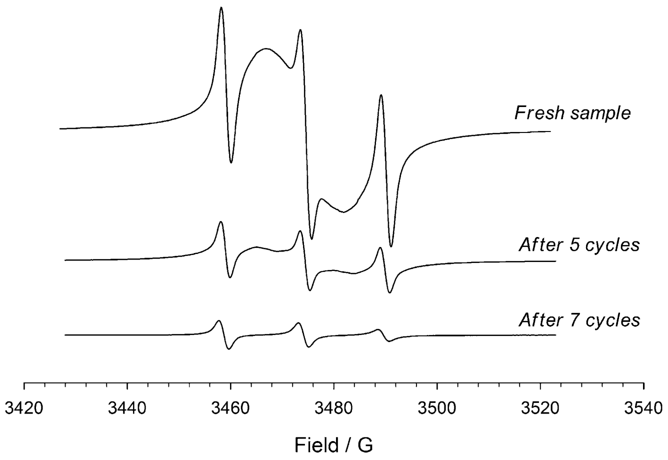


Figure 3. EPR spectra of fresh **4** (0.5 mM) and **4** after five and seven cycles in THF.

Conclusions

For the first time, fullerene has been employed successfully as a molecular support in the preparation of C_{60}-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) systems employed as active catalysts for the oxidation of primary and secondary alcohols to aldehydes and ketones. The main advantage of this approach is to have highly loaded homogeneous catalytic systems that can be recovered easily through a simple and fast silica pad, which combines the benefits of homogeneous catalysis with recyclability and cost abatement. The catalysts were active at just 1 mol% loading (based on TEMPO) in at least seven cycles with almost no loss in activity. Moreover, the success of the present approach may pave the way toward the extensive use of fullerene as a molecular support for other kinds of organometallic and organocatalysts as well as for their use as model compounds to understand the behavior of other nanocarbon-supported catalysts. In addition, especially in the case of C_{60}-T_{12} (**4**), this exotic octahedral polynitroxide system can also find application in organic radical batteries,[25] for magnetic resonance and EPR imaging,[26] or as a building block for the preparation of materials with magnetic, conducting, and optical properties,[27] among others.

Experimental Section

EPR spectroscopy

EPR spectra were recorded at RT by using an ELEXYS E500 spectrometer equipped with a NMR gaussmeter to calibrate the magnetic field and a frequency counter for the determination of *g* factors. Nitroxide concentrations were measured with respect to a solution of DPPH of known concentration using the signal from a ruby crystal as internal standard.

Synthesis of C_{60}-TEMPO systems

Synthesis of 1: A solution of 4-hydroxy-TEMPO (3.55 mmol, 610 mg) in 1,2-dichloroethane (12 mL) in a single-necked round bottom flask was degassed with dry Ar. Pyridine (3.55 mmol, 285 mL) was added to the solution at RT, and the reaction mixture was cooled to 0 °C. Then, malonyl chloride (1.77 mmol, 173 mL) was added dropwise under Ar, and the solution was stirred at 0 °C for 1 h. The reaction mixture was left overnight at RT. A saturated solution of $NaHCO_3$ (15 mL) was added to the mixture, which was extracted with DCM (3×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by flash chromatography (SiO_2, ethyl acetate/petroleum ether 2:8) to recover 450 mg (61%) of **1** as an orange solid. FTIR (film): $\tilde{\nu} = 2977$, 2940, 1735 (C=O), 1465 (N–O), 1365, 1337, 1243, 1180, 1150, 1015, 1061 cm^{-1}; MS (EI): *m/z*: calcd for $C_{21}H_{36}N_2O_6$ 412.2, found 412.4 *m/z*.

Synthesis of 2 and 3: To a solution of fullerene C_{60} (0.387 mmol, 279 mg), CBr_4 (0.774 mmol, 257 mg), and **1** (0.387 mmol, 160 mg) in chlorobenzene (22 mL), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 1.55 mmol, 236 μL) was added at RT, and the mixture was stirred for 24 h. The crude product was purified by column chromatography (SiO_2), unreacted C_{60} was recovered by hexane/toluene (3:1), whereas the monoadduct **2** was eluted with DCM and dried under reduced pressure. Subsequently, **3** was eluted with DCM/MeOH (9:1) and dried under reduced pressure. Finally, pure **2** (124 mg, 28%) and **3** (29 mg, 10%) were collected after precipitation from $CHCl_3$ with MeOH as dark solids.

Compound 2: FTIR (KBr): $\tilde{\nu} = 2973$, 2936, 1747 (C=O), 1465 (N–O), 1364, 1231, 1177, 1114, 1061, 740, 705, 527 cm^{-1} (C_{60}); MS (ESI): *m/z*: calcd for $C_{81}H_{34}N_2O_6{\cdot}H^+$ 1131.1, found 1131.2.

Compound 3: FTIR (KBr): $\tilde{\nu} = 2976$, 2939, 1746 (C=O), 1464 (N–O), 1364, 1231, 1180, 1107, 1057, 740, 527 cm^{-1} (C_{60}); UV ($CHCl_3$): $\lambda =$ 258, 324, 426, 474 nm; MS (ESI): *m/z*: calcd for $C_{102}H_{68}N_4O_{12}{\cdot}H^+$ 1542.6, found 1542.7; calcd for $[C_{102}H_{68}N_4O_{12}{\cdot}2\,H]^{2+}$ 772.2, found 772.1.

Synthesis of 4: To a solution of fullerene C_{60} (0.0833 mmol, 60 mg), CBr_4 (4.165 mmol, 1.38 g), and **1** (0.833 mmol, 345 mg) in chlorobenzene (9.2 mL), DBU (1.667 mmol, 250 μL) was added at RT, and the mixture was stirred for 72 h. The crude solution was purified by column chromatography (SiO_2); unreacted C_{60} was recovered by using hexane/toluene (3:1), excess **1** was recovered with DCM/MeOH (9:1), and the desired compound **4** was eluted with DCM/MeOH (8:2). After removal of the solvent under reduced pressure, the pure product was precipitated from $CHCl_3$ with hexane to afford 140 mg (54%) of an orange solid. FTIR (KBr): $\tilde{\nu} = 2975$, 2938, 1744 (C=O), 1634, 1464 (N–O), 1365, 1225, 1178, 964, 714, 528 cm^{-1} (C_{60}); UV ($CHCl_3$): $\lambda = 246$, 279, 342 nm; MS (ESI): *m/z* calcd for $C_{186}H_{204}N_{12}O_{36}{\cdot}Na^+$ 3206.4, found 3206.1; calcd for $[C_{186}H_{204}N_{12}O_{36}{\cdot}Na_2]^{2+}$ 1614.4, found 1614.5.

Preparation of reduced 4 (*N*-hydroxylamine form): To **4** (10 mg, 3.1 μmol), a 1:1 mixture of acetone/water (2 mL) and 85% $Na_2S_2O_4$ (0.7 mg, 3.4 μmol) were added. After stirring for 0.5 h at RT, acetone was removed under reduced pressure. The remaining aqueous solution was extracted with diethyl ether. The organic layers were dried over anhydrous Na_2SO_4. The solution was filtered, and the solvent was removed under reduced pressure. The so-obtained sample was employed to record NMR spectra. ^1H NMR (250 MHz, $CDCl_3$): $\delta = 3.79$ (bs, 12H), 2.67 (s, 24H), 2.94 (s, 24H), 1.29 ppm (s, 144H).

General procedures for oxidation

Oxidation with BAIB: BAIB (0.88 mmol) was added to a solution of alcohol (0.8 mmol) and catalyst (1 mol% based on TEMPO) in DCM (2 mL). The reaction mixture was stirred at RT and monitored by TLC. After 16 h the solvent was removed under reduced pressure to obtain the crude product, which was purified by simple filtration through a pad of silica (AcOEt/petroleum ether), and the conversion of the product was calculated by ^1H NMR spectroscopy after careful determination of its weight.

Oxidation with oxygen: A mixture of alcohol (0.8 mmol), *tert*-butyl nitrite (15 mol%), and catalyst (1 mol% based on TEMPO) in H_2O (0.5 mL) was prepared in a single-necked round-bottomed flask. The flask was then filled with pure oxygen (balloon filled), and the resulting mixture was stirred at 50 °C under an oxygen atmosphere. After 4 h, the reaction mixture was cooled to RT, and Et_2O (3×5 mL) was added. The mixture was stirred for 5 min, and the organic layers were separated and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give the crude product, which was purified by simple filtration through a pad of silica (AcOEt/petroleum ether). The conversion of the product was calculated by ^1H NMR spectroscopy after careful determination of its weight.

Oxidation with NaClO (Anelli): A mixture of alcohol (0.8 mmol), catalyst (1 mol% based on TEMPO), and aq KBr (0.16 mL, 0.5 M) in DCM (2 mL) was prepared in a single-necked flask. The mixture was cooled to 0 °C, NaOCl (2.86 mL, 0.35 M) was added, and the solution was buffered to pH 8.6 with $NaHCO_3$ (108 mg). The biphasic reaction mixture was stirred vigorously, and the temperature of the solution was maintained between 0–15 °C until total consumption of the starting alcohol (TLC). The solution was diluted with DCM (3×10 mL), and the organic layer was separated by extraction and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give the crude compound, which contained the catalyst and the carbonyl compound. The crude compound was further purified by simple filtration through a pad of silica, and the conversion of the product was calculated by ^1H NMR spectroscopy after careful determination of its weight.

Recycling procedure

The crude collected in the first cycle, after extraction and drying, was concentrated to a 1–2 mL volume and seeded in a short silica pad. Then, after atmospheric evaporation of the solvent, the carbonyl compound was isolated by elution with diethyl ether/petroleum ether (2:8), and the catalyst was recovered quickly with a mixture of methanol/ethyl acetate (2:8). The removal of the solvent allowed the recycling of the catalyst.

Acknowledgements

Financial support from the University of Palermo, the University of Bologna, and COST Action CM0905 ORCA are gratefully acknowledged.

Keywords: alcohols · EPR spectroscopy · fullerenes · organocatalysis · oxidation · TEMPO

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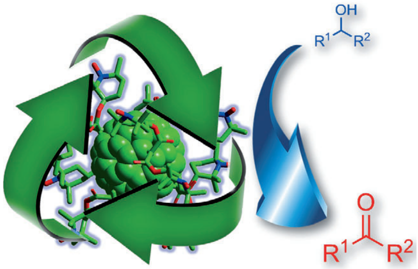
Received: April 22, 2014

A great couple: Fullerene and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) moieties combined in molecular assemblies give rise to excellent catalysts for the oxidation of a wide range of alcohols. These hybrids are easily recycled and maintain their activity after seven cycles.



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Fullerene as a Platform for Recyclable TEMPO Organocatalysts for the Oxidation of Alcohols