

THIN FILM OF CONJUGATED SCHIFF-BASE AS ULTRAHIGH DENSITY DATA STORAGE MATERIAL

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ABSTRACT

N-(3-nitrobenzylidene)-p-phenylenediamine (NBPDA) was used as ultrahigh density data storage medium by scanning tunneling microscope (STM) technique. Data marks of 1.4nm in diameter were written by applying voltage pulses between the STM tip and the substrate. Structures of single crystal and thin films were characterized by IR, UV-Vis, XRD, STM and verified by DFT quantum chemical calculation.

INTRODUCTION

Conjugated organic and polymeric systems with delocalized electrons have attracted increasing interests in their great potential for high-technology applications, especially ultrahigh density memory and information storage materials [1-3]. The highly polarizable electronic cloud is accompanied by a capability for ultrafast responses originating in the electron mobility, so that the conjugated systems are characterized by optimal electric activities as compared with inorganic crystals.

In recent years, much attention has been focused on conjugated organic charge transfer complexes, such as cyanuric acid melamine-7,7,8,8,tetracyanoquinodimethane (TCNQ) complex or Bis[2-butene-2,3-dithiolato(2-)-S,S']nickel (BBDN)-TCNQ complex, achieving data storage density of 4×10^7 bits/cm² [4,5]. In our laboratory, thin films from a complex of an electron acceptor, m-nitrobenzal malononitrile and a donor, 1,2-benzenediamine, were used as recording media [7,8]. Marks of 1.3nm in size were obtained with STM under ambient conditions. I-V characteristics of the film suggested that the recording mechanism be due to the conductance change of the films from insulating to conducting. In order to further clarify the mechanism and functionality process of such kind of recording media, we prepared a conjugated schiff-base N-(3-nitrobenzylidene)-p-phenylenediamine (NBPDA) with both electron donor and acceptor group located in a single molecule at opposite sites simultaneously. Recording process was successfully carried out to make marks of 1.4nm in diameter by applying voltage pulses between the STM tip and the substrate film. NBPDA crystal and film structure were characterized by IR, UV-Vis, XRD, STM and verified by DFT quantum chemical calculation. The possible mechanism of the recording process were tentatively discussed.

EXPERIMENTS

Materials and Thin Film Preparation

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N-(3-nitrobenzylidene)-p-phenylenediamine (NBPDA) was prepared by condensation reaction of equal molar amounts of 3-nitrobenzaldehyde with 1,4-benzenediamine, according to literature [9]. Thus, a solution of 0.1mmol 1,4-benzene-diamine in 10ml ethyl acetate was added to a solution of 0.1mmol 3-nitrobenzaldehyde in 10ml ethyl acetate. After standing at 0°C for 6 days, deep red crystals were obtained with melting point 146~147°C.

Ultrathin films of NBPDA were obtained by a thermal vacuum deposition method. The NBPDA crystals were placed in a glass crucible and heated under 9×10^{-4} Pa and deposited on a substrate kept at room temperature.

Recording Experiments by STM

Experiments were performed with a CSTM-9100 STM in a constant height mode. Ultrathin films were deposited on freshly cleaved highly ordered pyrolytic graphite (HOPG). The STM tips were 0.25mm in diameter Pt/Ir (80/20) wires snipped with a wire cutter. The recording experiments were carried out by applying voltage pulses between the tip and the substrate.

Structure Characterizations and Quantum Calculation

Crystal structure analysis data were collected with an ENTSSF-NONLUS CAD-4 diffractometer. FT-IR spectrum for NBPDA crystal pilled with KBr, and micro FT-IR spectrum for NBPDA thin film on HOPG substrate were both taken by a Nicolet Magna-IR 750. UV-Vis spectra were taken by a Shimadzo UV 250. The crystallinity of the thin film was examined by using a Riguku max/2400 X-ray diffractometer employing Ni-filtered $\text{CuK}\alpha$ radiation. Sample film was deposited on a glass substrate.

Quantum chemistry calculations were performed based on density functional theory (DFT) using Amsterdam Density Functional (ADF) 2.3.

RESULTS AND DISCUSSION

Fig.1 shows the molecular structure and the unit cell of NBPDA crystal. The crystal was monoclinic with lattice constants $a=0.9601\text{nm}$, $b=1.0229\text{nm}$, $c=1.2697\text{nm}$, and $\beta=110.33^\circ$. Element analysis for $\text{C}_{13}\text{H}_{11}\text{N}_3\text{O}_2$: %Calcd(Found): C:64.73(64.51), H:4.56(4.79), N:17.43(17.35).

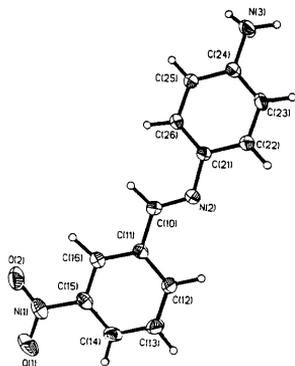


Fig.2 shows the FT-IR spectrum of NBPDA crystal and Micro FT-IR spectrum of NBPDA film. It seems that the composition of the film is about the same as the original crystal. No significant change of the characteristic absorption bands were observed as shown in Fig.1 and Table I.

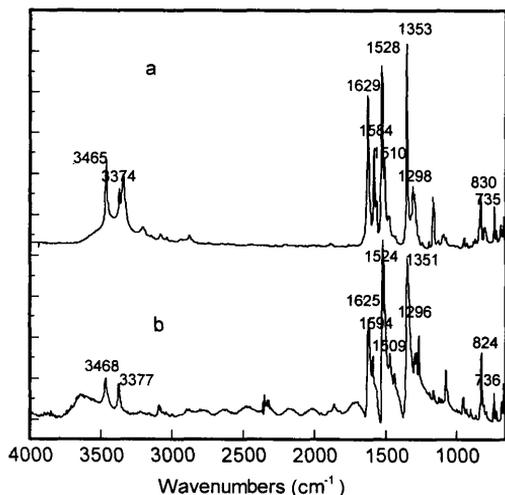


Fig.2 Infrared absorption spectra of (a) NBPDA crystal, (b) NBPDA film.

Table I. FT-IR characteristic absorption bands of NBPDA crystal and film.

Attributions	Wavenumbers (cm ⁻¹)	
	crystal	film
$\nu_{as}(\text{NH}_2)$	3465	3468
$\nu_s(\text{NH}_2)$	3374	3377
$\nu(\text{C}=\text{N})$	1629	1625
$\nu_{\phi}(\text{C}=\text{C})$	1584	1594
	1510	1509
$\nu_{as}(\text{NO}_2)$	1528	1524
$\nu_s(\text{NO}_2)$	1353	1351
$\nu(\text{C}-\text{N})$	1298	1296

Fig.3 shows the UV-Vis spectra of the NBPDA solution and NBPDA film. The red-shift and broadening of the peaks implied the possibility of intermolecular complexing. X-ray diffraction spectrum indicated that the thin films were highly stereo-regularly packed as shown in Fig.4.

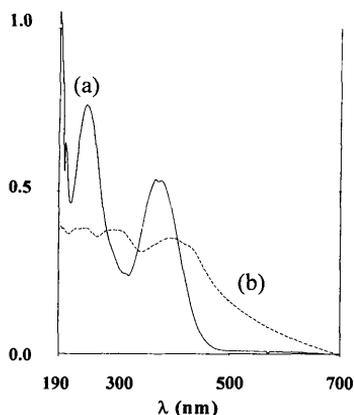


Fig.3 UV-Vis spectra of (a) NBPDA in ethyl alcohol; and (b) NBPDA film deposited on quartz.

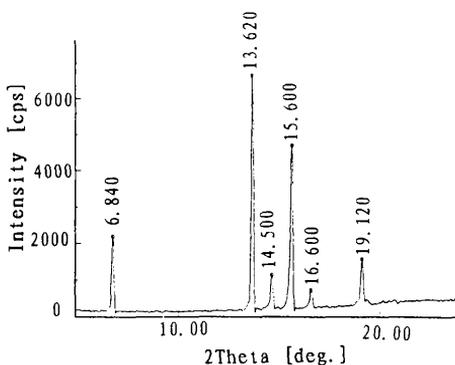


Fig.4 X-ray diffraction spectrum of NBPDA film.

A flat region without visible defects was selected for recording. Recording process was carried out by applying pulse voltage of 4V for 2ms. A typical $28 \times 28 \text{ nm}^2$ STM image of the NBPDA thin film with recorded marks is shown in Fig.5. The average size of recorded marks was 1.4nm in diameter. The distance between two neighboring marks could be 9nm or less, which corresponds to a data storage density of about 10^{12} bits/cm² or above.

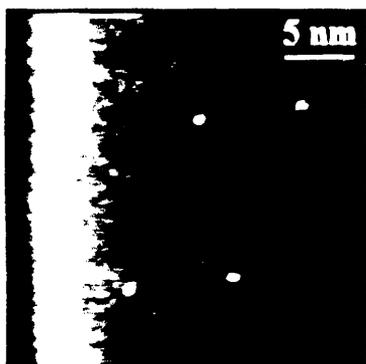


Fig.5 A $28 \times 28 \text{ nm}^2$ STM image on NBPDA thin film with recorded marks by applying pulse voltage of 4V for 2ms. $V_b=0.10\text{V}$, $I_t=0.19 \text{ nA}$.

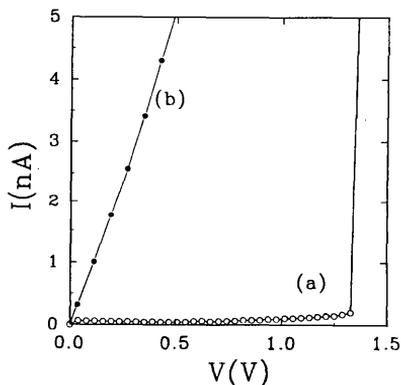


Fig.6 Typical I-V characteristics of the NBPDA film of (a) the unrecorded region and (b) the recorded region by STM.

I-V characteristics of the unrecorded region and recorded region were measured by STM as shown in Fig.6. Curve (a) shows that the medium is insulating when the applied voltage pulse is below the threshold 1.3V, and becomes conductive when above it. Curve (b) shows that the recorded region of the film is conductive.

Fig.7 gives a view of the nearest-neighbor packing of the NBPDA molecules. The molecules packed in a columnar manner, which was similar to the ring-double bond overlap of molecular planes in organic cation-TCNQ structures [10]. The zigzag linkage of C-C-N-C in the molecule was sandwiched between two phenyl groups of its two nearest-neighbor molecules with the interplanar spacings of 0.352nm and 0.345nm, respectively.

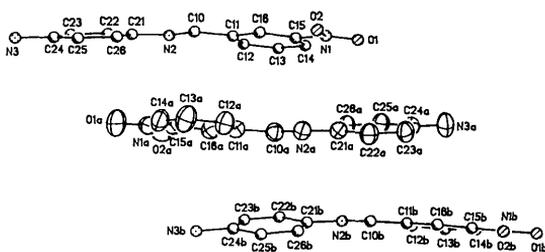


Fig.7 The nearest-neighbor packing of NBPDA molecules. Direction of view is along the molecular plane.

We calculated the three-nearest-neighbor-molecule system by DFT. Calculated Mulliken population for the $^1A_{1g}$ ground state of the molecules are summarized in Table II.

The Mulliken population analysis of the HOMO and LUMO suggested that the electron transfer would occur between the phenylenediamino group of the upper molecule and the nitro-

Table II. Mulliken population analysis for three-nearest-neighboring-molecule system of NBPDA.

	Energy levels ϵ (eV)	Mulliken population								
		upper			middle			lower		
		a*	b*	c*	a*	b*	c*	a*	b*	c*
HOMO	-4.882	0.16	0.28	1.32	0.02	0	0.02	0	0	0.06
LUMO	-3.295	0	0	0	1.92	0.02	0	0	0	0

*a: nitrobenzyl group; b: $-\text{C}=\text{N}-$; c: phenylamino group.

benzylidene group of the middle one. The Mulliken population of the lowest molecule of the three was comparatively small, which indicated that the electron transfer was constricted in two-nearest-neighboring-molecule system. So when appropriate amount of energy was added to the substance by voltage pulses using extremely thin STM tip, electron transfer would occur in certain constricted molecules from the HOMOs of certain amount of NBPDA molecules to the LUMOs of their neighboring ones. Usually, the transferred electrons would settle back shortly after the removal of applied energy, and the substance remained insulating again. In case of experiments performed by STM, the influence of the extremely short distance between the tip and the film (0.3~0.7nm), and the effect of conductive HOPG substrate should not be neglected [11]. The strong tip-sample interaction might stabilize the partial transition of electrons resulting in the expected conductance change. Further work dealing with the detailed electron transfer process and analysis of quantitative calculations are in progress.

CONCLUSIONS

Nanometer-scale recording on thin film of conjugated schiff-base N-[(3-nitrophenyl)methylene]-1,4-Benzenediamine (NBPDA) with STM under ambient conditions was presented. The films were fine enough to show the reproducible electrical bistability. The average size of recorded marks was 1.4nm in diameter. The distance between two neighboring marks could be 9nm or less, which corresponded to a data storage density of about 10^{12} bits/cm² or above. Characterizations of the crystal and thin films indicated that the composition of thermal vacuum deposited films was almost the same as the original NBPDA crystal. The existence of intermolecular charge transfer complexing was verified by UV-Vis. Quantum chemistry calculation of the three-nearest-neighboring-molecule system by density functional theory showed the theoretical feasibility of the electron transfer between two neighboring NBPDA molecules, which would result in the conductance change of thin films after applying voltage pulses by STM tip and consequently, the formation of recorded marks.

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REFERENCES

1. W.R.Salaneck, I.Lundstrom and B.Ranly ed. Conjugated Polymers and Related Materials—the Interconnection of Chemical and Electronic Structure. Proceedings, 81st Nobel Symposium, 13 (June 18, 1991, Lulca), (Oxford University Press, Oxford, 1993), pp. 502.
2. M.H.Lyons ed., Materials for Non-Linear and Electro-optico, (IOP publishing Ltd., Bristol and N.Y., 1989).
3. R.S.Potember, T.O.Poehler, R.C.Hoffman, in Molecular Electronic Devices II, (edited by F.L.Cartex, Marcel Dekker Inc. New York & Basel, 1988), pp. 97-110.
4. W.Xu, G.R.Chen and Z.Y.Hua, *Vac.Sci.Tech.(China)*, **15** (6), 363-367 (1995).
5. W.Xu, G.R.Chen, and Z.Y.Hua, *Appl.Phys.Lett.* **67**(15), 2241-2242 (1995).
6. K.Yano, R.Kuroda, Y.Shimada, S.Shido, M.Kyogaku, H.Matsuda, K.Takimoto, K.Eguchi and T.Nakagiri, *J.Vac.Sci.Technol.* **B14**(2),1353-1355 (1996).
7. L.P.Ma, Y.L.Song. H.J.Gao, W.B.Zhao, H.Y.Chen, Z.Q.Xue, S.J.Pang, *Appl.Phys. Lett.* **69**(24), 1-2 (1996).
8. H.J.Gao, L.P.Ma, H.X.Zhang, H.Y.Chen, Z.Q.Xue and S.J.Pang, *J.Vac.Sci.Technol.* **B 15**(4), 1581-1583 (1997).
9. J.H.Hodgkin and J.Heller, *J.Polym.Sci.: Part C*, **29**, 37-46 (1970).
10. C.J.Fritchie, *Acta.Cryst.* **20**, 892-898 (1966).
11. C.Julian Chen, Introduction to scanning tunneling microscope. (Chinese Light Industry Press, 1996), pp. 189-205.