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Enhanced Raman scattering provided by endometallofullerene nanoclusters.

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The search for novel molecules displaying optimal nonlinear optical properties (NLO) is currently an intense area of research in both academia and industry. Fullerenes and its derivatives are intriguing candidates for study as NLO chromophores by virtue of their highly delocalized p-electron systems.

In this paper NLO photo-physical properties of $M@C_{2n}$ ($M = Gd, Ce, La$) were studied. Examined endometallofullerenes were produced by composite graphite rods evaporating in DC electric arc discharge at helium atmosphere followed by extraction in polar solvents. Mass-spectrometry measurements show that our $M@C_{2n}$ was in anion form. Microscopic investigations indicate that $M@C_{2n}$ formed nanoparticles (50-60 Å in diameter) in solutions and on the substrate surface

From the literature it is known that the $M@C_{2n}$ dominant absorption and luminescence peaks corresponding to HOMO-LUMO transitions are situated at IR-region. We found that $M@C_{2n}(-)$ dimethylformamide (DMF) solutions show photoluminescence emissions in the visible region. Significantly (10^6) enhanced Raman scattering from $M@C_{2n}$ nanoparticles was revealed. Giant Raman scattering effect took place only in or near the $M@C_{2n}$ DMF solution luminescence wavelength region. We demonstrated that conducting polymer- poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene (MEN-PPV) doped with endometallofullerenes exhibits novel photo-induced characteristics. If we formed on the MEN-PPV surface gradient doping layer with $M@C_{2n}$ its luminescence efficiency significantly enhanced. A mechanistic pathway for the Raman scattering amplification and luminescence efficiency enhancement is discussed.