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The structural transitions in a nematic liquid crystals doped with magnetically labeled carbon nanotubes

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The 4-(trans-4'-n-hexylcyclohexyl)-isothiocyanatobenzene (6CHBT) liquid crystal was doped with carbon nanotubes and magnetically labeled carbon nanotubes. The prepared samples were characterized by infrared (IR) spectroscopy, transmission electron microscopy (TEM), optical microscopy and by magnetic measurements. The electric and magnetic Fredericksz transition were measured for pure liquid crystal for liquid crystal doped with multi-walled carbon nanotubes (MWNTs) and with magnetically labeled MWNTs (volume concentration $\phi = 2 \times 10^{-3}$).

Introduction. Since their discovery in 1991 by Iijima, carbon nanotubes have been of great interest, both from a fundamental point of view and for future applications. The most eye-catching features of these structures are their electronic, mechanical, optical and chemical characteristics, which open a way to future applications. Carbon nanotubes are molecular-scale nanofibers with fullerene like structure. One of the most important applications of nanotubes based on their properties will be as reinforcements in composite materials. However, there have not been many successful experiments that show that nanotubes are better fillers than the traditionally used carbon fibers. The main problem is to create a good interface between nanotubes and the polymer matrix, as nanotubes are very smooth and have a small diameter, which is nearly the same as that of a polymer chain. Secondly, nanotube aggregates, which are very common, behave different to loads than individual nanotubes do. Limiting factors for good load transfer could be sliding of cylinders in MWNTs and shearing of tubes in SWNT ropes. To solve this problem the aggregates need to be broken up and dispersed or cross-linked to prevent slippage. A main advantage of using nanotubes for structural polymer composites is that nanotube reinforcements will increase the toughness of the composites by absorbing energy during their highly flexible elastic behavior. Other advantages are the low density of the nanotubes, an increased electrical conduction and better performance during compressive load. Another possibility, which is an example of a non-structural application, is filling of photoactive polymers with nanotubes. PPV (Poly-p-phenylenevinylene) filled with multi-walled carbon nanotubes (MWNTs) and single-walled carbon nanotubes (SWNTs) is a

composite, which has been used for several experiments. These composites show a large increase in conductivity with only a little loss in photoluminescence and electro-luminescence yields. Another benefit is that the composite is more robust than the pure polymer. Liquid crystals can be orientated under magnetic or electric field due to their anisotropic properties but the response of liquid crystals to an external magnetic field is weak due to small value of the anisotropy of diamagnetic susceptibility. Brochard and de Gennes [1] proposed doping liquid crystals with fine magnetic particles to increase this sensitivity, i.e. they created so called ferronematics. Ferronematics are stable colloidal suspensions of fine magnetic particles in nematic liquid crystals. They attract considerable interest of investigation because their response to the external magnetic field exceeds sufficiently that of pure nematics. The most essential feature of these systems is an orientational coupling between the magnetic particles and the liquid crystal matrix. The influence of the magnetic field depends on the type of anchoring that is characterized by value of density of anchoring energy and initial orientation between liquid crystals molecules (characterized by unit vector \mathbf{n} - director) and magnetic moment of magnetic particles (\mathbf{m}).

In our previous work [2] we studied 6CHBT liquid crystal doped with magnetic particles of different shape (spherical, rod-like and chain-like). The obtained result have motivated us to study the same liquid crystal doped with carbon nanotubes with aim to generate a complex of geometry of liquid crystal molecules with respect to doped nanoparticles in order to study the influence of shape on the structural Freedericksz transition. The first part of this paper is devoted to preparation and characterisation of magnetically labeled MWNTs. In the second part are described some first results obtained form measurements of prepared liquid crystal doped with MWNTs and with magnetically labeled MWNTs with aim to investigate the influence of doping on electrical and magnetic Freedericksz transition. To our knowledge, this is first work on composite systems liquid crystal-MWNTs and liquid crystal-MWNTs/Fe₃O₄.

1. Experimental

1.1. Synthesis of MWNTs/Fe₃O₄ Chemical vapor deposited (CVD) multi-walled carbon nanotubes (MWNTs) were purchased from Sigma Aldrich Co. (length was from 0.5 μm to 2 μm , outer diameter was from 20 nm to 30 nm, wall thickness was from 1 nm to 2 nm). The other reagents (FeCl₃.6H₂O, FeCl₂.4H₂O, NH₄OH, HNO₃, and H₂SO₄) were analytical grade. MWNTs/Fe₃O₄ were prepared in two steps:

(i) Functionalization of MWNTs (Figure 1): The inert and pristine surface of as-prepared MWNTs makes it difficult for attachment of metal precursors by wet impregnation. Only extensive dispersion of various functional groups such as hydroxyl, carboxyl and carbonyl on MWNTs surface could provide active sites for metal ions to attach. We used carboxyl groups for functionalization of MWNTs. First, 0.1 g of MWNTs was added to a mixture of concentrated nitric acid (10 ml) and sulfuric acid (30 ml) and ultrasonicated over 8 hours. Then was added 90 ml of distilled water into the mixture. The dispersion was then centrifuged, washed with distilled water until it turned neutral and dried at 50°C over night.

(ii) Synthesis of MWNTs/Fe₃O₄ (Figure 2): After drying, 45 mg of functionalized MWNTs were dissolved in 30 ml of distilled water by ultrasonic irradiation for 20 min. Then 40.5 mg of FeCl₃.6H₂O was added under stirring. After the mixture was stirred vigorously for 30 min under nitrogen atmosphere, 60 mg of

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was added and keep stirring under nitrogen atmosphere for 30 min. Then 24 ml of 6% NH_4OH aqueous solution was added into the mixture drop by drop at 60°C during 1 hour and reacted for another 2 hours. The whole process must be under nitrogen atmosphere. The reaction mixture was then centrifuged, washed with distilled water and dried at 50°C for 24 hours.

1.2. Experimental methods The morphology and size distribution of the prepared MWNTs and magnetically labeled MWNTs were measured by transmission electron microscopy (TEM Tesla BS 500). The sample dispersed in diluted ethanol was dropped on a copper grid and dried on the air. Infrared spectra were observed by using IR spectrometer Avatar 330 in the range from 400 to 4000 cm^{-1} using KBr pellets. Magnetic properties of the products were obtained from hysteresis loops recorded in a vibrating sample magnetometer (VSM) at room temperature. The thermotropic nematic 4-(trans-4'-n-hexylcyclohexyl)-isothiocyanatobenzene (6CHBT) was used for doping with prepared particles. The 6CHBT is a low-melting enantiotropic liquid crystal with high chemical stability [3]. The temperature of the nematic-to-isotropic transition (clearing point) of the studied nematic is $T_{N-I} = 42.8^\circ\text{C}$. The nematic samples were doped with prepared MWNTs and magnetically labeled MWNTs. The doping was simply done by adding this particles, under continuous stirring, to the liquid crystal in the isotropic phase. The phase diagram of the mixture of 6CHBT and particles was determined with using polarizing microscope. No influence of the admixture of prepared particles on the temperature of the nematic-to-isotropic transition have been observed. The calorimetric scans were performed by using a DSC instrument Mettler FP80HT at a scan rate 4°C min^{-1} in the temperature range from 20°C up to 90°C . The electric and magnetic Fredericks transitions in prepared samples were indicated by capacitance measurements in a capacitor made of ITO-coated glass electrodes. During measuring of electric and magnetic Fredericksz transition, the external electric and magnetic field were applied perpendicularly to the surface of electrodes. In measurements obtained in combined electric and magnetic field, the bias electric field was perpendicular to the surface of electrodes and magnetic field was parallel. Before starting measurements the high magnetic field (12 T) parallel with surface of electrodes was applied on all samples with aim to obtain good alignment of molecules of liquid crystal and nanotubes. The capacitor with the electrode area approximately $0.5\text{cm} \times 0.5\text{cm}$ was connected to a regulated thermostat system, the temperature was stabilized with the accuracy of 0.05°C . The distance between the electrodes (sample thickness) was $D = 5\mu\text{m}$. The capacitance was measured at the frequency of 1 kHz by the high precision capacitance bridge Andeen Hagerling.

2. Results and discussion Figure 3 display typical TEM images of MWNTs, and MWNTs/ Fe_3O_4 . As is shown in Figure 3 a, the used MWNT contains few defects in sheets of nanotubes. It can be seen from Figure 3 b that the magnetite nanoparticles are close to cubic and the particle size is distributed from 10 to 15 nm, and the mean particle size is about 12 nm. Figure 4 illustrates IR spectrum of the MWNTs/ Fe_3O_4 . The presence of magnetite nanoparticles can be seen by strong absorption band at 573 cm^{-1} [4]. The O-H stretch appears in the region $1440\text{--}1395\text{ cm}^{-1}$, and the C-O bond is characterized by 1200 cm^{-1} . Absorption band at 1580 cm^{-1} is assigned to nanotube phonon modes [5].

Magnetic properties of the products were obtained from hysteresis loops recorded in a vibrating sample magnetometer (VSM) at room temperature (Figure 5). The

measured data were fitted by system of three Langevin functions. The size distribution of measured sample was obtained from this fit with following results: 20.7% of particles is 5.5 nm, 45.6% of particles is 14 nm and 33.7% is 21.5 nm. The obtained values are in good agreement with values observed by TEM.

Figure 6 shows the 6CHBT liquid crystal doped with MWNTs observed under the polarizing microscope. The sample was deposited between two glass slides heated from nematic phase (left picture) to isotropic phase. The clusters of MWNTs are observed in this sample. The right picture shows droplets of nematic phase in isotropic phase near the clearing point. Figure 7 shows the 6CHBT liquid crystal doped with MWNTs/Fe₃O₄ in nematic phase observed under the polarizing microscope. If compare with left picture of Figure 6, in this case no clusters of MWNTs are observed. From these observations we can conclude that labelling of MWNTs with magnetic nanoparticles avoids of forming clusters. The electric and magnetic Fredericksz transitions were studied in the following experimental geometry: the molecules of liquid crystal were oriented parallel with the surface of cell and the electric field or magnetic field were applied perpendicular to the surface of capacitor electrodes. The measured capacitance dependences on the external electric or magnetic field reflect the re-orientation of the nematic molecules. Figure 8 shows reduced capacitance dependence of pure 6CHBT and 6CHBT doped with MWNTs and magnetically labeled MWNTs on external electric field. It is clear seen that doping with MWNTs and MWNTs/Fe₃O₄ shifts the critical value of electric Fredericks transition to the lower values. The critical value of electric field voltage for structural changes is calculated as

$$U_C = \pi \sqrt{\frac{K_i}{\epsilon_0 \epsilon_a}}. \quad (1)$$

where D is thickness of sample, K_i is corresponding Frank modulus and ϵ_a is anisotropy of dielectric permittivity. Decreasing of value of critical electric field could be due to decreasing of Frank modulus or increasing of anisotropy of dielectric permittivity. So measuring of anisotropy of dielectric permittivity will be aim of our next work.

From Figure 9 it is seen that there is no influence of presence MWNTs and MWNTs/Fe₃O₄ on magnetic Fredericksz transition. But situation is changing if bias voltage is applied on the same samples. Figure 10 shows the reduced capacitance dependence of 6CHBT doped with MWNTs and magnetically labeled MWNTs on external magnetic field measured at bias voltage $U_{bias}=6$ V. During measurements the bias electric field was applied perpendicular to the capacitor electrodes and the external magnetic field was applied perpendicular to the bias electric field. The dependence of the measured capacitance on the external magnetic field reflects the re-orientation of the nematic molecules in the strong magnetic field. From this figure it is seen that due to doping of liquid crystal with MWNTs the value of magnetic Fredericksz transition is shifted to lower value but due to doping with MWNTs/Fe₃O₄ the value of critical magnetic field is shifted to higher value. Such behaviour could be result of some complicated orientation of liquid crystal molecules and MWNTs in prepared samples and could be different in the case of doping with MWNTs and with MWNTs/Fe₃O₄. At the present time it is difficult to describe this orientation, but it will be aim of our future investigations.

3. Conclusion. The composite systems liquid crystal-MWNTs and liquid crystal-MWNTs/Fe₃O₄ were successfully prepared. The results obtained from measuring of electric Fredericksz transition showed that doping with MWNTs

and MWNTs/Fe₃O₄ shifts the critical value of electric Fredericks transition to the lower values. In order to decide reason for such behaviour, the anisotropy of dielectric permittivity will be measured. Also measurements of structural transitions in combined electric and magnetic field will be performed for different values of bias voltage.

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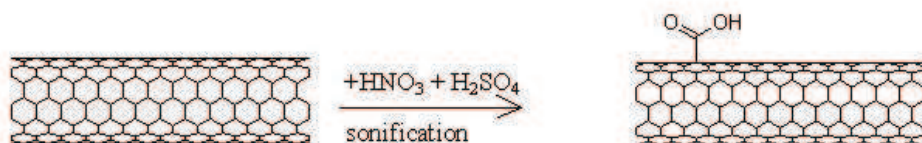


Figure 1: The scheme of functionalization of MWNTs.

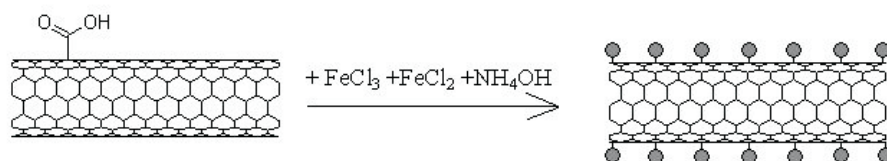


Figure 2: The scheme of preparing of MWNTs/Fe₃O₄.

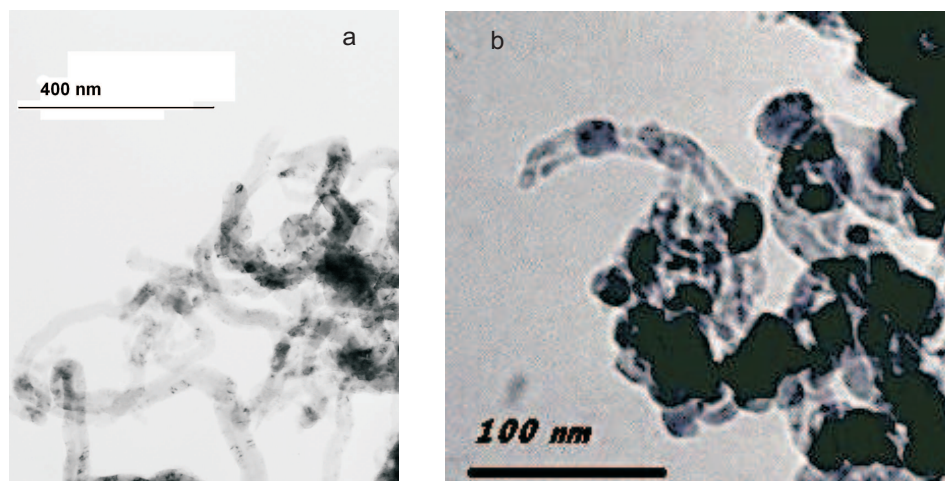


Figure 3: TEM images of (a) MWNTsTEM and (b) MWNTs/Fe₃O₄.

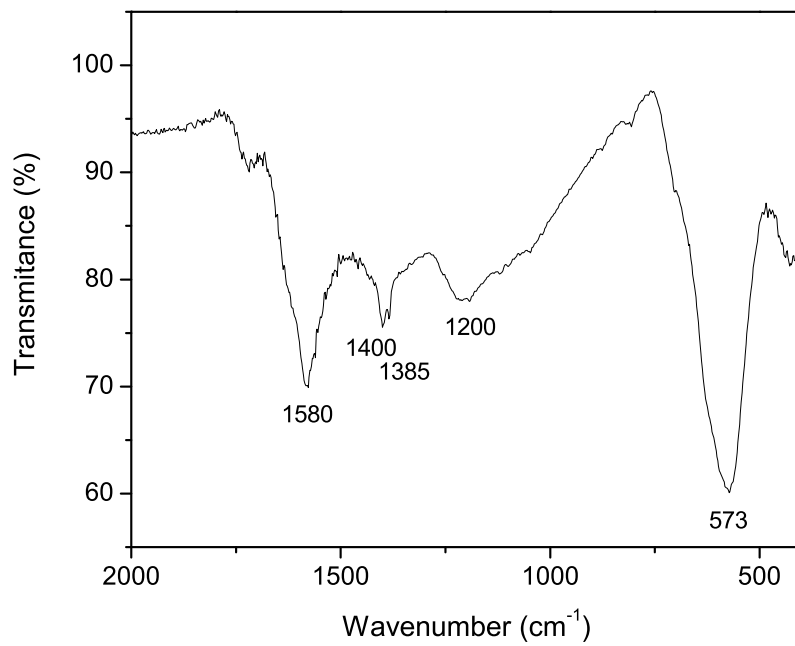


Figure 4: Infrared spectrum of MWNTs/Fe₃O₄.

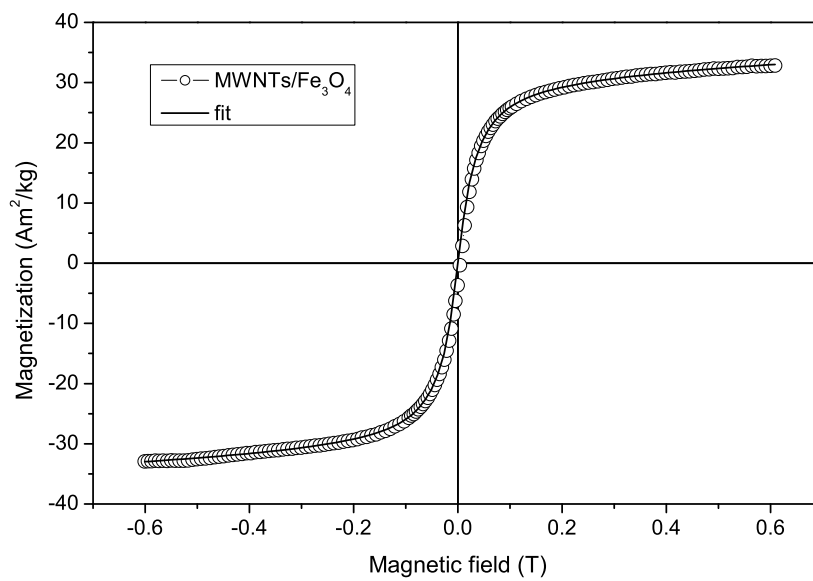


Figure 5: Magnetization curve of MWNTs/Fe₃O₄.

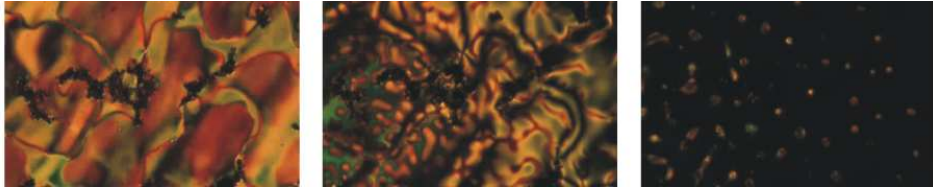


Figure 6: 6CHBT liquid crystal doped with MWNTs observed by polarizing microscope.

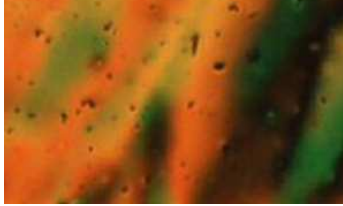


Figure 7: 6CHBT liquid crystal doped with MWNTs/ Fe_3O_4 observed by polarizing microscope.

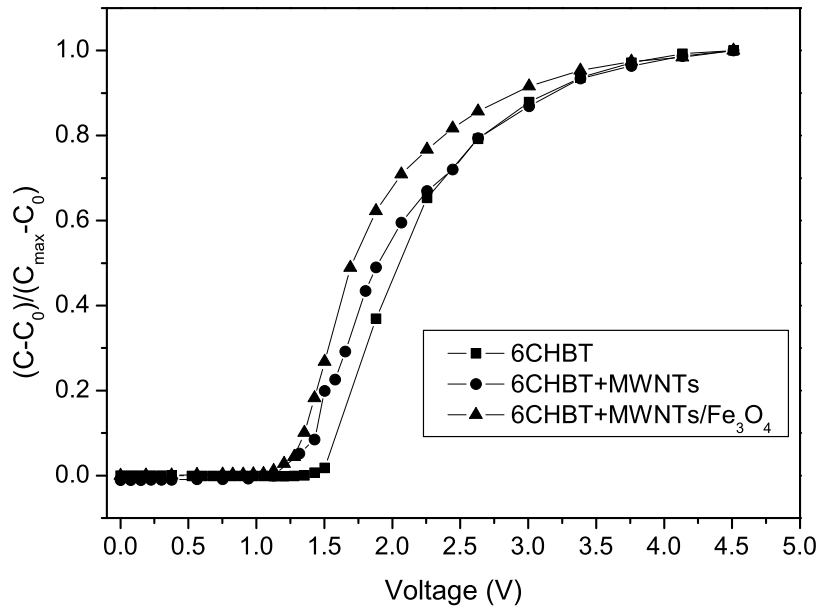


Figure 8: The reduced capacitance dependence of pure 6CHBT and 6CHBT doped with MWNTs and magnetically labeled MWNTs on external electric field.

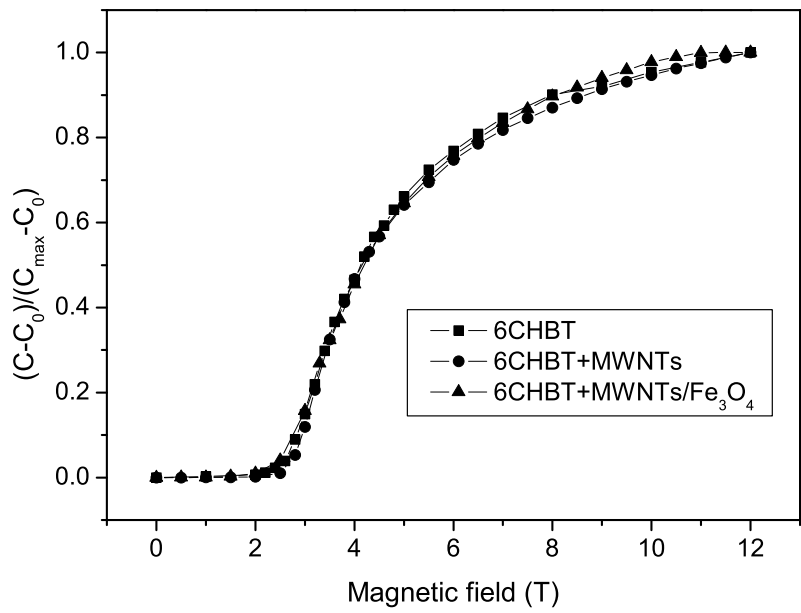


Figure 9: The reduced capacitance dependence of pure 6CHBT and 6CHBT doped with MWNTs and magnetically labeled MWNTs on external magnetic field.

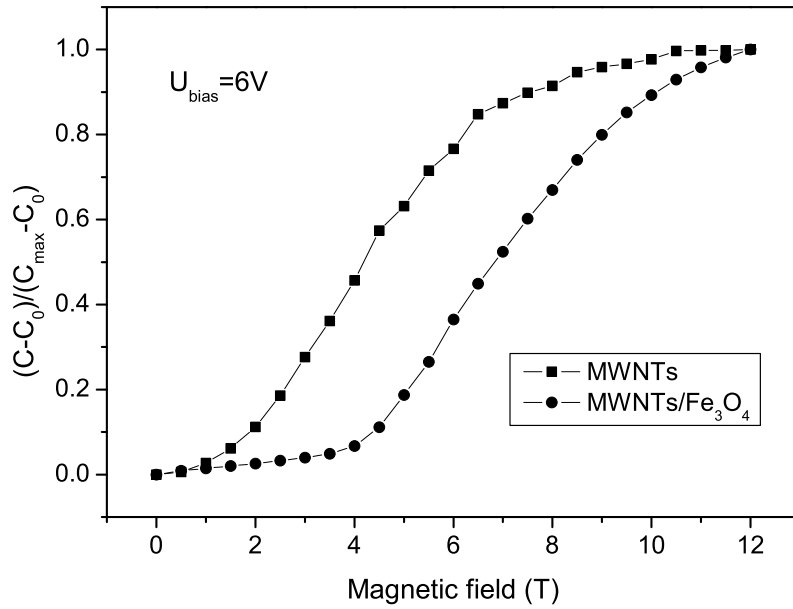


Figure 10: The reduced capacitance dependence of 6CHBT doped with MWNTs and magnetically labeled MWNTs on external magnetic field measured at bias voltage $U_{\text{bias}}=6\text{ V}$.