Non-linear optical properties of the inorganic cluster $[(\eta\text{-}C_5H_5)CoFe_2SSe(CO)_6]$

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Non-linear refraction and absorption have been studied in a mixed-metal, mixed chalcogenide cluster. The cluster displays optical limiting significantly superior to that displayed by C_{60}.

The relentless search for materials with good non-linear optical response has led to impressive strides in understanding existing materials as well as the design and synthesis of new types of molecules.[1] In particular, there has been great interest in finding better non-linear media for the process of optical limiting.[2] Organic systems like dyes, porphyrins and fullerenes have been explored in considerable detail.[2–4] Some transition-metal cluster compounds have also been investigated for their potential for response comparable to or exceeding that of C_{60}.[5–8]

Cluster compounds which contain one or more bridging chalcogen ligands have recently been attracting considerable attention.[9] It is possible to design the construction of certain classes of mixed-metal clusters in which different combinations of chalcogen ligands can be incorporated.[10] Recently we have synthesised and structurally characterised the first example of a mixed-metal cluster containing both S and Se ligands $[(\eta\text{-}C_5H_5)CoFe_2(CO)_6(\mu_3\text{-}S)(\mu_3\text{-}Se)]$.[11] Here, we report on its optical limiting characteristics. Among the key requirements for a good optical limiter are (*a*) large transmission at low intensities followed by low transmission at high intensities and (*b*) a low threshold for the onset of non-linear attenuation of the input beam.[2] We show that, on both these counts, the present cluster displays superior performance compared to other materials.

The linear absorption spectrum of a solution of $[(\eta\text{-}C_5H_5)CoFe_2SSe(CO)_6]$ in *n*-hexane is shown in Fig. 1. There is weak absorption in the visible and near-IR regions. Commonly used laser wavelengths (Nd-YAG, dye and diode) exist in these regions and hence limiting applications are important here. The non-linear optical properties of the solution were measured by the *Z*-scan technique[12] at 1064 and 532 nm using an Nd-YAG laser emitting 35 ps pulses at a 10 Hz repetition rate. Typical *Z*-scans are shown in Fig. 2. The large peak to valley difference (nearly 40%) in the closed aperture case [Fig. 2(*a*)] indicates considerable non-linear refraction and the occurrence of the peak at positive *z* indicates positive non-linearity or self-focussing. The non-linear refraction coefficient γ can be extracted from the difference in transmission between the peak and the valley.[12] Table 1, which summarises the experimental parameters and the extracted non-linear coefficients, indicates that our γ value at 532 nm is two orders of magnitude larger than the values reported by Shi and coworkers for other inorganic clusters at the same wavelength.[13] The γ at 1064 nm for our

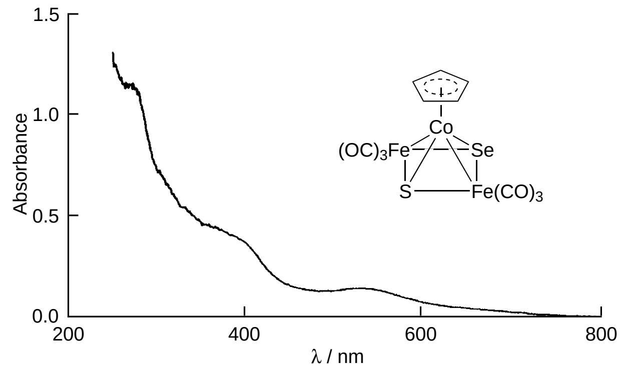

Fig. 1 Linear absorption spectrum of $[(\eta\text{-}C_5H_5)CoFe_2SSe(CO)_6]$ in *n*-hexane. The inset shows the structure of this cluster.

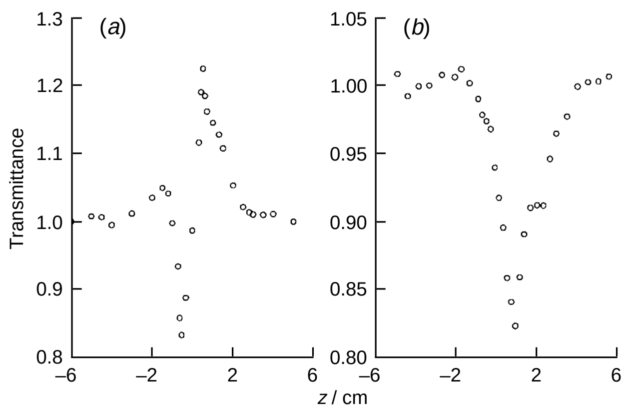

Fig. 2 Results of a *Z*-scan at 532 nm. A lens with 50 cm focal length was used, giving a focussed spot radius of about 25 µm. The sign convention for *z* is as defined in ref. 12. *z* = 0 is the focus. The fluence at focus is 0.80 J cm^{-2}. (*a*) Non-linear refraction, (*b*) non-linear absorption.

Table 1 Experimentally determined values for $[(\eta\text{-}C_5H_5)CoFe_2SSe(CO)_6]$ and those reported for other materials. The maximum (at focus) intensity in our *Z*-scan experiment was 23 GW cm^{-2}, corresponding to a maximum fluence of 0.8 J cm^{-2}. The sample concentration was 50 µmol ml^{-1}; γ is the non-linear refractive index coefficient (see ref. 12). F_t is the limiting threshold fluence at 532 nm

Material	γ (532 nm)/ m^2 W^{-1}	γ (1064 nm)/ m^2 W^{-1}	F_t (with ap.)/ J cm^{-2}	F_t (no. ap.)/ J cm^{-2}	Ref.
$[(\eta\text{-}C_5H_5)CoFe_2SSe(CO)_6]$	2.7×10^{-14}	-5.8×10^{-18}	2.1×10^{-3}	11.0×10^{-3}	This work
C_{60}	-9×10^{-17}	—	—	175×10^{-3}	14, 15
$[MoOS_3(CuNCS)_3]^{2-}$	-2.3×10^{-16}	—	—	7.0	13, 16
$[Mo_8O_8Cu_{12}S_{24}]^{4-}$	-3.5×10^{-16}	—	—	—	13
$[Cu_4(SPh)_6]^{2-}$	5.0×10^{-17}	—	—	—	13

cluster is also of a significant magnitude (no other data exist for a comparison to be made at this wavelength). Note that the sign of the non-linearity changes at 1064 nm, where the non-linear refraction is found to be due to self-defocussing. Moving on to the open aperture data [Fig. 2(*b*)], it is evident that there is non-linear absorption, indicated by the dip in the transmission as the sample is moved towards the focus. The non-linear absorption of about 16% at the maximum fluence of 0.80 J cm^{-2}, is significant considering the low fluence levels we have used. The solvent *n*-hexane did not give any signals. It is also clear from Table 1 that the γ is considerably superior to that measured for C_{60}.[14]

The significant non-linear refraction as well as non-linear absorption displayed by this cluster have been used to design optical limiters with and without apertures. Fig. 3 shows the measurements of transmission at 532 nm as a function of input energy density (fluence) with an aperture of 1 mm in the output beam. The input pulse was focussed by a lens with a focal length of 50 cm. The concentration of the sample was adjusted such that the transmission of the limiter at low fluences is quite large (80%). The transmission starts decreasing as the input increases to a fluence of 1.0 mJ cm^{-2} (28 MW cm^{-2}) and comes down to 30% at 3.5 mJ cm^{-2}. The onset of non-linear transmission in other inorganic clusters has been found to occur at values that are two orders of magnitude larger than that for the present cluster.[7] The benchmark limiting material, C_{60}, also shows onset of non-linear transmission at 80 mJ cm^{-2}.[15] The threshold for limiting,[2] defined as the fluence at which the transmission decreases to half of the value at low input fluences, is found to be 2.1 mJ cm^{-2} for our cluster. This value is about 250 times smaller than the smallest value obtained for other inorganic clusters studied recently.[16] Even without an aperture (the open aperture case), our limiting threshold is 11 mJ cm^{-2}, which is a factor of over 45 times smaller compared to the other clusters[16] and about 15 times smaller than that for C_{60}. An additional advantage of our cluster is that it has a large transmission at low input intensities, a characteristic required for an ideal optical limiter.

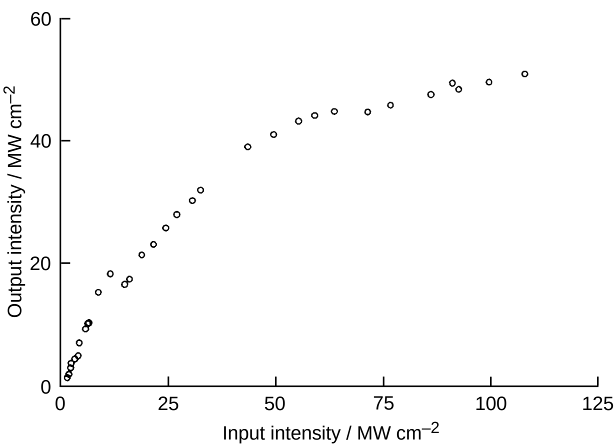

Fig. 3 Output–input characteristics of a solution of the cluster in *n*-hexane at 532 nm with an aperture of 1 mm in the transmitted beam. Linear (low intensity) transmission of the limiter was 80%. The sample was contained in a 1 mm path length quartz curvette.

In conclusion, we have shown that the mixed-metal, mixed chalcogenide cluster $[(\eta\text{-}C_5H_5)CoFe_2SSe(CO)_6]$ displays large optical non-linearity. We have demonstrated that it has optical limiting characteristics which are considerably superior to C_{60} and other recently investigated inorganic clusters.

Footnotes

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Received, 4th November 1996; Com. 6/07485E