

SAMPLE PREPARATION AND CHARACTERIZATION

Synthesis of $\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{32}$, $[\text{Ti}_{16}]$. A mixture of 33.4 mmol of $\text{Ti}(\text{OEt})_4$ dissolved in 7 mL of ethanol and 16.7 mmol of neutral water was placed in a steel autoclave at 100°C for 2 weeks. Crystals were isolated from the solution after slow cooling (1K/h) and further dried and stored in an inert atmosphere.

Synthesis of $[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{24}(\text{OEMA})_8]$. $[\text{Ti}_{16}]$ (0.40 mmol) was dissolved in 10 mL of toluene, an excess of 2-hydroxyethyl methacrylate (25.6 mmol) was added and this mixture was placed at 50°C for 3 days. The final product is recovered after vacuum evaporation of the volatiles.

Preparation of the hybrid organic-inorganic nanomaterials. For UV curing the 2-hydroxy-2-methyl-1-phenyl-1-propanone (Darocur 1173) photoinitiator was used in a concentration of 4% wt. The mixtures were applied to a mould 1 mm-thick and polymerized with a polychromatic (312 nm, 360 nm, 410 nm, 440 nm, 550 nm, 575 nm) UV lamp 120 W/cm during 108 s.

Determination of conversion by Near FT-IR spectroscopy. Near InfraRed spectra were recorded on a Bruker Equinox 55 spectrometer. The conversion, defined as the percentage of total reacted double bond, was evaluated by the disappearance of first harmonic band of C-H of the methacrylic double bond between 6,098 and 6,238 cm^{-1} .

Dynamic mechanical analyses. Viscoelastic properties were determined using a RSA II rheometer from Rheometric Scientific in tensile mode on thin films applying a dynamic strain of 0.05% at a given frequency of 1Hz. Measurements were performed during a temperature ramp from -100°C to 200°C at 4K.min⁻¹. The dimensions of specimens were 23×5×1 mm³.

Transmission Electron Microscopy. TEM, was performed using a Philips CM120 microscope from Philips on microtomed sections of the cured polymethacrylate polymer and related nanomaterials.

NMR spectroscopy. ¹⁷O spectra were recorded on a Bruker Avance 400 MHz spectrometer equipped with a 10-mm broadband probe head.

FTIR spectroscopy. The FTIR spectra were recorded on Nicolet Magna-IR Spectrometer 550 in the 4000-300 cm^{-1} frequency range. Wavenumbers are expressed in reciprocal centimetres.

EPR spectroscopy. EPR spectra of the irradiated samples were recorded on a Bruker ESP 300E instrument at 77 K.

Characterization of [Ti₁₆O₁₆(OEt)₂₄(OEMA)₈]

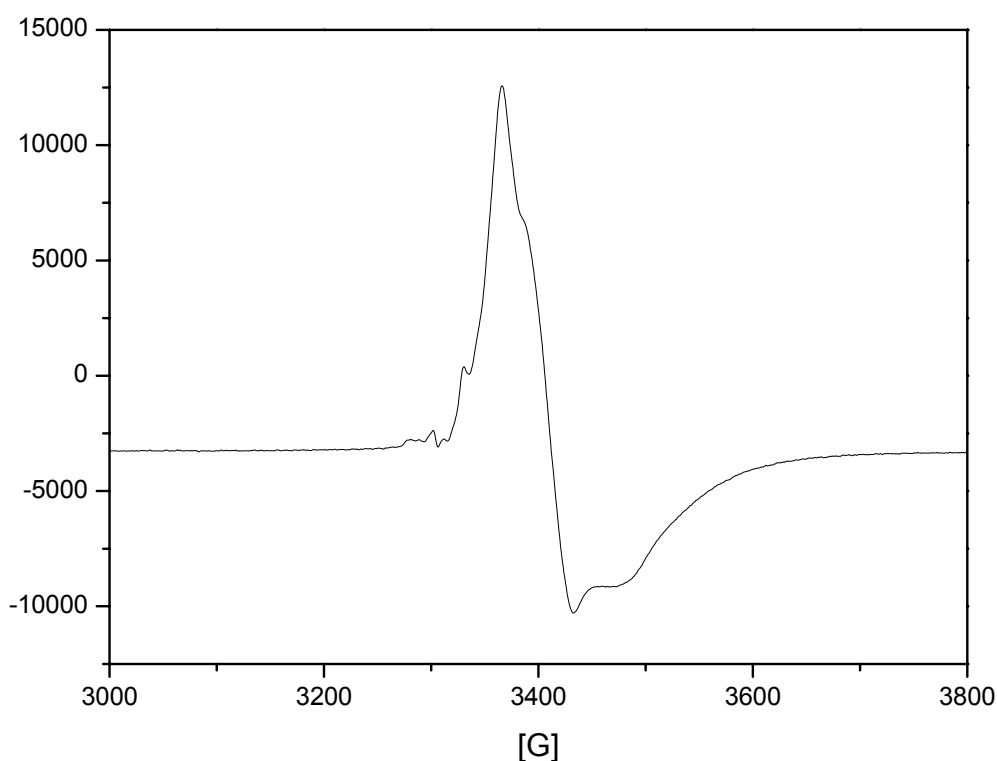
¹⁷O NMR (C₆D₆, δ ppm): 750 (4 μ₂O), 570, 555 (8 μ₃O), 380 (4 μ₄O).

FTIR: 2950, 2880: ν(CH₂,CH₃), 1720 ν(COO), 1638 ν(C=C), 1472 ν(CH₃ asym), 1462 δ(CH₂), 1377, 1356, 1296: δ(CH), 1210-1048 ν(C-OTi), large bande 580 ν(Ti-O-Ti). No vibrations due to carboxylate groups bonded to titanium, ν_s(COO)=1453, ν_{asym}(COO)=1538, were observed.

Characterization of irradiated [Ti19.2] polymer

The EPR spectrum of irradiated hybrid material is shown in Fig. S1. These measurements were conducted at T=77 K. A comparison with results from Refs [1,2] gives evidence of a strong resonance due to Ti³⁺ with correspondent perpendicular and parallel components g_⊥=1.961 and g_{||}=1.998.

Fig. S1: EPR spectrum of irradiated [Ti19.2] polymer



- 1 R. F. Howe and M. Grätzel, *J. Phys. Chem.*, 1985, **89**, 4495.
- 2 M. Grätzel and R. F. Howe, *J. Phys. Chem.*, 1990, **94**, 2566.