EPR studies of free radical reactions of C₆₀ embedded in mesoporous MCM-41 materials in aqueous solution

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The channels of the molecular sieve MCM-41 are employed as nanoreactors to study free radical attacks on C_{60} in aqueous media. Samples of C_{60} embedded in the nanochannels of mesoporous materials were prepared by the chemical binding of C₆₀ to the amino-modified surface of MCM-41 solids. The spin trapping/EPR technique was employed to study the reactions of hydroxyl and methyl radicals with the embedded C_{60} in the nanochannels. The study enables us to examine the chemistry of C₆₀ in aqueous solution, and the efficacy of free radical scavenging by C60 embedded in the nanochannels. The study further reveals the proximity effect of free radical reactions in a nano-restricted environment.

Introduction

The extended double bonds of C₆₀ are susceptible to multiple additions of electron-rich reagents including free radicals.1 Multiple additions of benzyl radicals to form $(C_6H_5CH_2)_n\dot{C}_{60}$ (n = 1 to at least 15) have been identified in an EPR study. The spin adducts with n = 3 and 5 are stable above 50 °C. The unpaired electrons are highly localized on the C₆₀ surface. It has also been shown in a mass spectrometric study that as many as 34 methyl radicals were added to C_{60} . Thus, C₆₀ has been characterized as a "radical sponge" Furthermore, radical additions to C_{60} are rapid and lead to highly functionalized C_{60} .^{2,3} However, C_{60} is sparingly soluble only in organic solvents. The chemical reactions of C_{60} in aqueous solution have not yet been reported.

Previously, we reported free radical reactions of water-soluble C_{60} derivatives, fullerenols⁴ and carboxyfullerene (trismalonic acid- C_{60}).^{5,6} These studies showed that water-soluble C₆₀ derivatives are potent free radical scavengers and provide protective potency toward neurons under oxidative stresses. These medical applications of water-soluble C_{60} derivatives and other recent studies of free radical reactions of fullerenes^{7,8} prompt us to further explore possible free radical reactions of native" C₆₀ in a hydrophilic environment.

Toward this goal, we recently successfully prepared C_{60} embedded in the nanochannels of amino-modified MCM-41 mesoporous materials which show hydrophilicity.9 The MCM-41 solids consist of hexagonal arrays of uniform 2 to 10 nm sized cylindrical pores.^{10,11} The amino-modified MCM-41 solids provide accessibility for anchoring other substrates, including transition metals ions, for many physical and chemical studies.¹² Thus, the amino-modification of the MCM-41 surface provides not only the binding sites for C_{60} , but also the hydrophilicity that enables us to study the free radical reaction of C60 in aqueous media. Furthermore, "single molecular chemistry" taking place in nano-restricted environments has recently aroused much interest in the chemical community.13 Reactions in which molecules are physically constrained could lead to much new fundamental understanding of the use of local environment to control chemical reactions. Among these, radical reactions are most intriguing

because of the possibility of reducing the random combination of radical species. For example, Turro recently described the photochemistry of dibenzyl ketones adsorbed on many zeolites.14 The reaction pathway becomes much restricted due to constrained diffusion of the intermediate radical species.

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In an attempt to explore the radical reactions of C₆₀ in aqueous solution and in confined space to mimic and understand the site specific reactivity in biological system, we undertook EPR studies of the free radical reactions of C₆₀ embedded in the nanochannels of amino-modified MCM-41 materials. These materials possess not only the above-mentioned hydrophilicity but also the following unique features: (1) large surface area, (2) specificity of rigid binding with C_{60} , and (3) selectivity of catalytic site, such as Fe²⁺ sites for the oxidation of H_2O_2 . The hydrophilicity of these materials is especially important for the study of hydroxyl radicals, an important class of free radical in biological systems.

Experimental

Methods of preparation: C₆₀ embedded in surface modified MCM-41 materials

The over-all methods of preparation consist of several steps: the preparation of MCM-41, surface functionalization, and the covalent attachment of C_{60} or C_{60}^{-} to the surface functional group. Since the procedure for the preparation of MCM-41 mesoporous materials has been given previously,15 below we briefly describe the last two steps of the preparation.

(1) The synthesis of amine-modified MCM-41 (MCM41-NH₂). The MCM-41 with amine functional group was synthesized in the following steps: 0.5 g of the calcined MCM-41 was placed in 100 ml toluene and stirred for 30 min. 2.5 g of 3-aminopropyltrimethoxysilane (APTS) was added to the resulting mixture. The above reaction was allowed to run overnight at 110 °C. The solids were washed twice with pure toluene and acetone, filtered, and dried under vacuum.

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(2) Binding of C_{60} and C_{60}^{-} on the amine-modified MCM-41 channels (MCM41-NH-C₆₀H). In order to increase the loading of C₆₀ in the hydrophilic MCM41-NH₂ channels, we prepared C₆₀ in a more hydrophilic form by one-electron reduction with mercury, which could then have higher affinity to the amine-functionalized pores. Thus, we adopted the following synthetic strategy to prepare the fulleride ions to bind with amines. The hydrophilic anion C_{60}^{-} species was prepared by mixing 40 mg C₆₀ with 130 mg tetrahexylammonium bromide in 40 ml THF and 2-3 drops Hg. The solution was heated to and maintained at 80 °C for 3 h under nitrogen atmosphere. The solution became dark red at the end of 3 h, which is the characteristic color of $C_{60}{}^-$ and $C_{60}{}^ N^+$ (hex)_4 radical ions. Next we prepared the target material by mixing the above solution with 200 mg MCM41-NH₂. After stirring the mixture for 12 h under nitrogen atmosphere, the solids were washed twice with toluene and acetone, filtered, and dried under vacuum.

EPR measurements

We employed an X-band EPR spectrometer (Bruker ER300) for our EPR measurements. A flat rectangular quartz sample cell (volume = 400 μ l) was used to measure the EPR spectra of aqueous liquid mixtures. A quartz tube of 4 mm OD was used for the solid sample. The spectrometer is equipped with a variable temperature set-up, which allows us to perform low temperature experiments (100 K to room temperature). A DPPH solid sample (g = 2.0037) was used as the reference standard for the g-value determination. Typical spectrometer parameters are: microwave frequency: 9.74 GHz, microwave power: 1–2 mw, modulation amplitude: 1–5 G (depends on the line width), multiple scans were often required to obtain good signal/noise ratio.

Generation and detection of hydroxyl radicals ('OH)

Hydroxyl radicals were generated via the Fenton reaction $(Fe^{2+} + H_2O_2)$. Since 'OH radicals are short-lived species, we employed a spin-trapping agent DMPO (5,5-dimethyl-1-pyroline N-oxide) to trap 'OH radicals and convert to stable nitroxides, DMPO-OH. The concentrations of the reagents used in the experiments were as follows: 100 mM DMPO, 5 mM H₂O₂, and 1 mM FeSO₄. The composition of a typical mixture of reagents used in an experiment was: 30 µl DMPO, 100 μ l H₂O₂, and 400 μ l FeSO₄. The mixture was vigorous shaking for 15 s, and the EPR spectrum of the liquid was taken 4 min after the mixing. The free radical scavenging capacity of MCM41-NH-C₆₀H, proportional to the decrease of EPR intensity, was measured by introducing the above reagents in proper order into 0-60 mg MCM41-NH-C₆₀H solids. A syringe filter was employed to extract the liquid from the liquid-solid mixture for EPR measurements.

Generation and detection of methyl radicals ('CH₃)

Methyl radicals were generated from the attack of hydroxyl radicals on dimethylsulfoxide (DMSO).^{16–18} Even though this is a secondary reaction, the reaction of ***OH** radical with DMSO is practically diffusion controlled with a bimolecular rate constant of $k = 7.2 \times 10^9$ M⁻¹ s⁻¹.¹⁹ Thus, it is feasible to generate *****CH₃ quantitatively for our scavenging studies. Since the lifetime of *****CH₃ radicals is extremely short (<200 ns at room temperature),²⁰ again we employed the spin-trapping agent DMPO to trap *****CH₃ radicals.

The concentrations of the reagents used in the experiments were 100 mM DMPO, 10 mM H_2O_2 , and 10 mM $FeSO_4$. The composition of a typical mixture of reagents used in the experiment was 400 µl DMSO, 30 µl DMPO, 300 µl $FeSO_4$, and 100 µl H_2O_2 . The mixture was vigorous shaking for 15 s and the EPR spectra of the liquid were taken 5 min after the

mixing. A portion of 0-50 mg MCM41-NH-C₆₀H was added to the mixture to examine its effect on the EPR intensity. A syringe filter was used to extract the liquid from the mixture.

Results and discussion

Physical properties of C_{60} embedded in surface modified MCM-41 materials

Previously, our spectroscopic studies (EPR, NMR, XRD, FTIR and UV–vis) showed that C_{60} molecules are embedded in the channels of the solids.^{9,12} Below we briefly summarize three of the physical properties of C_{60} embedded in the channels of MCM41-NH₂ solids to facilitate our discussion of the results: (1) The elemental analysis shows MCM41-NH-C₆₀H solids contain 5.41% C_{60} (equivalent to 0.75 µmol C_{60} per 10 mg of solid), (2) the surface area is 234 m² g⁻¹ for MCM41-NH-C₆₀H solids, a substantial reduction in comparison with 1015 m² g⁻¹ for the unmodified MCM-41, and (3) the pore diameter of the mesoporous material has also been reduced from 2.7 nm (unmodified) to 1.7 nm (high C_{60} loading). A schematic structure of MCM41-NH-C₆₀H solid is displayed in Scheme 1.

We shall discuss the attack of 'OH and ' CH_3 radicals on C_{60} with respect to the localization of free radical generation sites (Fe²⁺) either on the inner surface of nanochannels or in the bulk solution (outer surface of the channels).

Attack of 'OH free radicals on C_{60} embedded in nanochannels of MCM41-NH- C_{60} H solids

The formation of 'OH radical and its subsequent fate in the presence of DMPO are given in the following chemical reactions:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH(Fenton reaction)$$
 (1)

$$DMPO + OH \rightarrow DMPO-OH$$
 (2)



Scheme 1 Schematic structure of MCM41-NH-C₆₀H solids.

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Fig. 1 EPR spectra of 'OH radicals generated from the Fenton reaction in the presence of DMPO. The spectra were taken in a flat quartz cell (volume = 400 μ l). Solids were removed before the EPR measurements. (a) No MCM41-NH-C₆₀H was added, (b) Fe²⁺ was added to the 10 mg MCM41-NH-C₆₀H solids in the final step of the Fenton reaction, and (c) Fe²⁺ was added to the 10 mg MCM41-NH-C₆₀H solids at the beginning to form catalytic sites in the channel of mesoporous materials, and H₂O₂ was added to the mixture 1 min later to initiate the Fenton reaction. The spectrometer settings and the amounts of sample were kept the same for each of the above 3 spectral measurements.

The EPR spectrum of the **'DMPO-OH** spin adducts displays a characteristic 1:2:2:1 hyperfine splitting pattern $(a_{\rm N} = a_{\rm HB} = 14.96$ G, Fig. 1a).

Next we examine the efficacy of 'OH scavenging by C_{60} embedded in the channel of MCM41-NH-C₆₀H mesoporous materials by monitoring the signal intensity of 'DMPO-OH spin adducts. We compare two EPR spectra of a given composition under the exact experimental conditions except that the order of adding the reagents to the mixture was different: (1) Fe^{2+} solution was added to the mixture (DMPO+ $H_2O_2 + MCM41$ -NH-C₆₀H) as the *final* component in the generation of 'OH radicals (Fig. 1b), and (2) Fe²⁺ was added to MCM41-NH-C₆₀H solids *first*, after shaking for 1 min, DMPO and H_2O_2 were then added to the mixture (Fig. 1c). The purpose of the second EPR measurement was to allow Fe²⁻ to enter the channels and anchor on the surface (bound with amino-groups) in the vicinity of C₆₀ sites. The Fenton reaction was initiated by further addition of H₂O₂ to generate 'OH radicals. Thus, these two experiments allow us to examine the proximity effect of the Fe^{2+} sites ('OH source) relative to the C₆₀ sites (sink) on the scavenging capacity of MCM41-NH-C₆₀H.

The EPR intensity (based on the signal height of the second peak) as a function of the amount of MCM41-NH-C₆₀H solids present in the Fenton reaction is shown in Fig. 2. Note that the solids were removed before the EPR spectra were taken. We observed that the intensity decreased to nearly zero when Fe^{2+} was added as the final component to 50 mg MCM41-NH-C₆₀H solids, containing the liquid mixture of all other substrates as given in the Experimental section (Fig. 2a). On the other hand, it required only 10 mg MCM41-NH-C₆₀H to produce the same effect when Fe^{2+} was added to MCM41-NH-C₆₀H at the very beginning (Fig. 1c and 2b). Under the same spectrometer settings, experimental conditions and sample volume (400 µl), the observed EPR signal intensity is



Fig. 2 EPR intensity of *****DMPO–OH radical (height of the 2nd peak, see Fig. 1) *vs.* the amount of MCM41-NH-C₆₀H added to the Fenton reaction. The spectra were taken in a flat quartz cell (volume = 400 µl). Solids were removed before the EPR measurements. (a) Fe^{2+} was added to the MCM41-NH-C₆₀H solids in the final step of the reaction, and (b) Fe^{2+} was added at the beginning of the reaction to prepare the catalytic site in the proximity of C₆₀ sites. The spectrometer settings and the amounts of sample were kept the same for each of the above spectral measurements.

proportional to the steady state concentration of the **'DMPO-OH** spin adducts (reaction (2)), we are able to quantify the efficacy of free radical scavenging in these two different runs: they differ by a factor of five.

The reported rate constant for the addition reaction of 'OH to DMPO $2.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (reaction (2)),^{21,22} which is about one order of magnitude greater than the rate of many addition reactions of free radicals to C₆₀(10⁸ M⁻¹ s⁻¹).^{2,3} Thus,'OH radicals can be trapped by DMPO more effectively than C₆₀ in a given time after the initiation of the Fenton reaction. Below we further examine the difference between these two procedures:

(1) When Fe^{2+} was added to the mixture in the final step, the 'OH radicals were generated instantaneously upon the addition of Fe^{2+} . These radicals could be readily trapped by DMPO in the solution. The bulky 'DMPO–OH spin adducts may then enter the channel of mesoporous material at a slower rate and react with the C₆₀ embedded in the MCM41-NH-C₆₀H solids.

(2) When Fe^{2+} was added to the mesoporous materials before the introduction of all other components, Fe^{2+} was allowed to complex with $-NH_2$ groups of the modified channel surface in the vicinity of C_{60} sites. When H_2O_2 was introduced into the mixture, H_2O_2 diffuses into the channels and reacts with Fe^{2+} to generate multiple 'OH radicals, which can be readily scavenged by the nearby C_{60} sites.

It has been reported that the efficiency of hydroxyl radical generation in the Fenton reaction varies with the nature of the iron chelators used. For instance, a strong ligand, such as diamine group in EDTA, has a higher rate constant than a poor ligand, such as diphosphate group in ADP.²¹ Thus, one expects that the ligation of Fe^{2+} with NH₂ groups will enhance the generation of 'OH, not diminish it, a counter-intuitive effect. Nevertheless, we attribute the decrease of 'DMPO–OH intensity to the close proximity of Fe^{2+} and

 C_{60} on the surface of the mesoporous channels providing nano-restricted environments (nanoreactor), which could facilitate (a catalytic effect) the attack of 'OH radicals on C_{60} , even though we may underestimate the ligation effect. Consequently, less 'OH will be available to react with DMPO and the EPR signal intensity will therefore be reduced.

Free radical scavenging capacity of acidified MCM41-NH- C_{60} H solids

In order to confirm that the catalytic site of Fe^{2+} is situated inside the channel of MCM41-NH-C₆₀H solids, we performed another experiment by acidifying the wall surface with 0.4 M H₂SO₄ solution to convert the free -NH₂ (the original unbound $-NH_2$, see Scheme 1) to $-NH_3^+$. When the wall surface is positively charged upon acidification, the positively charged Fe²⁺ ions can no longer enter the channels easily due to the electrostatic repulsive force, *i.e.*, the added Fe^{2+} will remain on the outside of the channels and in the bulk solution. Then the order of addition of Fe^{2+} to the reaction mixture to generate 'OH radicals was immaterial, and the amount of MCM41-NH-C₆₀H solids present in the mixture to scavenge a given amount of 'OH radicals was the same, based on the EPR signal intensity (Fig. 3). This is strikingly different from the above observation where Fe^{2+} was preloaded onto the channel inner surface, near the C₆₀ sites, and was ready to react with the nascent 'OH free radicals.

Attack of 'CH₃ radicals on MCM41-NH-C₆₀H solids

As mentioned previously, ${}^{\circ}CH_3$ can be generated from the reaction between DMSO and ${}^{\circ}OH.^{15-17}$ The formation of ${}^{\circ}CH_3$ radical and its subsequent fate in the presence of DMPO may be described by the following reactions:

$$(CH_3)_2SO + {}^{\bullet}OH \rightarrow (CH_3)_2(OH)SO^{\bullet}$$
 (3)

$$DMPO + (CH_3)_2(OH)SO^{\bullet} \rightarrow {}^{\bullet}DMPO - OS(OH)(CH_3)_2 \quad (4)$$

$$(CH_3)_2(OH)SO^{\bullet} \rightarrow {}^{\bullet}CH_3 + CH_3SO_2H$$
(5)

$$^{\bullet}CH_{3} + H_{2}O_{2} \rightarrow CH_{3}OH + ^{\bullet}OH$$
(6)

$$DMPO + CH_3 \rightarrow DMPO - CH_3$$
 (7)

The identity of ${}^{\bullet}CH_3$ radical as an intermediate spin adduct (reaction (5)) has been established previously.^{15–18}

The EPR spectra of DMSO attacked by 'OH radicals (generated from the Fenton reaction) in the presence of DMPO are shown in Fig. 4: (1) no MCM41-NH-C₆₀H was added (Fig. 4a), (2) Fe²⁺ was added to MCM41-NH-C₆₀H solids in the final step of the Fenton reaction (Fig. 4b), and (3) Fe²⁺ was added to MCM41-NH-C₆₀H solids at the beginning and was allowed to bind with the amino- functional groups forming the catalytic site for the decomposition of H₂O₂ (Fig. 4c). The observed hyperfine splittings of the sample with zero amount of MCM41-NH-C₆₀H solids are assigned to two major spin adducts:⁶ (1) 'DMPO-OS(OH)(CH₃)₂ (reaction (4)), $a_{\rm N} = 15.0$ G and $a_{\rm H} = 10.2$ G, and (2) 'DMPO-CH₃ (reaction (7)), $a_{\rm N} = 16.4$ G and $a_{\rm H} = 23.7$ G (g = 2.00540).

The rate constant for the addition reaction of 'OH to DMSO (reaction (3))¹⁸ is 7.2×10^9 M⁻¹ s⁻¹ which is faster than those for reactions (2) and (7). The EPR intensity is proportional to the steady state concentration which is governed by the formation and disappearance of 'CH₃ in the following pathways: (1) formed by the unimolecular dissociation of (CH₃)₂(OH)SO' (reaction (5)), (2) reacted with excess amount of H₂O₂ to yield CH₃OH and 'OH (reaction (6)) and with DMPO to form 'DMPO–CH₃ (reaction(7)),⁶ and (3) removed effectively by MCM41-NH-C₆₀H (the reaction of 'CH₃ with C₆₀).¹² Since the steady concentration of 'DMPO–CH₃



Fig. 3 EPR intensity of the 'DMPO–OH radical (height of the 2nd peak) *vs.* the amount of surface acidified MCM41-NH-C₆₀H solids (pretreated with 400 μ l of 0.4 M H₂SO₄, see text) added to the Fenton reaction. The spectra were taken in a flat quartz cell (volume = 400 μ l). Solids were removed before the EPR measurements. (a) Fe²⁺ was added to the acidified MCM41-NH-C₆₀H solids in the final step of the Fenton reaction, and (b) Fe²⁺ was added to the acidified MCM41-NH-C₆₀H at the beginning of the Fenton reaction. There is little difference between these two sets of experiments due to the fact that Fe²⁺ cannot enter the channels. Note that the channel surface of the acidified solid is occupied by positively charged –NH₃⁺which is electrostatically repulsive to Fe²⁺.



Fig. 4 EPR spectra of DMSO attacked by 'OH radicals (from the Fenton reaction) in the presence of DMPO. The spectra were taken in a flat quartz cell (volume = 400 µl). Solids were removed before the EPR measurements. (a) no MCM41-NH- C_{60} H was added, (b) Fe²⁺ was added to the 10 mg MCM41-NH- C_{60} H solids in the last step of the Fenton reaction, and (c) Fe²⁺ was added to the 10 mg MCM41-NH- C_{60} H solids at the beginning to form catalytic sites for the decomposition of H₂O₂. The spectrometer settings and the amounts of sample were kept the same for each of the above 3 measurements.

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Fig. 5 EPR intensity of 'DMPO-CH₃ vs. the amount of MCM41-NH-C₆₀H added to the mixture. The spectra were taken in a flat quartz cell (volume = 400 μ l). Solids were removed before the EPR measurements. (a) Fe²⁺ was added in the final step, and (b) Fe²⁺ was added at the beginning of the free radical reaction. The spectrometer settings and the amount of samples were kept the same for each of the above measurements.

decreased to nearly zero when Fe^{2+} was introduced in the final step of the Fenton reaction in the presence of 25 mg MCM41-NH-C₆₀H solids (Fig. 5a), we infer that the scavenging potency of MCM41-NH-C₆₀H solids is relatively high. On the other hand, it took 10 mg MCM41-NH-C₆₀H to observe the same effect when Fe^{2+} was introduced in the initial step (Fig. 5b). That is the scavenging of °CH₃ by MCM41-NH-C₆₀H is a factor of 2.5 more effective when Fe^{2+} ions were added initially to the mesoporous mixture. Thus, we observed a similar proximity effect in the free radical reactions of C₆₀ taking place in the nanoreactor.

The catalytic site of iron in MCM41-NH2 and MCM41-NH- $\mathrm{C_{60}H}$ solids

In order to confirm that Fe^{2+} or Fe^{3+} (oxidized) is securely bound on the channel surface of mesoporous solids to initiate the Fenton reaction, we performed the following experiments to characterize the catalytic sites. A mixture of Fe^{2+} and MCM41-NH₂ or MCM41-NH-C₆₀H solid was stirred for 2 min, filtered, washed thrice with water, filtered and dried under vacuum. Since Fe^{2+} is easily oxidized to Fe^{3+} upon exposure to the air, we monitored the Fe^{3+} coordination in the following solid-state EPR measurements at 100 K:

(1) Fe³⁺ in MCM41-NH₂ solids: We observed two strong broad signals at $g_1 = 4.30$ and $g_2 = 2.00$ (Fig. 6a). These two signals are the characteristic signature of iron-containing zeolites, where Fe³⁺ may be either on the framework of the zeolites or extraframework.²³ Since we washed the solids with water to remove excess Fe³⁺ on the outer surface, we can ascertain that the signals must arise from Fe³⁺ complexing with –NH₂ on the surface of the mesoporous materials (extraframework). The signal at $g_2 = 2.00$ has been assigned to Fe³⁺ in octahedral²⁴ or tetrahedral coordination,^{23,25} and the signal at $g_1 = 4.30$ to Fe³⁺ in tetrahedral coordination with strong rhombic distortion.²⁴⁻²⁶

(2) Fe^{3+} in MCM41-NH-C₆₀H solids: The binding of bulky C₆₀ on the surface of the nanochannels of MCM41-NH₂ solids



Fig. 6 EPR spectra of Fe^{3+} ions in the following solids at 100 K: (a) MCM41-NH₂, and (b) MCM41-NH-C₆₀H.

will reduce the amount of Fe^{3+} ions that may bind on the surface of mesoporous solids for the following two reasons: (a) Some of the amine groups are already bound with C_{60} , so the amount of amine available to bind with Fe^{3+} will be less. (b) The bulky C_{60} in the nanochannels will further restrict the pathway and provide less room for Fe^{3+} to bind on the surface.

The reduced Fe³⁺ concentration in the MCM41-NH-C₆₀H solids therefore yields poor signal/noise ratio in the EPR spectra of the sample (*cf.* Fig. 6a and b). Nevertheless, we still observed two signals at g = 4.30 and 2.00. We further observed a new intense sharp peak at $g_3 = 2.002$ which has been assigned to fulleride radicals (Fig. 6b).^{8,27,28} Thus, we infer that iron ions can bind with the amine groups in the channels of MCM41-NH-C₆₀H solids and serve as the catalytic sites for the decomposition of H₂O₂.

Conclusion

We have demonstrated several important effects in employing MCM-41 as a "nanoreactor" in this study. Firstly, the reaction of C₆₀ is performed in otherwise inaccessible aqueous media. Proper surface functionalization of MCM-41 mesoporous materials with amino-groups allows C₆₀ to bind to the channel surface which provides hydrophilicity and makes the study of free radical reactions of C₆₀ in aqueous solution feasible. Secondly, we can control the distribution of reactants in proximity, where C₆₀ (radical scavenging sites) and Fe^{2+} (free radical generating sites, a catalytic site) are prepared in close proximity in the nanochannels. The modified MCM-41 samples thus allow us to study the scavenging efficiency of C₆₀ for hydroxyl and methyl radicals in aqueous solution and in nano-restricted environments. We observed a substantial enhancement of radical scavenging by C₆₀ when Fe^{2+} is located in close proximity. Thus, we may apply a synthetic strategy to generate free radicals or other reactive species inside the channels of mesoporous materials to facilitate the reaction and yield the desired products. We may also control the reaction pathways in a confined space if there exist complex chemical reactions. Thirdly, the reactions are isolated in separate channels, which effectively makes the concentration much higher where avoiding the random attacks between fastreacting free radical species. Nanoreactors therefore open the possibility of "single molecule chemistry",29 otherwise accessible only in extreme dilution. Thus, these mesoporous materials with 2 to 10 nm pores provide the means and opportunity to

probe complex chemical reactions of C_{60} and other bulky substrates in nanoreactors.

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References

- (a) P. J. Krusic, E. Wasserman, P. N. Keizer, J. R. Morton and K. F. Preston, *Science*, 1991, **254**, 1183; (b) P. J. Krusic, E. Wasserman, B. A. Parkinson, B. Malone, E. R. Holler, P. N. Keizer, J. R. Morton and K. F. Preston, *J. Am. Chem. Soc.*, 1991, **113**, 274.
- 2 C. S. Foot, Top. Curr. Chem., 1994, 169, 347.
- 3 N. M. Dimitrijvic, Chem. Phys. Lett., 1992, 194, 457.
- 4 L. L. Dugan, J. K. Gabielsen, S. P. Yu, T.-S. Lin and D. W. Choi, *Neurobiol. Dis.*, 1996, 3, 129.
- 5 L. L. Dugan, D. M. Turetsky, C. Du, D. Lobner, M. Sheeler, R. Almli, C. F.-F. Shen, T.-Y. Luh, D. W. Choi and T.-S. Lin, *Proc. Nat. Acad. Sci. USA*, 1997, **94**, 9434.
- 6 T.-S. Lin, L. L. Dugan and T.-Y. Luh, *Appl. Magn. Reson.*, 2000, 18, 321.
- 7 I. V. Koptyug, A. G. Goloshevsky, I. S. Zavarine, N. J. Turro and P. J. Krusic, J. Phys. Chem. A, 2000, 104, 5726.
- 8 C. A. Reed and R. D. Bolskar, Chem. Rev., 2000, 100, 1075.

- 9 C.-H. Lee, T.-S. Lin, H.-P. Lin, Q. Zhao, S.-B. Liu and C.-Y. Mou, *Microporous Mesoporous Mater.*, submitted.
- 10 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, T. W. Chu, D. H. Olson, E. W. Sheppard, S. B. Higgins and J. L. Schlenker, J. Am. Chem. Soc., 1992, 114, 10834.
- 11 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
- 12 C.-H. Lee, MS Thesis, National Taiwan University, July, 2001.
- 13 M. Antonietti, K. Landfester and Y. Mastai, Israel J. Chem., 2001, 41, 1.
- 14 N. J. Turro, Acc. Chem. Res., 2000, 33, 637.
- 15 H.-P. Lin, Y.-R. Cheng, C.-R. Lin and F.-Y. Li, et al., J. Chin. Chem. Soc., 1999, 46, 495.
- M. K. Eberhardt and R. Colina, J. Org. Chem., 1988, 53, 1071.
 J. Woodward, T.-S. Lin, Y. Sakaguchi and H. Hayashi, J. Phys.
- Chem. A, 2000, **104**, 557. 18 J. Woodward, T.-S. Lin, Y. Sakaguchi and H. Hayashi, Appl.
- Magn. Reson., 2000, **18**, 333. 19 G. Meissner, A. Henglein and G. Beck, Z. Naturforsch. B, 1967,
- 22, 13.
 20 D. M. Bartels, R. G. Lawler and A. D. Trifunac, *J. Chem. Phys.*, 1985, 83, 2686.
- 21 (a) I. Yamazaki and L. H. Piette, J. Biol. Chem., 1990, 265, 13589; (b) J. Am. Chem. Soc., 1991, 113, 7588.
- 22 E. Finkelstein, G. M. Rosen and E. J. Rauckman, J. Am. Chem. Soc., 1980, 102, 4994.
- 23 D. Goldfarb, M. Bernardo, K. G. Strohmaier, D. E. W. Vaughan and H. Thomann, J. Am. Chem. Soc., 1994, 116, 6344.
- 24 W. A. Carvalho, M. Wallau and U. Schuchardt, J. Mol. Catal. A, 1999, **144**, 91.
- 25 J. W. Park and H. Chon, J. Catal., 1992, 133, 159.
- 26 J. Matta, J. F. Lamonia, E. Abi-Aad, E. A. Zhidinskaya and A. Aboukais, *Phy. Chem. Chem. Phys.*, 1999, 1, 4975.
- 27 R. Taylor, M. P. Barrow and T. Drewello, *Chem. Commun.*, 1998, 2497.
- 28 P. Paul, R. D. Bolskar, A. M. Clark and C. A. Reed, *Chem. Commun.*, 2000, 1229.
- 29 M. Antonietti and K. Landfester, ChemPhysChem, 2001, 2, 207.