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Quinoline-based azo derivative assembly: Optical limiting property and enhancement mechanism

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To further investigate the dependence of optical limiting properties on molecular structures, especially the strong intermolecular influence, *such as* the influences of hydrogen bond, dipole-dipole interaction and their synergetic effect on optical limiting properties, three polar D- π -A conjugated quinoline-based heterocyclic azo derivatives (**3a**, **3b** and **3c**) with different hydrogen-bond recognition abilities were designed and synthesized. Their structures and properties were characterized and evaluated by infrared spectroscopy, thermogravimetric analysis, and ultraviolet-visible spectrometry. The strengthening mechanism of optical limiting property was investigated in detail based on theoretical calculation and experimental results of molecular assembly induced by synergetic effect of hydrogen bond and dipole-dipole interaction. The results indicate that the optical limiting properties of these polar D- π -A conjugated optical materials were significantly affected by molecular structure, strong intermolecular interaction and their synergetic enhancement effect.



TOC Graph

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Abstract: To further investigate the dependence of optical limiting properties on molecular 10 structures, especially the strong intermolecular interactions, such as the influences of hydrogen bond, 11 dipole-dipole interaction and their synergetic effect on optical limiting properties, three polar D- π -A 12 conjugated quinoline-based heterocyclic azo derivatives (3a, 3b and 3c) with different 13 hydrogen-bond recognition abilities were designed and synthesized. Their structures and properties 14 were characterized and evaluated by infrared spectroscopy, thermogravimetric analysis, and 15 ultraviolet-visible spectrometry. The strengthening mechanism of optical limiting property was 16 investigated in detail based on theoretical calculation and experimental results of molecular assembly 17 induced by synergetic effect of hydrogen bond and dipole-dipole interaction. The results indicate that 18 the optical limiting properties of these polar D- π -A conjugated optical materials were significantly 19 affected by molecular structure, strong intermolecular interaction and their synergetic enhancement 20 effects. 21

Keywords: Quinoline-based azo derivative; Self-assembly; Optical limiting; Mechanism; Hydrogen
 bond; Synergetic effect

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1. Introduction

Optical materials, in particular, optical limiting materials for protection of human eyes, optical 26 sensors, and sensitive optical components from laser damage in both civilian and military 27 applications [1-4], have attracted more and more considerable interest in recent years with the fast 28 development of modern laser technologies. Different conjugated organic materials that exhibit strong 29 optical limiting property and fast response time have been designed and synthesized, i.e., azo 30 compounds[5, 6], porphyrins[7], phthalocyanines[8], polydiacetylenes[9] and polyacetylenes[10] and 31 so on. The results show that extending the conjugation length[11], introducing strong electron donor 32 (D) and acceptor (A) groups to the conjugated system[12], strengthening the molecular planarity[13] 33 and making the system multi-branch[14], multi-dimension or dendrimer[3] can all improve the 34 optical limiting properties. Recently, Li[15] proposed the concept of "suitable isolation group" based 35 on the facts that the nonlinear optical (NLO) effect would be enhanced dramatically with further 36 increases in loading density [16, 17], meaning that the frequently observed asymptotic dependence of 37 electro-optic activity on the chromophore number density could be overcome through rational design. 38 The proposed concept would provide some useful information for the rational design of new NLO 39 materials. The basic principle is to extend more π -delocalization, which results in the lower energy 40 gap between the highest occupied molecular orbits (HOMO) and the lowest unoccupied molecular 41 orbits (LUMO) and effective intermolecular charge transfers (ICT). However, the above 42 investigations are mainly based on the molecular structural design. The influence of intermolecular 43 interactions, *i.e.*, hydrogen bond, dipole-dipole interaction and their synergetic enhancement effect, 44 on optical limiting properties was not completely understood. 45

In this work, three polar D-π-A conjugated heterocyclic azo molecules with different terminal
hydrogen bond recognition abilities: 6-quinaldinyl-4'-[N,N-dimethyl-amino]azo-benzene (3a),
6-quinaldinyl-4'-[N-methyl-N-hydroxyethyl amino] azo-benzene (3b), and 6-quinaldinyl-4'-[N,
N-di-hydroxyethyl amino]-azo-benzene (3c), in which quinolyl groups are used as electron acceptors

(A) and aniline derivative groups as electron donors (D), are designed and synthesized for further investigating the influence of molecular structure, hydrogen bond, dipole-dipole interaction and their synergetic enhancement effect on optical limiting properties.

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54 **2. Experimental**

⁵⁵ 2.1. *Reagents and apparatus*

⁵⁶ 4-Nitro aniline, crotonaldehyde, sodium nitrite, N,N-dimethyl-aniline, N-methyl-N-hydroxyethyl
 ⁵⁷ aniline, N,N-dihydroxyethyl aniline and all the other reagents were of analytical grade and purchased
 ⁵⁸ from Shanghai Chemical Reagent Company. They were used directly without any further
 ⁵⁹ purification.

FT-IR spectra were recorded as KBr pellets on a Perkin Elmer Model 882 infrared spectrometer 60 by infrared spectrometer scanning from 4000-500 cm⁻¹. ¹H NMR (300 MHz) and ¹³C NMR (100 61 MHz) spectra were recorded using a Bruker AMX-500 spectrometer operating at 400 MHz, with 62 tetramethyl-silane(TMS) as the reference and chloroform-d as solvent. Elemental analyses were 63 conducted with an Elemental Vario EL-III apparatus. Mass spectra were carried out by using 64 Shimadzu GCMS-QP2010 Spectrometry. The aggregation morphologies were visualized using a 65 CMM-88E metallographic electron optical microscope (OM). Thermogravimetric analyses (TGA) 66 were performed on a Perkin Elmer TGA under nitrogen at a heating rate of 10 °C/min. 67 Ultraviolet-visible (UV-vis) spectra were recorded on a Lambda 35 UV/Vis spectrometer (Perkin 68 Elmer Precisely) using a 1-cm square quartz cell. The optical limiting properties were measured in 69 DMSO solutions. Testing was performed using a frequency-doubled, Q-switched, mode-locked 70 Continuum ns/ps Nd:YAG laser, which provided linearly polarized 4 ns optical pulses at 532 nm 71 wavelength with a repetition of 1 Hz. The transverse mode of the laser pulses was nearly Gaussian. 72 The input laser pulses were split into two beams by an attenuator (Newport). One was employed as 73 reference to monitor the incident laser energy, and the other was focused onto the sample cell by 74

using a lens with 40 cm focal length. The sample was housed in quartz cells with a thickness of 4
mm. The incident and transmitted laser pulses were monitored by utilizing two energy detectors, D1
and D2 (Rjp-735 energy probes, Laser Precision). The optical limiting properties of the samples were
carried out using the same laser system at the input energy 184 mJ. The experimental set up was
similar to that given in the literature[18].

80 2.2. Synthesis and self-assembly

⁸¹ The target heterocyclic azo-derivatives with different terminal hydrogen bond recognition abilities

were prepared according to **Scheme 1**[5, 19, 20].

Insert Scheme 1

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⁸⁶ 2.2.1 Preparation of 6-nitro-quinaldine (1)

A 100 mL three-necked bottle was charged with hydrochloride (44.8 mL, 6 mol/L), 4-nitro aniline 87 (1232 mg, 8.9 mmol) and acetic acid (0.5 mL, 8.9 mmol), which was refluxed at 100 °C for 0.5 h. 88 After iodine/potassium iodide (50 mg/132 mg, 0.4 mmol/0.8 mmol) and 10 mL toluene added, a 89 mixture of toluene (2 mL) and crotonaldehyde (1.5 mL, 17.8 mmol) was added drop wise over a 90 period of 1 h and refluxed for another 6 h. The reaction mixture was cooled to room temperature, and 91 adjusted to alkaline using aqueous ammonia for precipitating the product completely. The 92 precipitation was filtered and purified by column chromatography on silica gel (eluent: petroleum 93 ether/ethyl acetate = 1:5.5, v/v) to give light yellow crystal 6-nitro-quinaldine 1. 94

Yield, 93.1%. IR (KBr), υ (cm⁻¹): 3096 (Ar-H), 2959 (CH₃), 1534, 1382 (-NO₂). ¹H NMR (400 MHz, CDCl₃) δ : 8.12 (s, J=8.4 Hz, 1 H, H⁵), 7.97 (d, J=2.4 Hz, 1 H, H⁴), 7.95 (d, J=2 Hz, 1 H, H³), 7.53 (d, J=8.2 Hz, 1 H, H⁸), 7.38 (d, J=8.4 Hz, 1 H, H⁷), 2.78 (s, 3 H, CH₃). Anal. Calcd. for C₁₀H₈N₂O₂: C, 63.82; H, 4.28; N, 14.89. Found: C, 63.93; H, 4.27; N, 14.74.

⁹⁹ 2.2.2 Preparation of 6-amino-quinaldine (2)

To a 50 mL round bottom bottle, glacial acetic acid (10 mL) and 6-nitro quinaldine (1) (400 mg, 2.13 mmol) were added. The mixture was then stirred and added iron powder (480 mg, 8.60 mmol) slowly. After turning to light yellow completely, the reaction mixture was filtered and washed thoroughly with ethanol. The filtrate was distilled to dryness under reduced pressure conditions and the residue was purified by column chromatography on silica gel (eluent: ethyl acetate) to give white crystal 6-amino quinaldine **2**.

Yield, 71.9%. IR (KBr), υ (cm⁻¹): 3462, 3428 (NH₂), 2920 (CH₃). ¹H NMR (400 MHz, CDCl₃) δ : 7.93 (d, J=8.4 Hz, 1 H, H³), 7.76 (d, J=8.5 Hz, 1 H, H²), 7.73 (d, J=4.2 Hz 1 H, H⁷), 7.32 (d, J=4.8Hz, 1H, H⁸), 7.26 (s, 1 H, H⁵), 5.02 (s, 2 H, NH₂), 2.739 (s, 1H, CH₃). Anal. Calcd. for C₁₀H₁₀N₂: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.03; H, 6.41; N, 17.80.

¹¹⁰ 2.2.3 Preparation of 6-quinaldinyl-4'-[N,N-dimethyl-amino] azobenzene (**3a**)

6-Aminoquinaldine (2) (316 mg, 2 mmol) was dissolved in an ice-water solution of sodium nitrite 111 (170 mg, 2.5 mmol) in 3 mL of water. After cooling to 0 °C, concentrated hydrochloric acid (1.2 mL) 112 was added to the solution under continuous stirring for 30 min. The excess nitrous acid was 113 destroyed with about 5 mg urea. The mixture was then added drop wise to 10 mL buffered aqueous 114 solution (acetic acid/sodium acetate, pH \approx 6) containing N,N-dimethyl aniline (267 mg, 2.2 mmol) 115 and stirred for another 2 h at 0-5 °C. The resultant precipitation was filtered and rinsed with enough 116 water. The crude product was purified by column chromatography on silica gel (eluent: petroleum 117 ether/ethyl acetate = 1:1, v/v) to provide red crystal **3a**. 118

Yield, 87.1%. IR (KBr), υ (cm⁻¹): 3056 (ArH), 2923 (CH₃), 1599 (N=N). ¹H NMR (400 MHz, CDCl₃) δ : 8.76 (s, 1H, H⁵), 8.43 (d, J=7.9 Hz, 1 H, H⁴), 8.24 (d, J=7.8 Hz, 1 H, H³), 8.14 (d, J=8.8 Hz, 2 H, H⁸), 7.94 (d, J=8.8 Hz, 2 H, H⁷), 7.35 (d, J=8.4 Hz, 2 H, H⁹), 6.79 (d, J=8.8 Hz, 2 H, H¹⁰), 3.12 (s, 6 H, N-CH₃), 2.82 (s, 3H, Ar-CH₃). ¹³C NMR(100MHz, CDCl₃) δ : 159.8, 154.3, 151.1, 149.2, 145.8, 136.6, 131.7, 126.9, 126.2, 126.1, 125.8, 123.0, 122.9, 112.7, 112.7 (Ar-C), 42.3, 42.3(N-CH₃), 24.3(ArCH₃). MS: *m/z* 290.4 [M]⁺. Anal. Calcd. for C₁₈H₁₈N₄: C, 74.46; H, 6.25; N,

- ¹²⁵ 19.30. Found: C, 74.53; H, 6.29; N, 19.39.
- $_{126}$ 2.2.4 Preparation of 6-quinaldinyl-4'-[N-methyl-N-hydroxyethyl amino] azo benzene (**3b**)

3b was prepared as above from N-methyl-N-hydroethyl aniline and 6-Aminoquinaldine. The 127 product was red crystal. Yield, 84.7%. IR (KBr), υ (cm⁻¹): 3363 (OH), 2922 (CH₃), 1599 (N=N). ¹H 128 NMR (400 MHz, CDCl₃) δ: 8.27 (d, J=7.8 Hz, 1 H, H⁴), 8.15 (d, J=7.9 Hz, 1 H, H³), 7.93 (s, 1 H, 129 H⁵), 7.91 (d, J=8.5 Hz, 2 H, H⁸), 7.37 (d, J=8.4 Hz, 2 H, H⁷), 6.85 (m, J=3.2 Hz, 4 H, H^{9,10}), 3.90 (t, 130 J=8.4Hz, 2 H, CH₂OH), 3.64 (t, J=8.6Hz, 2 H, N-CH₂), 3.33 (s, 1H, OH), 3.15 (s, 3H, N-CH₃), 2.82 131 (s, 3H, ArCH₃). ¹³C NMR(100MHz, CDCl₃) δ: 159.9, 152.3, 151.0, 149.3, 144.8, 136.6, 131.7, 126.8, 132 125.8, 125.1, 125.1, 124.8, 122.9, 111.8, 111.8 (Ar-C), 64.0(N-CH₂-), 58.8(O-CH₂-), 41.9(N-CH₃), 133 24.3(ArCH₃). MS: *m/z* 320.2 [M]⁺. Anal. Calcd. for C₁₉H₂₀N₄O: C, 71.23; H, 6.29; N, 17.49. Found: 134 C, 71.16; H, 6.33; N, 17.55. 135

¹³⁶ 2.2.5 Preparation of 6-quinaldinyl-4'-[N,N-dihydroxyethyl amino]azobenzene (**3c**)

3c was prepared as above from N,N-dihydroxyethyl aniline and 6-Aminoquinaldine. The product 137 was red crystal. Yield, 85.8%. IR (KBr), v (cm⁻¹): 3346 (OH), 2921 (CH₃), 1597 (N=N). ¹H NMR 138 (400 MHz, CDCl₃) δ: 8.19 (d, J=7.8 Hz, 1 H, H⁴), 8.01 (d, J=7.9 Hz, 1 H, H³), 7.91 (s, 1 H, H⁵), 7.89 139 (d, J=8.5 Hz, 2 H, H⁸), 7.33 (d, J=8.4 Hz, 2 H, H⁷), 6.79 (m, J=2.2 Hz, 4 H, H^{9,10}), 3.97 (t, J=7.6Hz, 4 140 H, CH₂OH), 3.74 (t, J=7.5Hz, 4 H, NCH₂), 3.59 (s, 2H, OH), 2.77 (s, 3H, CH₃). ¹³C NMR(100MHz. 141 $CDCl_3$ δ : 159.8, 151.8, 151.0, 149.2, 144.8, 136.6, 131.6, 126.8, 125.1, 125.1, 124.8, 123.0, 122.8, 142 111.6, 111.6 (Ar-C), 61.8, 61.8(N-CH₂-), 58.9, 58.9(O-CH₂-), 24.5(ArCH₃). MS: m/z 350.5 [M]⁺. 143 Anal. Calcd. for C₂₀H₂N₄O₂: C, 68.55; H, 6.32; N, 15.99. Found: C, 68.51; H, 6.37; N, 16.04. 144

145 2.2.6 Self-assembly procedure

According to the reported method in the literature [4, 21], in a typical experiment, injection of 5 mL +**3a**, **3b** or **3c** solutions with the concentration of 10^{-4} mol·L⁻¹ in tetrahydrofuran solution (THF, a good solvent for **3a**, **3b** and **3c**) into water (a bad solvent for **3a**, **3b** and **3c**) got a mixture. The mixture was sonicated to disperse evenly in water-bath urtrasonic apparatus at room temperature for

- $_{150}$ 0.5 h and then all the mixtures were on standing for 48 h for self-assembly effectively. After that, the assemblies were filtered and stored at room temperature (20 °C).
- 152 2.2.7 Preparation of the samples

To measure the UV-vis absorption spectra and the optical limiting properties of **3a**, **3b** and **3c** in solutions, the above self-assemblies of **3a**, **3b** and **3c** were dissolved in DMSO to get 1.0×10^{-4} mol·L⁻¹ solutions, respectively. According to our recent research result [4], we conclude that there must be the existence of supramolecular self-assemblies for **3b** and **3c** to some extent, especially for **3c** in its solution with the increasing terminal hydrogen bond recognition ability.

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159 **3. Results and discussion**

¹⁶⁰ *3.1. Synthesis of* **3a**, **3b** and **3c**

Three polar quinoline-based heterocyclic azo derivatives (3a-3c) with different terminal hydrogen bond recognition groups were designed and synthesized through a multi-step reaction route shown in Scheme 1[5, 19, 20]. 6-Nitroquinaldine was synthesized using crotonaldehyde and p-nitroaniline as raw materials in the presence of acetic acid and toluene. It was found that the optimal reaction conditions for diazotization of 6-aminoquinaldine with N,N-bis-substituent aniline derivatives were in the buffer solution of acetic acid and sodium acetate (pH~6), which could keep diazo salt in high concentration and gave quinoline-based azo derivatives 3a~3c in high yields.

All the intermediates and target compounds were characterized by FT-IR, ¹H NMR and element analysis and satisfactory analysis data corresponding to their molecular structures were obtained as shown in section 2.

¹⁷¹ 3.2. Characterization of the hydrogen bond between polar $D-\pi$ -A azo molecules (**3a**, **3b** and **3c**)

Theoretically, when the hydrogen-bond proton donor is the same, the higher alkaline and the less space steric effect of the proton acceptor, the more easily and strongly hydrogen bonds can be formed. As the alkaline of N-atom in quinoline ring is stronger and its space steric effect is less than those of O-atom in the terminal hydroxyl group, the intermolecular hydrogen bond interaction

mainly happens between the terminal hydroxyl groups as proton donors and N-atoms in quinoline
rings as proton acceptors in polar 3a, 3b or 3c molecules based on the thermodynamic equilibrium
and kinetic effect, does not bring forth between two of the terminal hydroxyl groups (shown in
Figure 1).

Insert Fig. 1

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It is well known that FT-IR spectroscopy is a suitable technique for investigating particular intermolecular interaction owing to the fact that any alteration in intermolecular and/or intramolecular interaction can induce the corresponding FT-IR absorption change in its strength, peak position or peak area of the characteristic functional group[4]. To certify the intermolecular hydrogen bonding distribution in **3a**, **3b** and **3c**, their FT-IR spectra were recorded at room temperature first and shown in **Figure 2**, respectively.

Insert Fig. 2

From Figure 2, it is easy to find that there is no absorbance for **3a** in the region of $3100 \sim 3800 \text{ cm}^{-1}$, 192 *i.e.*, the interaction force between **3a** molecules is weak dipole-dipole interaction and van der waals 193 force only. For **3b** and **3c**, the absorbance at *ca*. 3600 cm⁻¹, which belongs to the O-H stretching 194 vibration of free hydroxyl groups, is very weak. It means that there are few free hydroxyl groups in 195 solid **3b** and **3c**. Moreover, we can find two obvious absorption peaks at ca. 3415 and 3269 cm⁻¹, 196 respectively. The peak at 3415 cm⁻¹ is assigned to the "oligomers" resulting from hydrogen bond 197 interaction between two molecules of 3b or 3c, whereas the one at 3269 cm⁻¹ is attributed to the 198 formation of "polymeric" species[4]. The peak intensity at 3269 cm⁻¹ becomes stronger in 3c than 199 that in **3b**, hinting that the stronger H-bond interaction happens in **3c** than that in **3b**. Simultaneously, 200

it is also found that the absorbance peak attributing to C=N stretching vibration changes from 1590 cm^{-1} for **3a** to 1597 cm⁻¹ for **3b**, and further to 1599cm⁻¹ for **3c** (Fig. 2), due to the strengthening electron- attractive ability of the N-atom in the quinoline ring once the formation of H-bonds. It also declares the N-atom in the quinoline ring has participated in forming H-bonds in **3b** and **3c**. The FT-IR spectra of **3b** and **3c** at 60 °C were also recorded shown in **Figure 3**.

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Insert Fig. 3

At 60 °C, for **3b**, the peak intensities at 3415 cm⁻¹ and 3269 cm⁻¹ both decrease compared with those at room temperature but their relative intensities change inversely (Figure 3a), exhibiting that "polymeric species" possesses higher stability than "oligomers" pattern. That is, the hydrogen bond intensity in the "polymeric species" pattern is stronger and more stable than that in "oligomers" pattern. The similar conclusion can be drawn from FTIR spectra of **3c** (Figure 3b).

Another proof for the formation of hydrogen bond interactions with different intensities in **3a**, **3b** and **3c** is their thermal properties, which are directly related to the strength of intermolecular interaction and the regularity of molecular arrangement[22, 23]. Thermal decomposition temperatures (T_d , 5 wt % loss) of **3a**, **3b** and **3c** are 166.5, 200.2, and 245.5 °C (shown in Figure 4), respectively.

Insert Fig. 4

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T_d improves with increasing terminal hydrogen bond recognition ability. Thermal properties of **3a**, **3b** and **3c** further confirm that the strength of intermolecular force and the regularity of molecular arrangements of **3a~3c** are in the order of 3c > 3b > 3a. It is consistent with analyses of FT-IR spectra. The intermolecular hydrogen bond interactions of **3a**, **3b** and **3c** with different intensities are

also confirmed directly by their induced aggregates morphologies. To do this, the morphologies of
 the resultant self-assemblies were examined by optical microscopy (OM) shown in Figure 5.

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Insert Fig. 5

From Figure 5 we can find that the morphology of **3a** agglomeration is random nano-particle shape owing to the weak van der waals interaction and dipole-dipole interaction between **3a** molecules. With the introduction of hydrogen bond group and increase of hydrogen bond recognition ability of group, the morphology of molecular agglomeration becomes from zero-dimensional nano particles for **3a**, to one-dimensional fibrous structure for **3b**, and further to two-dimensional line-like crystals for **3c**.

3.3. UV-vis absorption spectra

To illustrate the intermolecular interaction intensity in 3a, 3b and 3c, the UV-vis absorption 238 spectra of 3a, 3b and 3c in DMSO at room temperature were measured (Figure 6). As shown in 239 Figure 6, the UV-vis absorption peaks are at 446, 304 and 269 nm for 3a, 450, 308 and 270 nm for 240 **3b**, and 453, 313 and 273 nm for **3c**, respectively, *i.e.*, the corresponding absorption peaks are 241 red-shift to longer wavelength with increase in terminal hydrogen bond recognition ability. Optical 242 band gaps for 3a, 3b and 3c were calculated to be 2.32, 2.29 and 2.27 eV, respectively according to 243 the onset absorption edge at higher wavelength in the intensity of 5% λ_{max} as illustrated in the 244 literature reported[20]. 245

Insert Fig. 6

Red-shift of UV-absorption peaks and decrease in optical band gaps may be explained by the formation of much stronger intermolecular hydrogen bond interaction described above. It is well

²⁵¹ known that once the formation of hydrogen bond interaction, the electron-attractive ability of N-atom ²⁵² in quinoline ring will get stronger and the arrangement of molecules will be more regular, which ²⁵³ both facilitate electron dispersal in molecules and further result in larger π -electron delocalization. ²⁵⁴ The band gap between the highest occupied molecular orbits (HOMO) and the lowest unoccupied ²⁵⁵ molecular orbits (LUMO) is lowered, which facilitates intermolecular charge transfers (ICT) in the ²⁵⁶ excited state.

257 3.4. Optical Limiting Properties

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To further explore the influence of the intermolecular interaction on optical properties, the optical limiting properties of **3a**, **3b** and **3c** with the same nonlinear optical chromphore content in DMSO were evaluated by *Z*-scan technique under an open aperture configuration. As shown in Figure 6, **3a**, **3b** and **3c** in DMSO show nearly no linear absorption at 532 nm, which promises low intensity loss and little temperature change by photon absorption during the NLO measurements. In theory, the normalized transmittance for the open aperture configuration can be written as[24].

$$T(z, s = 1) = \sum_{m=0}^{\infty} \frac{[-q_0(z)]^m}{(m+1)^{3/2}}, \quad \text{for } |q_0| < 1$$
(1)

where $q_0(z) = \beta I_0(t) L_{\text{eff}} / (1 + z^2/z_0^2)$, β is the nonlinear absorption coefficient, $I_0(t)$ is the intensity of laser beam at focus (z = 0), $L_{\text{eff}} = [1 - \exp(-\alpha_0 L)] / \alpha_0$ is the effective thickness with α_0 the linear absorption coefficient, L is the sample thickness, z_0 is the diffraction length of the beam, and z is the sample position. The results from Z-scan experiments are demonstrated in **Figure 7**.

Insert Fig. 7

The solid lines in Figure 7 are theoretical curves from equation (1). The data collected under the open-aperture configuration indicate that they all exhibit obvious nonlinear absorption properties with effective β values of 0.989 × 10⁻¹¹ m W⁻¹ (**3a**), 1.41 × 10⁻¹¹ m W⁻¹ (**3b**), and 1.55 × 10⁻¹¹ m W⁻¹

(3c), respectively. The result is consistent with our report before [25] that nonlinear properties appear the trend of 3c > 3b > 3a with increasing the terminal hydrogen bond recognition ability, but are stronger than those of corresponding azobenzene-based dyes. The reason may be that the introduction of polar quinolyl group can make the electron cloud distribution of target molecules more uniformitive, which facilitates intermolecular charge transfers (ICT) in the excited state and improves their optical limiting characteristics.

Simultaneously, it is found that optical limiting characteristics of these materials are also influenced by the regularity of the supramolecular self-assemblies. Optical limiting behaviors of **3a**, **3b** and **3c** in DMSO are shown in **Figure 8**, evaluated at 532 nm using 4 ns laser pulses with the same linear transmittance (T=45%).

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- 286 287

Insert Fig. 8

The limiting threshold (incident fluence at which the output fluence starts to deviate from 288 linearity) and amplitude (maximum output fluence) of **3a**, **3b** and **3c** are 0.85 J/cm² and 0.37 J/cm², 289 0.52 J/cm² and 0.30 J/cm², 0.48 J/cm² and 0.27 J/cm², respectively. Just like UV-vis and nonlinear 290 absorption properties, the lowest limiting threshold and limiting amplitude of the three materials both 291 improve with increasing the terminal hydrogen bond recognition ability. With increase of 292 intermolecular interaction, the larger π -electron delocalization may be shown in molecules along 293 with lower energy gap between HOMO and LUMO, further facilitating intermolecular charge 294 transfers (ICT) in the excited state [26], and enhancing optical limiting property. 295

3.5. Theoretical calculations

To theoretically confirm the conclusions made above, calculation under the Gaussian 03 software suite with B3LYP/6-31G level of theory[27], has been carried out to examine the dipole moments,

LUMO & HOMO energy levels of compound **3** with and without the interaction of hydrogen bonding. For simplifying the calculation, the basic structural units of the materials were selected and the bonds at the end of the structural units were saturated with hydrogen atoms. The results are shown in **Figure 9**.

Insert Fig. 9

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From Figure 9, it is easy to find that, electron cloud is mainly grouped on the electron-donor 306 amino-terminal segments for D- π -A-typed azo compounds 3 without the hydrogen bond interaction, 307 *i.e.*, electron cloud is unevenly distributed, molecular dipole moment is large (6.1032 D), and the 308 energy gap between the HOMO (-5.0325 eV) and the LUMO (-1.8533 eV) is high (3.1792 eV). 309 Once the formation of hydrogen bond interaction between N-atom in quinoline ring and H-atom of 310 hydroxyl group, the electron cloud distribution is maintained at equilibrium owing to the increasing 311 electron-withdrawing ability of quinolyl group. The total dipole moment of resultant 3 decreases to 312 4.5211 D, and the energy gap between the HOMO (-5.1240 eV) and the LUMO (-1.9779 eV) is also 313 reduced to 3.1641 eV, which facilitates intermolecular charge transfers (ICT) in the excited state and 314 improves its optical limiting characteristics. 315

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4. Conclusions

In conclusion, three new polar D- π -A conjugated quinoline-based heterocyclic azo derivatives with different terminal hydrogen-bond recognition abilities were designed and prepared. Owing to introducing basic quinolyl (which is a kind of strong basic proton-acceptor) and different terminal hydrogen bond recognition groups, the intermolecular interactions in the target organic molecules are greatly different, which results in different D- π -A conjugated degrees and molecular polarities. The results facilitate very well to enlarge the larger π -electron delocalization of molecules, to reduce

energy gap between HOMO and LUMO and so to facilitate intermolecular charge transfers. All these
 result in red-shift of linear absorption spectra and better optical limiting properties. This work will
 provide a new method to construct the building-in of optical limiting materials with nice property in
 the future.

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400	Figure Legends
401	
402	Scheme 1. Synthetic routes of the target quinoline-based squaraine dyes (3a, 3b and 3c).
403	
404	Fig. 1. The main hydrogen bonding formed in 3b (left) and 3c (right) in theory.
405	
406	Fig. 2. The FT-IR spectra of 3a, 3b and 3c at room temperature (25 °C).
407	
408	Fig. 3. Part of the FT-IR spectra of 3b (a) and 3c (b) at 60 °C and 25 °C, respectively.
409	
410	Fig. 4. TGA thermograms of 3a , 3b and 3c at a ramp rate of 10 °C/min in nitrogen flow, respectively.
411	
	Fig. 5. Optical microscopic images of salf assemblies 32, 3b and 3a amplified by 2000
412	Fig. 5. Optical incroscopic images of sen-assemblies 5a , 5b and 5c amplified by 2000×.
413	
414	Fig. 6. UV-vis spectra of DMSO solutions of 3a, 3b and 3c.
415	
416	Fig. 7. Normalized open-aperture Z-scan transmittance of 3a, 3b, and 3c in THF using 4 ns pulses at
417	532 nm. The curves have been vertically shifted for clarity. Solid lines represent theoretical fits.
418	
419	Fig. 8. Optical limiting responses to 4 ns, 1Hz pulses of 532 nm laser light in DMSO solutions of
	3a . 3c with a linear transmittance of 45%
420	Sa~Se with a micar transmittance of 4570.
421	
422	Fig. 9. The dipole moments, LUMO & HOMO energy levels of 3 with and without the formation of
423	H-bond implemented in the Gaussian 03 suite of program.

Highlights

> Three different polar D- π -A conjugated quinoline-based heterocyclic azo derivatives. > Optical limiting properties are affected by the molecular structures. > The affection mechanism is confirmed by means of experimental and theoretical proofs.> A well synergetic enhancement effect is confirmed between polar and H-bond. >















0 Z-position (mm)



Input fluence (J/on²)

CH3

℃H₃





a) R₁, R₂ = CH₃; b) R₁ = CH₃, R₂ = CH₂CH₂OH; c) R₁, R₂ = CH₂CH₂OH