

Supramolecular complexes of photoexcited functionalized fullerenes and spin labeled alkyl ammonium derivatives.

Carlo Corvaja^a, Elena Sartori^a, Antonio Toffoletti^a, Michele Maggini^b, and Luigi Garlaschelli^c

^a) Department of Physical Chemistry, University of Padova, via Loredan, 2, 35131 Padova (Italy)

^b) Department of Organic Chemistry, University of Padova, via Marzolo, 1, 35131 Padova (Italy)

^c) Department of Organic Chemistry, University of Pavia, viale Taramelli, 10, 27100 Pavia (Italy)

INTRODUCTION

With the aim to obtain materials which can exhibit new properties, functionalized [60]fullerene compounds have been incorporated in a variety of structures containing two counterparts as for example photoactive and electroactive groups. In order to exploit the versatility and reversibility of supramolecular interaction, new systems have been developed combining two interacting moieties linked through a noncovalent bond (1). The synthesis and the complexing ability towards primary alkyl ammonium ions of some methanofullerenes prepared from cyclic malonic esters were recently reported (2). In this work we present the results of a study performed using time resolved EPR (TR-EPR) on these compounds.

RESULTS AND DISCUSSION

A series of these [60] fullerenes crown malonates and a malonate-derived methanofullerene bearing a 18-crown-6 moiety (3) were photoexcited in chloroform solution to their lowest triplet state by visible laser light pulses. TR-EPR spectra were recorded in the microsecond time range with 100 ns resolution. The spectra consist of a broad line typical of triplet [60]fullerene derivatives. The signal life time is of the order of 5 μ s at room temperature. In the presence of nitroxide spin labeled derivatives, the recorded spectra are the superposition of the triplet line and of the three line spectrum, with hyperfine separation of about 1.5 mT, characteristic of nitroxide radicals in solution. Conversely, in the presence of spin labeled molecules containing a protonated amino group a quite different TR-EPR spectral pattern is observed. Three additional lines separated by 0.5 mT and centered at higher field appear.

Three lines with these characteristic features were observed in other cases, where a [60]fullerene triplet (electron spin $S=1$) and a nitroxide free radical ($S=1/2$) were covalently bound (4,5). The coupling of the two electron spins to form a quartet species ($S=3/2$) and the hyperfine coupling to the ^{14}N nuclear spin of the nitroxide account for this pattern.

For our systems the observation of the quartet spectrum when the photoexcited [60]fullerene derivative is in the presence of a spin labeled primary alkyl ammonium ion is a clear indication of the formation in solution of a host-guest supramolecular complex. Figure 1 shows typical TR-EPR spectra recorded for different types of systems.

With these systems we exploit the fact that in modified fullerene compounds the triplet spin is localized on the fullerene moiety and its distribution is weakly affected by the added groups. On the other hand, the unpaired electron of the spin labeled molecule is localized on the nitroxide group and it does not interfere with the ammonium group, which is involved in the host-guest

interaction with the macrocycle. Therefore, the electron spins present in the two partners are used simply as probes for studying the supramolecular interaction. The investigation is favored also by the relatively long lived triplet excitation and by the stability of the nitroxide free radicals.

In this work we analyze how the TR-EPR lineshape is affected by the chemical equilibrium between the unassociated triplet excited [60]fullerene compound and the spin labeled alkyl ammonium ion, and the possible information one gets about the dynamics of the association equilibrium.

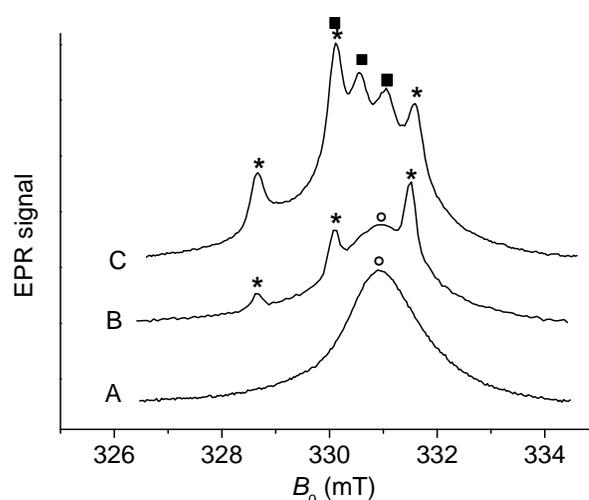


Figure 1. Typical TR-EPR spectra of 5 mM chloroform solution of [60]fullerene crown ether (A) and of the same compound in the presence of a nitroxide radical (B) and in the presence of an alkyl ammonium nitroxide radical (C). The open circle indicates the broad line due to the triplet excited species. Stars indicate the three lines due to the nitroxide radical and full squares the three lines due to the host-guest complex in the excited quartet state.

ACKNOWLEDGEMENTS

This work was supported by MIUR (Contract prot. MM031098284) and by CNR (legge 95/95).

REFERENCES

1. M. Gomez-Lopez, F. Diederich, *Chem. Soc. Rev.*, **28**, 263 (1999).
2. M. Carano, C. Corvaja, L. Garlaschelli, M. Maggini, M. Marcaccio, F. Paolucci, D. Pasini, P. P. Righetti, E. Sartori, A. Toffoletti, *Eur. J. Org. Chem.* in press.
3. E. Sartori, L. Garlaschelli, A. Toffoletti, C. Corvaja, M. Maggini, G. Scorrano, *Chem. Commun.*, 311, (2001).
4. C. Corvaja, M. Maggini, M. Prato, G. Scorrano and M. Venzin, *J. Am. Chem. Soc.*, **117**, 8857 (1995).
5. F. Conti, C. Corvaja, M. Maggini, F. Piu, G. Scorrano, A. Toffoletti, *Appl. Magn. Reson.*, **13**, 337 (1997).