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# Accelerated Optical Holographic Recording Using Bis-DNO

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**Abstract:** The design, synthesis and optical holographic recording properties of bis-DNO are reported. Bis-DNO is composed of two identical azobenzene oligoornithine segments (DNO) connected via a dipeptide linker. The two segments were assembled in a parallel fashion at the two amino groups of the dipeptide linker by Merrifield synthesis. Surprisingly, the response time of films of bis-DNOs was found to be much faster than that of their linear counterparts. © 1999 Elsevier Science Ltd. All rights reserved.

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Materials for optical holographic storage of huge quantities of information have been extensively investigated as an alternative to the conventional magnetic technology. In this regard, organic materials have attracted significant interest in recent years. [1] A wide range of organic materials that potentially offers major advantages such as easy processing and tailoring to fit the specific requirements (e. g., optical properties) of a given device includes azobenzene-containing polymers.[2]

Azobenzene peptides were introduced by Goodman and Kossoy more than thirty years ago.[3] Recently, it was found that holographic gratings with extraordinarily large first-order diffraction efficiencies[4] up to 80%) can be recorded in films of certain azobenzene-containing oligopeptides.[5] These peptides can be built from, e. g., ornithine units (DNO,[6] Fig 1) and were designed to stack azobenzenes in a manner similar to that of the bases in DNA or peptide nucleic acids (PNA)[7] (Fig 1) so as to impose orientational order on the chromophores.

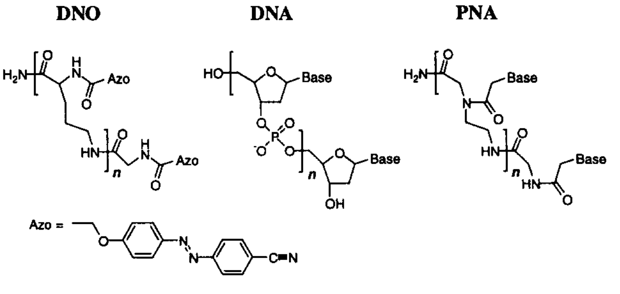

**Figure 1**

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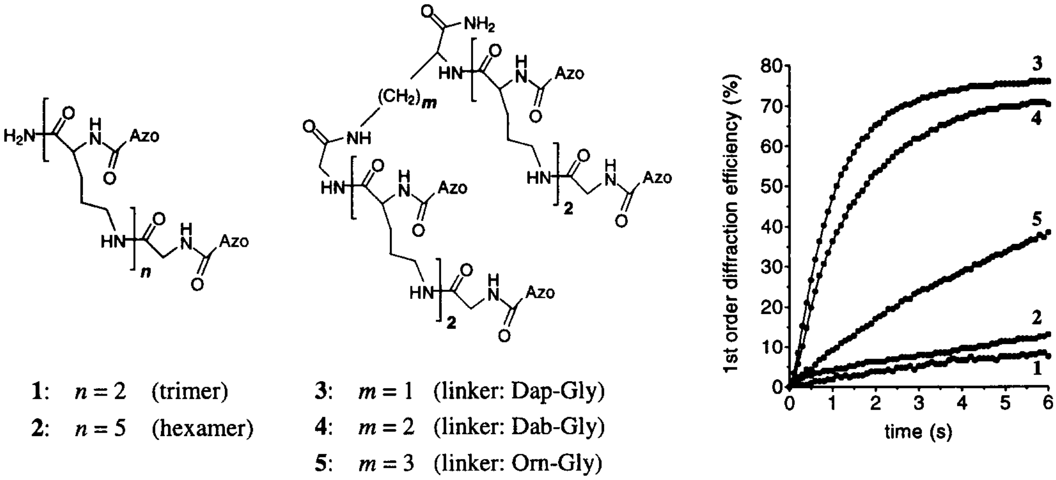
Holograms recorded in DNO oligomers also exhibit good thermal stability. However, a present limitation of ornithine-based DNOs is that the recording time[8] is long (on the order of minutes). Thus, an important challenge is to derive DNOs which permit shorter recording times, preferably on the order of milliseconds. We report here that a remarkable increase in recording speed can be achieved by linking together short DNOs. We show that suitably designed bis-DNOs can reach large diffraction efficiencies (50%) in about 1 s and thus exhibit recording speeds increased by up to a factor of 20 relative to linear DNOs made from the same number of chromophore units.

It is known from polymer systems that an azobenzene chromophore undergoes random reorientations through a number of *trans-cis-trans* isomerization cycles when it is exposed to polarized light in a certain wavelength range. This reorientation process continues until eventually the chromophore is aligned in a stationary orientation with its optical transition moment axis lying in the plane perpendicular to the polarization direction. The alignment of the chromophores results in a change in the material's refractive index which forms the basis for the storage process. The rationale behind the DNO work was to construct molecules in which two or more azobenzene groups are positioned in such a way that the transition moment axes are *non-parallelly oriented in planes parallel to one another* so as to reduce the number of stationary orientations possible. The extraordinarily large first-order diffraction efficiencies obtained with DNOs were thus rationalized on the basis of a more uniform alignment of the chromophores, resulting in higher refractive index changes.

The results obtained with DNOs made up of repeating ornithine units oligomerized through the $\delta$-amino groups and with azobenzene side chains attached to the the $\alpha$-amino groups (Fig 1), showed that the recording speed accelerates markedly with increasing oligomer size (up to about ten units). This suggests that the increased oligomer size may provide a stabilizing influence on the assumed stacking of the chromophores since that would make the coordinated reorientation of them more efficient. To examine the possibility of introducing a new type of conformational constraints on DNOs, oligomers, each of three units in length, were connected through different peptide linkers, producing a series of bis-DNO trimers (Fig 2), which presumably would be more compact than the parent ones. The three linkers consisted of glycine coupled to the 3-, 4-, and 5-amino groups of (2*S*)-2,3-diaminopropanoic acid (L-Dap-OH), (2*S*)-2,4-diaminobutanoic acid (L-Dab-OH) and L-ornithine, respectively.

The DNOs were prepared by standard Merrifield synthesis.[9] To obtain C-terminal amides, the DNOs were assembled on a benzhydrylamine-type polystyrene resin initially loaded with approximately 0.5 mmol *p*-methylbenzhydrylamino groups per gram resin. Bis-trimers (**3**), (**4**), and (**5**) were assembled as previously described[5] employing HBTU coupling of the backbone monomers $N^{\alpha}$-Fmoc-L-Dap($N^{\beta}$-Boc)-OH, $N^{\alpha}$-Fmoc-L-Dab($N^{\omega}$-Boc)-OH, $N^{\alpha}$-Fmoc-L-Orn($N^{\delta}$-Boc)-OH, and Boc-Gly-OH, respectively, and in situ DCC/Dhbt-OH coupling of the azobenzene side-chain monomer $NC\text{-}C_6H_4\text{-}N{=}N\text{-}C_6H_4\text{-}O\text{-}CH_2\text{-}COOH$ via its tetrabutylammonium salt. Trimer (**1**), hexamer (**2**) were assembled by an improved solid-phase procedure employing BOP coupling of both backbone and side-chain monomers (0.2 M monomer and 0.2 M BOP in $CH_2Cl_2$ containing 0.4 M DIEA, 2 h). Ninhydrin analyses indicated that the single BOP coupling of each residue proceeded with a coupling yield of >99%. The free oligomers were released from the resin with anhydrous HF under standard conditions. Since DNOs as well as bis-DNOs are insoluble in common organic solvents, the oligomers could not be characterized by NMR spectroscopy. However, they were shown to have the expected molecular mass by matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry.[10]

The recording properties of bis-DNOs were examined by polarization holography. A two-beam polarization holographic set-up[11] was used to record diffraction gratings in approximately 8 µm-thick films prepared from the different bis-DNOs by casting from hexafluoro-2-propanol-trifluoroacetic acid-methylene chloride (76: 18: 6 (v/v/v)) solutions as previously described. Two orthogonally circularly polarized beams at 488 nm from an argon ion laser, with a total intensity of 25 mW/mm$^2$, were used for recording holographic gratings with a spatial resolution of about 510 lines per mm. A 4.2 mW circularly polarized beam at 633 nm from a He-Ne laser was used for read-out.



1: $n = 2$ (trimer)
2: $n = 5$ (hexamer)
3: $m = 1$ (linker: Dap-Gly)
4: $m = 2$ (linker: Dab-Gly)
5: $m = 3$ (linker: Orn-Gly)

**Figure 2**

The bis-DNO trimers prepared were found to be surprisingly efficient. After the argon ion laser had been turned on for a few seconds they all gave first-order diffraction values much greater than that of the linear DNOs. Figure 2 shows the recording curves obtained with the linear DNOs (**1**) and (**2**) and the bis-DNO trimers (**3**), (**4**) and (**5**). It is seen that with **3** a first-order diffraction efficiency of 50% is reached in about 1 s and a maximum value of 75% is reached in 4 s. This is an increase in recording speed of more than a factor of 20 relative to **2**, which contains the same number of chromophores. Moreover, it is noted that the recording speed decreases with increasing flexibility in the spacer.

In summary, the present study demonstrates the dramatic effect which can be exerted on the recording properties of DNOs by constructing simple bis-DNOs. Thus, the present work provides a new strategy which may enable the development of superior DNO recording media for holographic storage. Work is in progress to optimize bis-DNO structures.

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10 MALDI-TOF MS (DHB): The linear DNO hexamer (**2**), *m/z* (M+ H$^+$) found (calcd) 2225.8 (2225.4); the DNO bis-trimer (**3**), *m/z* (M+ Na$^+$) found (calcd) 2334.5 (2333.4).

11 A general discussion on interference, diffraction, and holography can be found in "Optical Holography", R. J. Collier, C. B. Buckhardt and L. H. Lin, Academic Press, New York (1971).