

PHOTOCHEMICAL REDUCTION OF WATER-SOLUBLE C₆₀ DERIVATIVES (EPR STUDY)

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The photoinduced electron transfer to water-soluble C₆₀ mono-adducts and various bis-functionalized C₆₀ derivatives (Fig.1) was investigated by EPR spectroscopy in heterogeneous water/2-propanol TiO₂ system, and additionally, in aqueous solutions containing *L*-ascorbic acid as an electron donor. Upon continuous irradiation in both experimental photosystems radical species of identical nature were generated, which were attributed to the fullerenes anion-radicals [1].

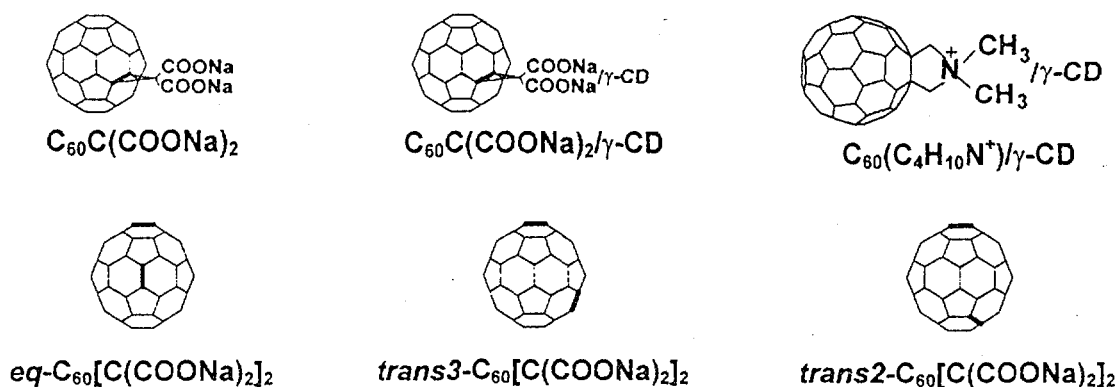


Figure 1

Fullerenes under study (bold bonds indicate $>C(COONa)_2$ functionalization).

Mono-functionalized C₆₀ derivatives encapsulated in γ -cyclodextrine (γ -CD) produced by irradiation an EPR signal A, characterized by $g_A = 2.0000$, peak-to-peak width, $pp_A = 0.095$ mT, assigned to the fullerenes mono-anion [2,3]. EPR signal A transforms with continuing irradiation into radical B and C ($g_B=2.0005$, $g_C=2.0009$). This behaviour is independent on the nature and electronic properties of the functionalizing addend, and is closely similar to the *in situ* reduction of pristine C₆₀ in organic solvents [2-4]. The yield of photochemical electron transfer to $C_{60}C(COONa)_2$ in aqueous solutions is quite low, because of the instantaneous formation of fullerene clusters [5].

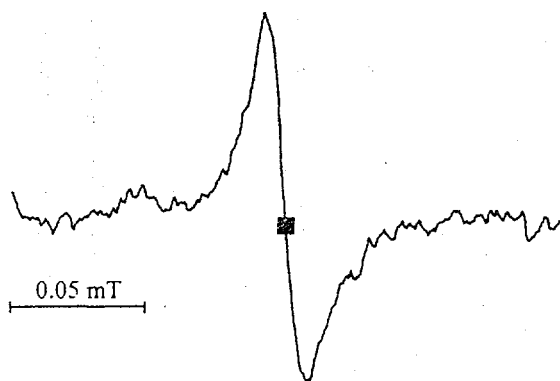


Figure 2

EPR spectrum observed upon continuous irradiation of 0.1 mM *eq*-C₆₀[C(COONa)₂]₂ in water/2-propanol (6:1 v/v) TiO₂ suspension (0.3 mg/ml TiO₂).

■...M, $g_M=2.0007$, $pp_M=0.01$ mT.

The photochemical reduction of three bis-functionalized C₆₀ derivatives resulted in the formation of a single radical product (Fig.2), characterized by relatively narrow EPR line ($g_M=2.0007$, $pp < 0.02$ mT). The observed EPR line narrowing probably reflect the partially broken symmetry in the bis-substituted fullerenes relative to pristine C₆₀ [6]. In the irradiated aqueous solutions containing *L*-ascorbic acid, in the addition to the EPR line related to bis-adduct mono-anion, also 6-line EPR spectrum of ascorbyl radical was observed. Consequently, the photoinduced formation of ascorbyl radical was attributed to the intermolecular quenching of fullerenes excited states [1].

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