Fractal Surfaces of 8-(hydroxyquinoline)zinc and their Relation to Electroluminescence Behaviour

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SUMMARY

A method has been developed for analysing the fractal surface behaviour of 8-(hydroxyquinoline)zinc (Znq2) using small-angle X-ray scattering (SAXS). The measurements indicated that the surface of Znq2 can be described by fractal and power-law decay of the scattering intensity I for values of the scattering vector q between 0.8 nm^{-1} and 5 nm^{-1} where $I(q) \sim q^{\alpha}$. The exponent is smaller than the four values given by Porod's law. The surface fractal dimension Ds was found to be 2.96 in agreement with surface fractals. We also report the fractal surface characteristics of 8-(hydroxyquinoline)aluminum (Alq3) and make a comparison between the fractal surface behaviours of Znq2 and Alq3. We believe that SAXS is the most appropriate technique for the determination of the fractal dimension and that it can be used to study the relations between the surface and electro-optical properties of organic materials.

INTRODUCTION

Currently, our knowledge of organic light-emitting diodes (OLEDs) made from organic materials is based on the work of Tang and Van Slyke[1] on devices using evaporated molecular films of tris(8-hydroxyquinoline)aluminium (Alq3) and on the work of Burroughes et al. with the spin-cast conjugated polymer poly(phenylene vinylene) (PPV)[2]. A device consists of two electrodes with one or more organic low molecular weight substances (or polymeric, polymer-organic low molecular) layers in between, in order to increase the electroluminescence (EL) characteristics of OLED. The polymer or organic small molecule is frequently used as the emitting material, electron transport layer or hole transport layer in a device structure. Therefore, the surface properties of the layer in the device structure closely relate to the carrier transport behaviour and EL characteristics. Alq3, 8-(hydroxy-quinoline)zinc (Znq2), PPV or organic small molecule will be used coordinately. Investigations of the surfaces of these materials must be very significant. Alq3 and Znq2 are often used as carrier transport material, emitting material and host material in the OLEDs because they have a good carrier transporting capability and strong electroluminescence. They also exhibit good stability in films (no crystal deposition with time), and offer heat resistance because of their high melting points. Thus Alq3 and Znq2 have attracted considerable attention in both basic research and commercial development, for example, OLEDs, optically and electrically pumped laser devices[3].

It is well known that the structure of organic materials is difficult to characterize in such a way as to help understand their electro-optical properties. Although electron micrographs have shown a richness in behaviour of organic materials dependent upon preparation techniques, the information is difficult to quantify. Small-angle X-ray scattering (SAXS) is a useful technique for investigating the structure of organic materials on a scale from about 0.5 to 200 nm. The external fractal surface behaviour can be determined by measurement of the SAXS intensity[4,5]. In this paper we report the SAXS study of Znq2, and its surface behaviour is discussed in the light of fractals.

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EXPERIMENTAL

The Znq2 sample used in the present study was prepared by the reaction of metal zinc and a ligand, such as 8-hydroxyquinoline. The Znq2 was purified using the train sublimation method. For the direct SAXS measurements, the powdered reaction product of Znq2 was compressed into cylindrical pellets having a diameter of 10 mm and a thickness which varied from 0.5 to 1 mm. The SAXS measurements were made using a position sensitive detector, a small-angle goniometer, and a step-by-step scanning technique. Nickel-filtered CuKa (λ = 0.154 nm) radiation and slit collimation were employed in all the measurements.

RESULTS AND DISCUSSION

The scattered intensity I(q) from a randomly oriented aggregate of N identical scattering objects is given by[6]:

$$I(q)=N\,I_0(qa)\,S(q) \qquad (1)$$

where $I_0(qa)$ is the scattered intensity from one scatterer. On condition that scattering from surface fractals Eq. (1) then becomes

$$I(q) = N\,I_0(qa) \qquad (2)$$

I(q) was proportional to a non-integral negative power of $q = 4\pi\lambda^{-1}\sin(\theta/2)$, where q is the modulus of the scattering vector, λ the x-ray wavelength, θ the scattering angle. N is the number of surface fractals in the scattering sample, $I_0(qa)$ is the scattered intensity from one scatterer, and a the diameter of a randomly oriented aggregate with N surface fractals in the scattering sample[7,8]. In the two-phase approximation from (2) and qa >> 1 we obtain

$$I(q) \sim q^{-(6-Ds)} \qquad (3)$$

where Ds is the surface fractal dimension and $2 \leq Ds \leq 3$. Equation (3) describes power-law scattering. Thus the magnitude of the power-law exponent from the SAXS measurement allows us to decide whether the scatterer is a surface fractal or not. If Ds = 2, for a smooth (nonfractal) surface then $I(q) \sim q^{-4}$, which is the familiar Porod's law. Figure 1 shows the logarithm of the SAXS intensity I(q) as a function of the modulus of the scattering vector q.

Figure 1 LnI(q) as a function of the modulus of the scattering vector

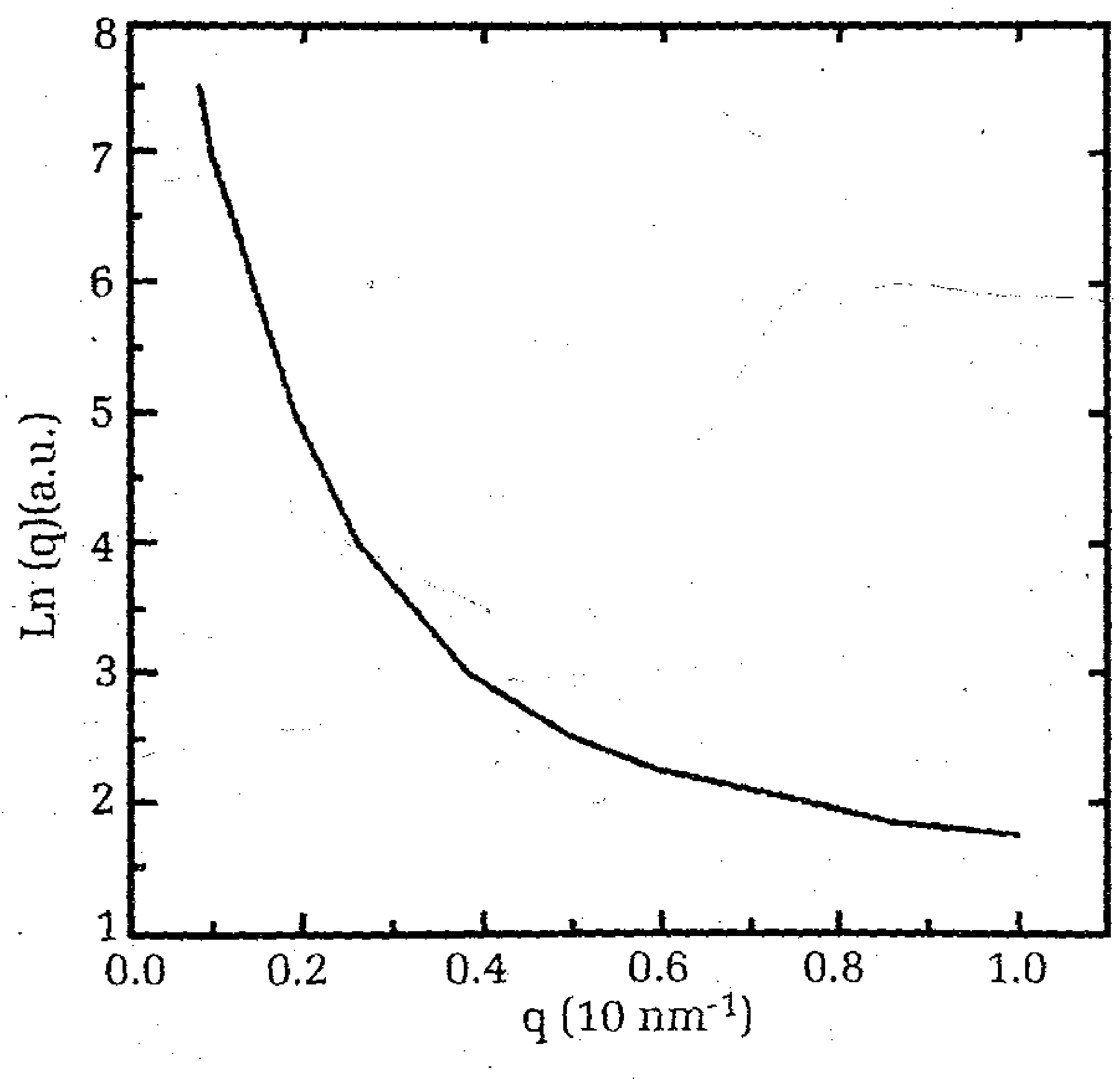
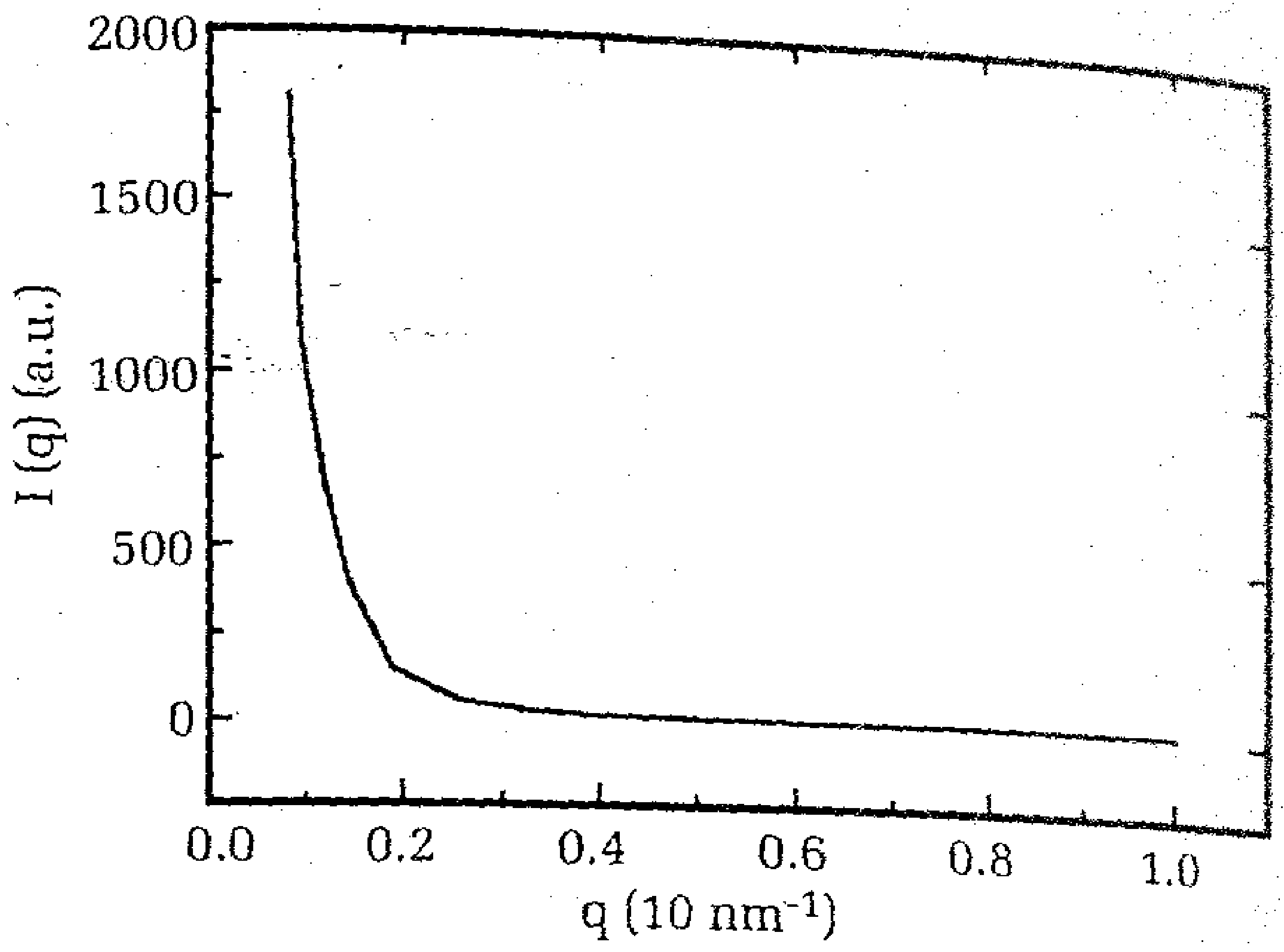
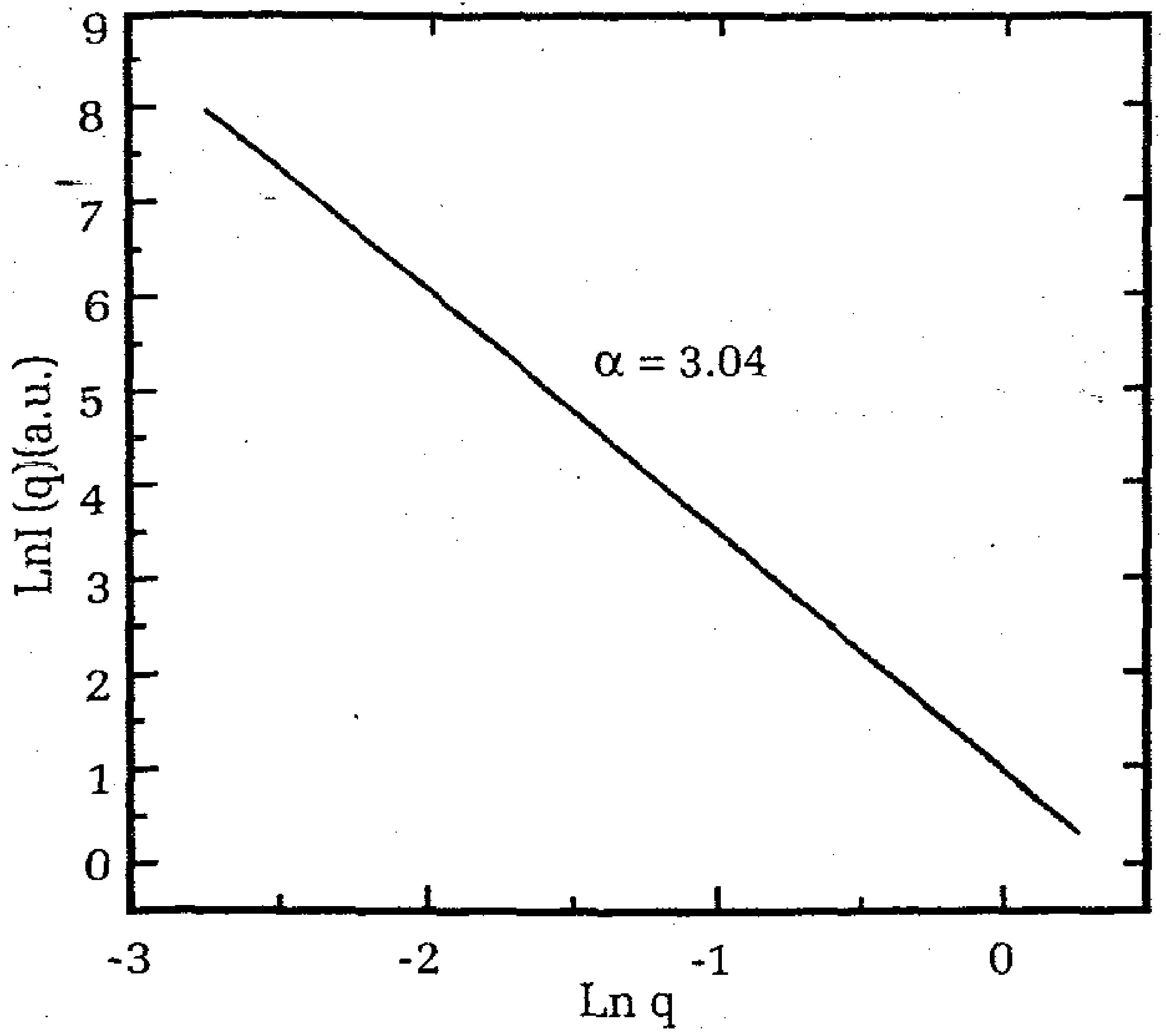


Figure 2 SAXS intensity as a function of the modulus of the scattering vector



From Figure 1 we can see that the scattering intensity first decreases rapidly with increasing q and then decreases slowly. It is characteric of non-crystalline Znq2. The SAXS intensity I(q) is shown in Figure 2 as a function of the modulus of the scattering vector q. The scattering intensity decreases rapidly with increasing q. In order to characterize the fractal behaviour of Znq2 from Figure 3, we can examine the straight line relation between I(q) and q in a Ln-Ln plot from 0.8 to 5 nm^{-1}. The relation follows the power law (3) and the slope of the straight line is α = -3.04, corresponding to a fractal dimension Ds = 2.96. This is in agreement with surface fractals. If $q \geq 5$ nm^{-1}, there is no straight line, because q has become so large that the scattering process deals with the problem of the size of individual atoms and the two-phase approximation is no longer valid. As we can see from Figure 2, the intensity is proportional to $q^{-3.04}$ for a wide range of q values. This kind of curve can be explained by the fractal behaviour of the Znq2 surface with a fractal dimension of 2.96. A rough order of magnitude estimate of fractal surface lengths can be

Figure 3 SAXS intensity as a function of q on a Ln-Ln scale



obtained from the condition that the scattering at a given value of q is associated with a distance π/q. Since the curve is linear for q between approximately 0.8 and 5 nm^{-1}, we conclude that the fractal surfaces have a fractal dimension 2.96 on a length from about 3.9nm down to at least 0.6nm. Figure 4 shows the change of LnI(q) with the square of the scattering vector q^2 for the Znq2.

From Figure 4, a linear region within a more or less extended q domain can be observed. If it is assumed that the system is composed of identical particles, the intensity change of x-rays scattered at low angles follows Guinie's law[8],

$$I(q) = B \exp(-R^2q^2/3) \qquad (4)$$

where B is a constant and R is the average (electronic) radius of gyration of the particles, respectively. We can calculate R ~ 0.7nm using Eq. (4) and the linear portion of Figure 4. The Alq3 is also a non-crystal material and its surfaces have the fractal characteristics. The fractal dimension of the Alq3 has been found by Raman light scattering[9] to be 2.67. The fractal dimension will characterize the interaction between the molecules. Therefore, the relations between the surface behaviour and the luminescent properties will be studied further through SAXS measurements of Znq2 (or Alq3).

Figure 4 Plot of LnI(q) versus q^2 of the SAXS curve

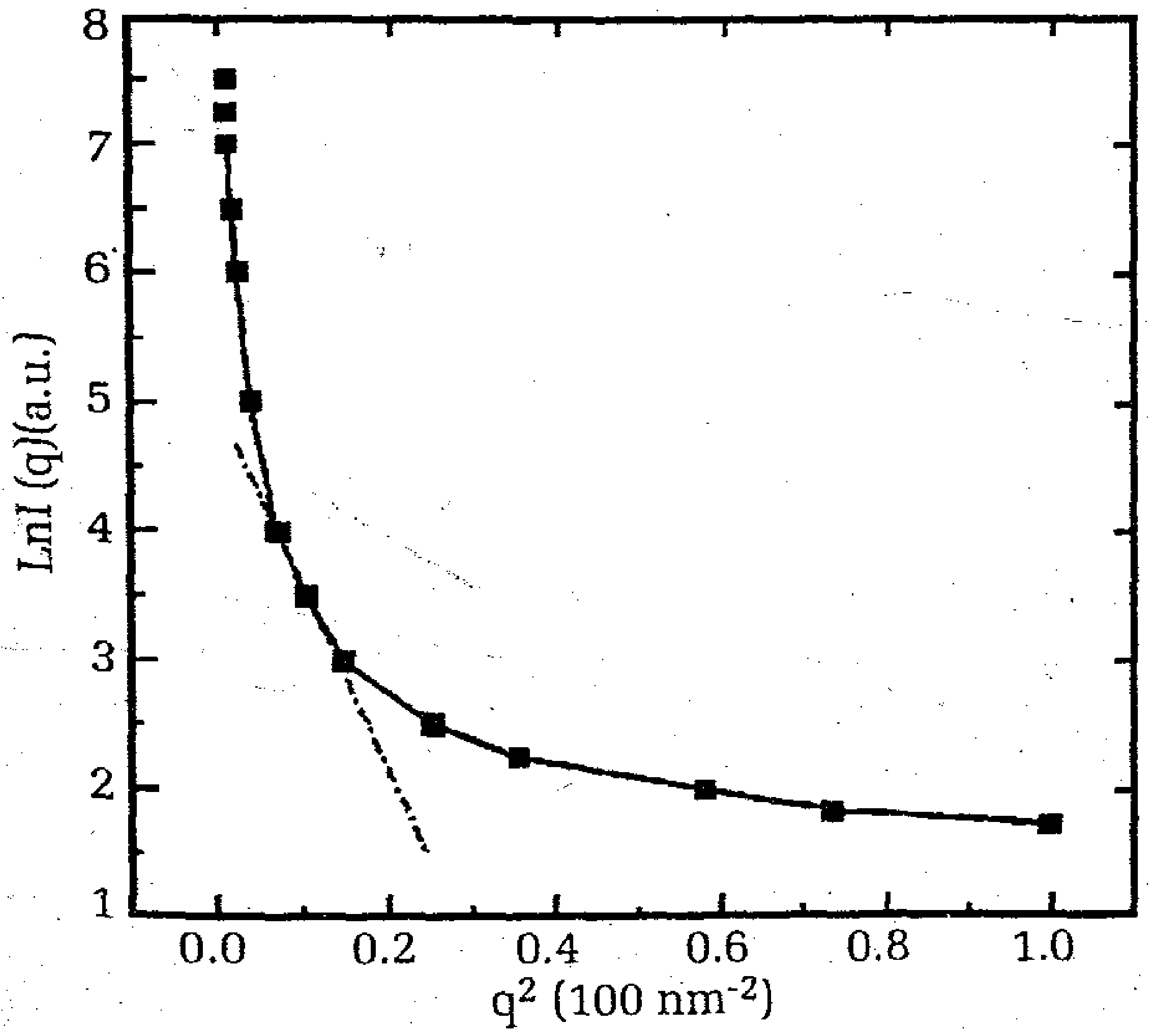
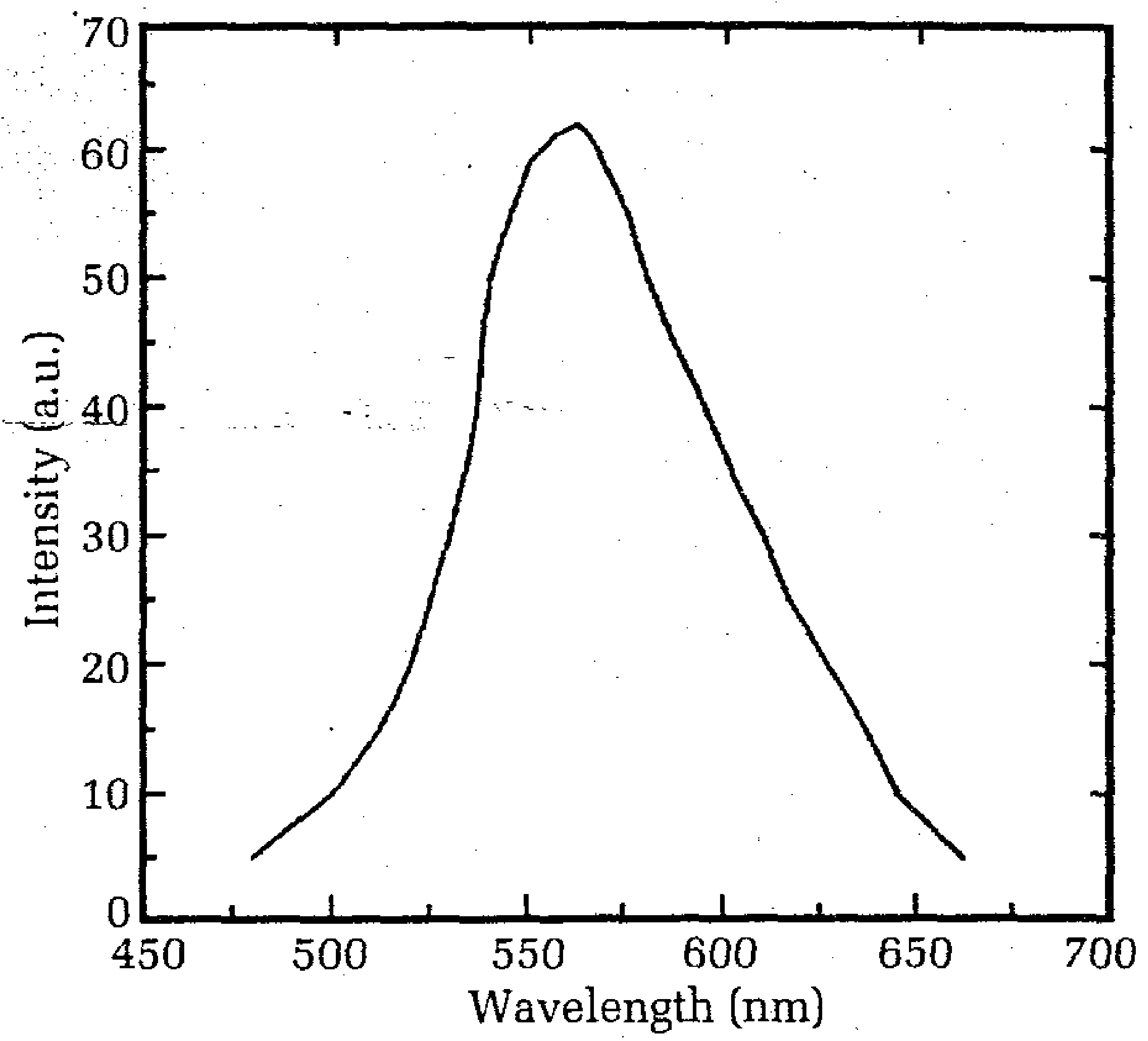


Figure 5 Electroluminescent spectrum of the ITO/PVK/ Znq2.Al



The EL spectrum of the ITO/PVK/Znq2/Al is shown in Figure 5. The excited voltage is 17.3 V. The current density is 6.5 mA/cm^2. The Znq2 and PVK are used as an emitter and a hole transport layer, respectively. EL emission originates from Znq2. The experiments indicate the change in fractal dimension with change in EL properties. Therefore, it may be used to study the relations between surface and EL properties of Znq2 (or Alq3) through the measurement of the fractal dimension. Thus, EL properties of Znq2 should be optimised for high performance EL devices.

CONCLUSIONS

In conclusion, the SAXS experimental results demonstrate that the Znq2 surface shows fractal behaviour. From a measurement of the fractal dimension we found a value of 2.96 in agreement with surface fractals. We therefore believe that the SAXS is the most appropriate technique for the determination of the fractal dimension and may be used to study the relations between surface and electro-optical properties of organic luminescent materials.

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