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Molecular glasses of azobenzene for holographic data storage applications

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ABSTRACT

A series of D-N=N-A type molecular glasses where the electron acceptor part (A) contains several electron withdrawing substituents, but the electron donating part (D) of the glassy azochromophores contains amorphous phase promoting non-conjugated bulky triphenyl or hydroxyl groups have been synthesized and investigated. Results showed that the azodye physical properties depend not only on the incorporated electron withdrawing substituents but are also influenced by the bonding type of covalently attached bulky moieties. Synthesized glassy azocompounds showed glass transition temperatures up to 106 °C and thermal stability up to 312 °C.

The ability to form holographic gratings in spin-cast thin films of the glassy azodyes was investigated using 532 nm and 633 nm lasers obtaining diffraction efficiency up to 57%, self-diffraction efficiency up to 15% and photosensitivity as high as 3.7 J/(cm^2%). Surface relief grating (SRG) depths reached 1.1 μm and in some cases even exceeded the thickness of the films.

1. Introduction

Since the first demonstration of the surface-relief grating (SRG) formation phenomenon in organic polymer films as a result of laser irradiation in 1995 [1–3], it has attracted considerable attention of many scientists due to the additional mechanical (light weight and flexibility) properties of organic materials, as light weight, flexibility and low-cost fabrication possibility [1,4]. Several mechanisms have been proposed for the surface structure modulation formation [1,4–8]. However, the main requirement for such organic materials is the presence of azobenzene fragment in their structure which undergoes continuous and reversible *trans-cis-trans* photoisomerization cycles [1,4–10]. Due these properties of photoisomerization and grating formation azobenzene materials are widely applicable in practical applications for nonlinear optics [11–14], optical switches [7,15], waveguides and Bragg reflectors in distributed feedback polymer lasers [16], optical storage devices [1,14,17] and polarization holograms [6,8,18]. A wide range of synthetic methods has provided numerous approaches for the placement of azobenzene fragment in the chemical structures of organic materials, most often in the side chain and/or main chain of various polymers [1,4–6,8,18–20]. Additionally, azobenzene fragment containing low-molecular weight organic chromophore can be incorporated within the structures of dendrimers [21,22] or doped in the polymer matrix producing the host-guest systems [17,23,24].

The design of recording medium for efficient polarization hologram and surface relief hologram recording is complicated and still remains a challenge as the potential material requires maximum refractive index and surface relief change modulation (diffraction efficiency), high sensitivity towards photonic irradiation and high free volume for mass-transport processes [25]. One way to increase the diffraction efficiency is introduction of hydroxyl groups which can form intermolecular hydrogen bonds and enhance the stability of formed relief gratings [26]. Another approach is to maximize the active azochromophore content within the material through utilization of low-molecular weight glassy organic compounds [13,27].

Previously we have demonstrated [27–29] that the low-molecular mass organic compounds with incorporated bulky triphenyl moieties form amorphous structure in their solid state by solution-processing [13,27–29] and show potential as holographic

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information storage materials [27,29]. Synthetic methods provide functionalization possibilities of azobenzene derivatives with amorphous phase promoting triphenyl functional groups. So far, the improvement of holographic recording medium properties has been related to the synthesis and design of chromophore molecules. However, there may be still undiscovered enhancement possibilities based only of the structure bonding type of the amorphous state promoting moieties. Therefore, in order to provide a better understanding on the relation between the azochromophores and different chemical incorporation of triphenyl moieties with the diffraction efficiency and irradiation sensitivity of molecular-type organic holographic-recording materials, glassy derivatives of azobenzene with bromine, cyano and carbonyl electron withdrawing substituents as well as with hydroxyl groups have been synthesized and investigated.

2. Experimental

Full preparation, characterization and relevant references of all organic compounds are available within the supplementary information.

2.1. Characteristics of synthesized azodyes

4-((4-(-2-(4-(Bis(2-(trityloxy)ethyl)amino)phenyl)-1-cyanovinyl)phenyl)diazenyl)-3-bromobenzonitrile (**ZGD-1**). Yield: 8% for a single step synthesis and 40% for a different pathway, two-step synthesis; m.p. 202 °C; IR (paraffin oil) υ, cm^{-1}: 3469, 3079, 3067, 3024, 2924, 2876, 2780, 2731, 2204, 1959, 1608, 1574, 1521.^{1}H NMR (300 MHz; $CDCl_3$) δ, ppm: 3.32 (4H, t, $^3J = 5.5$ Hz), 3.61 (4H, t, $^3J = 5.8$ Hz), 6.55 (2H, d, $^3J = 8.7$ Hz), 7.20–7.40 (30H, m), 7.65–7.78 (7H, m), 8.02 (3H, m). Elemental analysis: calcd. for ZGD-1 ($C_{64}H_{50}BrN_5O_2$): C, 76.79; H, 5.03; N, 7.00; found: C, 76.65; H, 5.08; N, 7.04.

4-((4-(2-(4-(Bis(5,5,5-triphenylpentyl)amino)phenyl)-1-cyanovinyl)phenyl)diazenyl)-bromobenzonitrile (**ZGD-1T**). Yield: 21.4%; m.p. 216 °C; IR (paraffin oil) υ, cm^{-1}: 3469, 3083, 3046, 3017, 2937, 2870, 2230, 2203, 1959, 1607, 1574, 1520, 1491.^{1}H NMR (300 MHz; $CDCl_3$) δ, ppm: 1.02 (4H, m), 1.48 (4H, s), 2.51 (4H, m), 3.06 (4H, m), 6.52 (2H, m), 7.10–7.25 (30H, m), 7.48 (1H, s), 7.65 (2H, m), 7.78 (4H, m, $^3J = 8.8$ Hz), 7.99 (3H, m). Elemental analysis: calcd. for ZGD-1T ($C_{68}H_{58}BrN_5$): C, 76.67; H, 5.70; N, 6.83; found: C, 76.83; H, 5.74; N, 6.90.

4-((4-(2-(4-((4-(Bis(2-(trityloxy)ethyl)amino)phenyl)diazenyl)phenyl)-1-cyanovinyl)phenyl)diazenyl)-3-bromobenzonitrile (**ZGD-2**). Yield: 23.9%; m.p. 222 °C; IR (paraffin oil) υ, cm^{-1}: 3469, 3156, 3085, 3064, 3033, 2954, 2928, 2876, 2781, 2730, 2228, 2214, 1959, 1598, 1581, 1561, 1511.^{1}H NMR (300 MHz; $CDCl_3$) δ, ppm: 3.33 (4H, t, $^3J = 5.4$ Hz), 3.64 (4H, m), 6.59 (2H, d, $^3J = 8.8$ Hz), 7.10–7.25 (31H, m), 7.62–7.76 (3H, m), 7.84–7.98 (6H, m), 8.02–8.08 (4H, m). Elemental analysis: calcd. for ZGD-2 ($C_{70}H_{54}BrN_7O_2$): C, 76.08; H, 4.93; N, 8.87; found: C, 76.02; H, 5.02; N, 8.71.

2,2'-(4-(2-(4-((2-Bromo-4-cyanophenyl)diazenyl)phenyl)-2-cyanovinyl)phenylazanediyl)bis(ethane-2,1-diyl) bis(3,3,3-triphenylpropanoate) (**ZGD-1Q**). Yield: 51.7%; m.p. 126 °C. IR (paraffin oil) υ, cm^{-1}: 3468, 3087, 3061, 3034, 2927, 2852, 2777, 2205, 1734, 1606, 1569, 1518.^{1}H-NMR (300 MHz; $CDCl_3$) δ, ppm: 3.09 (4H, t, $^3J = 5.5$ Hz), 3.64 (4H, s), 3.79 (4H, t, $^3J = 5.6$ Hz), 6.50 (2H, d, $^3J = 8.8$ Hz), 7.10–7.25 (30H, m), 7.46 (1H, s), 7.66 (2H, m, $^3J = 8.3$ Hz), 7.78 (4H, t, $^3J = 8.4$ Hz), 7.96–8.03 (3H, m). Elemental analysis: calcd. for ZGD-1Q ($C_{68}H_{54}BrN_5O_4$): C, 75.27; H, 5.02; N, 6.45; found: C, 75.13; H, 5.12; N, 6.54.

2,2'-(4-((4-(2-(4-((2-Bromo-4-cyanophenyl)diazenyl)phenyl)-2-cyanovinyl)phenyl)diazenyl)phenylazanediyl)bis(ethane-2,1-diyl) bis(3,3,3-triphenylpropanoate) (**ZGD-2Q**). Yield: 35.4%; m.p. 169 °C. IR (paraffin oil) υ, cm^{-1}: 3468, 3086, 3056, 3032, 2935, 2857, 2781, 2263, 2226, 1736, 1597.^{1}H-NMR (300 MHz; $CDCl_3$) δ, ppm: 3.12 (4H, m), 3.64 (4H, s), 3.79 (4H, m), 6.54 (2H, d, $^3J = 8.4$ Hz), 7.10–7.25 (31H, m), 7.66–7.74 (3H, m), 7.84–7.92 (6H, m), 7.98–8.08 (4H, m). Elemental analysis: calcd. for ZGD-2Q ($C_{74}H_{58}BrN_7O_4$): C, 74.74; H, 4.92; N, 8.24; found: C, 74.77; H, 5.11; N, 8.15.

5,5,5-Triphenylpentyl 4-((4-(2-(4-(bis(2-(trityloxy)ethyl)amino)phenyl)-1-cyanovinyl)phenyl)diazenyl)benzoate (**B-7**). Yield: 52%; IR (paraffin oil) υ, cm^{-1}: 3080, 3059, 3033, 2926, 2876, 2208, 1959, 1717, 1682, 1597, 1575, 1519, 1490, 1402.^{1}H-NMR (300 MHz; $CDCl_3$) δ, ppm: 1.24 (2H, m), 1.78 (2H, m), 2.62 (2H, m), 3.29 (4H, m), 3.60 (2H, m), 4.25 (2H, t, $^3J = 6.4$ Hz), 6.59 (2H, m), 7.10–7.30 (47H, m), 7.45–7.55 (2H, m), 7.70–7.80 (2H, m), 7.90–8.00 (3H, m, $^3J = 8.6$ Hz), 8.05 (2H, d, $^3J = 8.4$ Hz). Elemental analysis: calcd. for B-7 ($C_{87}H_{74}N_4O_4$): C, 84.30; H, 6.02; N, 4.52; found: C, 84.03; H, 6.10; N, 4.33.

5,5,5-Triphenylpentyl 4-((4-(2-(4-(bis(2-hydroxyethyl)amino)phenyl)-1-cyanovinyl)phenyl)diazenyl)benzoate (**B-11**). Yield: 43%; IR (paraffin oil) υ, cm^{-1}: 3436, 3083, 3055, 3029, 2930, 2874, 2204, 1959, 1713, 1605, 1568, 1518, 1352, 1270, 1183, 1140, 1113.^{1}H-NMR (300 MHz; $CDCl_3$) δ, ppm: 1.22 (4H, m), 1.76 (2H, m), 2.60 (2H, m), 3.67 (4H, m), 3.87 (4H, m), 4.23 (2H, t, $^3J = 6.1$ Hz), 6.86 (2H, d, $^3J = 8.4$ Hz), 7.10–7.25 (15H, m), 7.49 (1H, s), 7.75 (2H, d, $^3J = 8.3$ Hz), 7.87 (4H, m), 7.95 (2H, d, $^3J = 8.4$ Hz), 8.02 (2H, d, $^3J = 8.2$ Hz). Elemental analysis: calcd. for B-11 ($C_{49}H_{46}N_4O_4$): C, 77.96; H, 6.14; N, 7.42; found: C, 77.78; H, 6.30; N, 7.32.

5,5,5-Triphenylpentyl 4-((4-(2-(4-(bis(2-hydroxyethyl)amino)phenyl)-1-cyanovinyl)phenyl)diazenyl)-3-bromobenzoate (**B-15**). Yield: 63%; IR (paraffin oil) υ, cm^{-1}: 3437, 2952, 2923, 2850, 2198, 1959, 1717, 1607, 1568, 1518, 1274, 1182, 1149.^{1}H-NMR (300 MHz; $CDCl_3$) δ, ppm: 1.20 (4H, wide s), 1.76 (2H, m), 2.60 (2H, m), 3.67 (4H, m), 3.90 (4H, m), 4.23 (2H, t, $^3J = 6.3$ Hz), 6.72 (2H, d, $^3J = 8.8$ Hz), 7.10–7.25 (15H, m), 7.49 (1H, s), 7.62 (1H, d, $^3J = 8.4$ Hz), 7.76 (2H, d, $^3J = 8.6$ Hz), 7.87 (3H, m), 8.01 (2H, d, $^3J = 8.7$ Hz), 8.26 (1H, s). Elemental analysis: calcd. for B-15 ($C_{49}H_{45}BrN_4O_4$): C, 70.58; H, 5.44; N, 6.72; found: C, 70.25; H, 5.75; N, 6.89.

3. Results and discussion

3.1. Investigated materials

Cyano- and bromine-substituents with an average electron withdrawing characteristics were selected for the desired materials to form neat films in their solid-state without aggregate formation which is usually caused by strong dipole-dipole interaction of molecules that leads to crystallization [29,35]. Synthesized glassy compounds are shown in Fig. 1. Azodye ZGD-1 where bulky amorphous phase promoting triphenyl moieties are attached to the chromophore through ether bonds was obtained according to known procedures [30–33]. Azodye ZGD-1T contains triphenyl moieties incorporated through methylene bonds [34].To evaluate the influence of additionally incorporated azobenzene fragments in connection to optical and thermal properties as well as holographic data storage parameters, two azogroups containing D-π-A dye ZGD-2 with triphenyl groups attached through ether bonds [29] has been synthesized. In one and two azogroup containing dyes ZGD-1Q and ZGD-2Q bulky triphenyl moieties are attached through ester bonds [34–36]. Additionally, different types of azodyes (B-type materials) with carboxyl substituent have been synthesized according to previously described procedures [30–32,34–36]. B-7 contains covalently attached three triphenyl moieties, which are necessary for the formation of amorphous films in the solid state