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# Study on new quinacridone derivatives with enhanced third-order nonlinear optical properties

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**Abstract:** Seven new quinacridone derivatives were designed and synthesized. The relationship between molecular structure and nonlinear optical properties was studied by cyclic voltammetry, DFT calculation and Z-scan. By introducing strong electron donating groups at the two sides of the quinacridone, and then introducing a strong electron withdrawing group dicyanoethylene group, the band gap of the molecule can be effectively reduced, and the intramolecular charge transfer can be promoted. The results shown that the HOMO/LUMO band gaps of the target compounds are all reduced, and **QA-F** has the best third-order nonlinear optical performance, and its  $\gamma$  ( $\gamma = 5.32 \times 10^{-33}$  esu) is 4.38 times that of **QA-1** ( $\gamma = 1.21 \times 10^{-33}$  esu).

**Keywords:** Second-order hyperpolarizability; Quinacridone derivatives; NLO materials; Z-scan technology.

# **1** Introduction

Nonlinear optical (NLO) materials have profound importance in some advanced technologies of contemporary significance such as optical limiting, optical data storage, laser medicine, image processing, all-optical switch and so on<sup>1-9</sup>. The molecular design and synthesis of novel organic compounds with superior third-order NLO properties has drawn a widely public attention<sup>10, 11</sup>. Compared with inorganic NLO materials, organic NLO materials have the advantages of short response time, low dielectric constant, high optical damage threshold, high molecular plasticity, excellent processing performance and high nonlinear polarizability<sup>10-13</sup>. The polarization of the organic NLO materials results from the delocalization of the  $\pi$  electrons in the backbone<sup>14-17</sup>. Partial  $\pi$ -conjugated polymers have good electrochemical properties, photochemical properties, and good mechanical properties and processing properties<sup>14, 18, 19</sup>. It is a good strategy to get high performance NLO materials by modifying the molecular structure <sup>20-22</sup>. Therefore, the organic conjugated compound having a delocalized large  $\pi$  structure can be preferred as third-order nonlinear optical materials<sup>12, 23-25</sup>.

As organic chromophores, QA and its derivatives are widely used in organic photovoltaic materials, organic light-emitting diodes, dye-sensitized solar cells and other fields because of their high fluorescence quantum yield, good photostability and chemical stability. QA, as an electron acceptor, has been used in molecular design of NLO materials together with some electron donors because of its highly delocalized system, which exhibits high nonlinear optical response<sup>26</sup>. At the same time, QA also has several modified active sites through which appropriate molecular modification can be carried out to improve intramolecular charge transfer (ICT) and reduce molecular band gap. It is helpful to improve the third-order nonlinear optical response of molecules<sup>27-29</sup>.

In previous works<sup>20</sup>, a series of D-A poly-quinacridone were applied to third-order nonlinear optical materials. However, the relationship between molecular structure and nonlinear response of quinacridone derivatives is still not very clear. According to the previous work, we believe that improving the electron-absorbing ability of quinacridone

structure and the electron-supplying ability of electron donors in material molecules will be beneficial to improving the third-order nonlinear response of materials. In this study, dicyanoethylene (DCN) was introduced into quinacridone structure to enhance the electron absorption ability of quinacridone structure, and triphenylamine and carbazole as electron donors were introduced to enhance the molecular dipole moment of material molecules. The purpose is to extend the p- $\pi$  conjugate system to make QA derivatives have push-pull structure, enhance intramolecular charge transfer, reduce molecular band gap, and improve the third-order nonlinear optical properties of molecules. In addition, we analyzed the effect of structure on the photophysical, electrochemical and third-order nonlinear optical properties of materials by UV and fluorescence spectrophotometer, cyclic voltammetry and Z-scan performance.

# **2** Experimental

#### 2.1 Materials and Instruments

All chemicals and solvents, unless otherwise stated, are commercially available, and were used without further purification.

The <sup>1</sup>H nuclear magnetic-resonance (<sup>1</sup>H NMR) spectra were recorded on a Varian XL-200 spectrometer with tetramethylsilane (TMS) as the internal standard. Infrared spectra were determined using a Vector 22 FT-IR spectrometer using KBr pellets. The Ultra-violete visible (UV-vis) absorption spectra of the synthesized compounds were recorded on a Shimadzu UV-2550 UV-visible spectrophotometer with a quartz cuvette (path length 1 cm).

#### 2.2 Synthesis

The main synthesis scheme of the all materials were shown as Scheme 1. The synthesis scheme of **Z-1**, **Z-2** were shown as Scheme S1.



Scheme 1. The synthetic procedure of the quinacridone derivatives.

2.2.1 N, N'- dodecane quinacridone (QA-1)

Reference article to synthesize **QA-1**<sup>20</sup>. Quinacridone (3.00 g, 9.60 mmol), Cs<sub>2</sub>CO<sub>3</sub> (9.39 g, 28.80 mmol), and tetrabutylammonium bromide (TBAB) (0.62 g, 1.92 mmol) were dissolved in DMSO (80 mL) and stirred at 30  $\Box$  for 4 hours, and then 1-bromosodecane (8.38 g, 33.62 mmol) was slowly added dropwise. The resulting mixture was allowed to react at room temperature for 20 h and then heated to 90 °C for 6 h. When cooled to room temperature, the reaction solution was poured into 250 ml of saturated brine and filtered under reduced pressure. The solvent was removed from filter cake by washing with methanol. The resulting crude product was purified by recrystallization from ethyl acetate to give an orange-red solid **QA-1** (4.98 g, 80%). M.p.: 138-139  $\Box$ .<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.69 (s, 2H), 8.52 (dd, J = 8.0, 1.6 Hz, 2H), 7.70 (m, J = 8.6, 6.9, 1.6 Hz, 2H), 7.46 (d, J = 8.8 Hz, 2H), 7.22 (t, J = 7.4 Hz, 2H), 4.61 - 4.27 (t, 4H), 2.07 - 1.88 (m, 4H), 1.62 (m, J = 15.4, 7.6 Hz, 4H), 1.47 (m, J =

15.2, 6.9 Hz, 4H), 1.42 – 1.26 (m, 12H), 0.91 (t, J = 6.9 Hz, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  177.99, 142.15, 135.58, 134.46, 127.98, 126.16, 121.02, 120.72, 114.57, 113.40, 46.35, 31.93, 29.67, 29.63, 29.60, 29.48, 29.35, 27.13, 27.04, 22.70, 14.12. HRMS (ESI) m/z calcd for C<sub>44</sub>H<sub>61</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> (M+H)<sup>+</sup> 649.47276, found 649.47253.

2.2.2 N, N'-dodecane-2,9-dibromoquinacridone (QA-2)

Reference article to synthesize **QA-2**<sup>20</sup>. Under a N<sub>2</sub> atmosphere, **QA-1** (0.50 g, 0.77 mmol) and *N*-bromosuccinimide (NBS) (0.48 g, 2.70 mmol) were add in 20 mL of DMF. The mixture was stirred at 90  $\Box$  for 24 h in a dark environment and then cooled to room temperature, and poured into a saturated aqueous solution of sodium chloride. After precipitated, filtered and washed with methanol, the filter cake was recrystallized from dichloromethane to give the dark-red solid **QA-2** (0.49g, 79%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.41 (s, 2H), 8.39 (d, *J* = 2.5 Hz, 2H), 7.68 (dd, *J* = 9.2, 2.5 Hz, 2H), 7.23 (d, *J* = 9.3 Hz, 2H), 4.36 (t, *J* = 16.4, 8.5 Hz, 4H), 2.00 – 1.81 (m, 4H), 1.60 (m, *J* = 15.3, 7.5 Hz, 4H), 1.46 (m, *J* = 14.8, 6.7 Hz, 4H), 1.36 (m, *J* = 21.2, 10.4, 5.3 Hz, 12H), 0.92 (t, *J* = 6.9 Hz, 6H). 2.2.3 *N*, *N*'-dodecane -2,9-diborate quinacridone(**QA-3**)

**QA-2** (2.01 g, 2.49 mmol), bornazolium diborate (2.21 g, 8.70 mmol), PdCl<sub>2</sub>(dppf) (0.17 g, 0.25 mmol), potassium acetate (0.85 g, 8.72 mmol) were add to 30 mL of 1,4-dioxane under an atmosphere of N<sub>2</sub>. The mixture was stirred at 80  $\Box$  for 12 h and then poured into saturated salt water. After filtered and washed with methanol, crude products were obtained by decolorization with activated carbon in dichloroethane and recrystallization from ethyl acetate to afford a dark-red solid **QA-3** (1.17 g, 76%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.00–8.93 (m, J = 1.5 Hz, 2H), 8.63 (s, 2H), 7.99 (dd, J = 8.7, 1.4 Hz, 2H), 7.36 (d, J = 8.8 Hz, 2H), 4.49–4.42 (m, 4H), 1.98–1.90 (m, J = 15.6, 8.9 Hz, 4H), 1.66–1.57 (m, J = 15.2, 7.6 Hz, 4H), 1.49–1.43 (m, J = 14.3, 7.2 Hz, 4H), 1.41 (s, 24H), 1.36–1.25 (m, 28H), 0.89 (t, J = 6.9 Hz, 6H).

2.2.4 5,12-didodecyl-2,9-diphenyl-5,12-dihydroquinolino[2,3-*b*]acridine-7,14-dione (**QA-A**)

**QA-3** (0.56 g, 0.62 mmol), bromobenzen (0.39 g, 2.48 mmol), K<sub>2</sub>CO<sub>3</sub> (0.35 g, 2.48 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.07 g, 0.06 mmol) were placed in 10mL of toluene and 50 mL of distilled water as solvent. The solution was stirred for 24 h under a N<sub>2</sub> atmosphere at 90  $\Box$ . After removal of the solvent under reduced pressure, the crude product was purified by silica chromatography, eluting with (V (petroleum ether) / V (dichloromethane) = 1/2) to obtain red solid **QA-A** (0.35

g, 70.5%). M.p.: 185.1-187.4 $\Box$ . <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ 8.70 (d, J = 2.4 Hz, 1H), 8.61 (s, 1H), 7.82 (dd, J = 8.9, 2.3 Hz, 1H), 7.69–7.63 (m, 2H), 7.50 (dd, J = 10.5, 4.8 Hz, 2H), 7.44–7.36 (m, 2H), 4.59–4.23 (m, 2H), 1.72 (s, 1H), 1.65 (dt, J = 15.3, 7.6 Hz, 2H), 1.56–1.44 (m, 2H), 1.43–1.21 (m, 17H), 0.93–0.84 (m, 4H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  177.84, 141.22, 139.36, 135.26, 133.09, 133.05, 128.94, 127.31, 126.69, 125.91, 125.27, 120.96, 115.26, 113.48, 46.41, 31.95, 29.70, 29.66, 29.63, 29.52, 29.37, 27.19, 27.08, 22.71, 14.12. HRMS (ESI) m/z calcd for C<sub>56</sub>H<sub>69</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> (M+H)<sup>+</sup> 801.53536, found 801.53564.

2.2.5

2,9-bis(4'-(diphenylamino)-[1,1'-biphenyl]-4-yl)-5,12-didodecyl-5,12-dihydroquinolino[2,3-*b*]acridine-7,14-dione (**QA-B**)

The synthetic procedures were almost the same as that of **QA-A**, except that compound **Z-1** (0.87 g, 2.17 mmol). The crude product was purified by silica gel column chromatography (V (petroleum ether) /V (dichloromethane) = 3/1) to give the red solid **QA-B** (0.52 g, 65%). M.p.: 212.1-219.4  $\Box$ . <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.81-8.73 (m, 1H), 8.69- 8.62 (m, 1H), 8.04 (dt, J = 7.0, 3.5 Hz, 1H), 7.78 (d, J = 8.2 Hz, 2H), 7.72 (dd, J = 17.1, 8.0 Hz, 2H), 7.58 (d, J = 9.1 Hz, 1H), 7.55-7.48 (m, 2H), 7.29 (dd, J = 13.9, 6.4 Hz, 5H), 7.17 (d, J = 7.7 Hz, 5H), 7.06 (dd, J = 20.1, 12.8 Hz, 2H), 4.66-4.40 (m, 2H), 1.69 (dt, J = 15.0, 7.6 Hz, 2H), 1.59 (s, 3H), 1.57-1.47 (m, 2H), 1.47 (s, 16H), 0.89 (t, J = 6.8 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  177.71, 147.68, 147.35, 141.13, 139.46, 137.52, 135.18, 134.34, 132.74, 132.44, 129.33, 127.60, 127.00, 126.86, 125.84, 124.91, 124.53, 123.86, 123.03, 120.94, 115.23, 113.43, 31.95, 29.72, 29.67, 29.65, 29.55, 29.38, 27.11, 22.71, 14.13. HRMS (ESI) m/z calcd for C<sub>92</sub>H<sub>95</sub>N<sub>4</sub>O<sub>2<sup>+</sup></sub> (M+H)<sup>+</sup> 1287.74495, found 1287.74451.

2.2.6

2,9-bis(4-(9H-carbazol-9-yl)phenyl)-5,12-didodecyl-5,12-dihydroquinolino[2,3-*b*]acridine-7, 14-dione (**QA-C**)

The synthetic procedures were almost the same as that of **QA-A**, except that compound **Z-2** (0.70 g, 2.17 mmol). The crude product was purified by silica gel column chromatography (V (petroleum ether) /V (dichloromethane) = 1/2) to give the red solid **QA-C** (0.53 g, 75%). m.p. 245.1-246.4  $\Box$ .<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.83 (d, J = 2.1 Hz, 1H), 8.77–8.69 (m, 1H), 8.19 (d, J = 7.8 Hz, 2H), 8.02 (dd, J = 8.8, 2.1 Hz, 1H), 7.91 (t, J = 8.1 Hz, 2H), 7.70 (t, J =

6.5 Hz, 2H), 7.60 (t, J = 8.3 Hz, 1H), 7.56–7.47 (m, 3H), 7.42 (dt, J = 26.5, 7.6 Hz, 2H), 7.33 (t, J = 7.4 Hz, 2H), 4.73– 4.47 (m, 2H), 1.78–1.66 (m, 2H), 1.64 (s, 3H), 1.60–1.49 (m, 3H), 1.48–1.22 (m, 19H), 0.89 (t, J = 6.8 Hz, 4H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  177.89, 140.83, 138.37, 136.96, 133.03, 128.00, 127.43, 126.04, 125.54, 123.53, 121.18, 120.38, 120.09, 115.55, 113.68, 109.85, 31.95, 29.72, 29.67, 29.56, 29.39, 27.14, 22.71, 14.13. HRMS (ESI) m/z calcd for C<sub>80</sub>H<sub>83</sub>N<sub>4</sub>O<sub>2</sub><sup>+</sup> (M+H)<sup>+</sup> 1131.65105, found 1131.64844.

2.2.7 2,2'-(5,12-didodecyl-5,12-dihydroquinolino[2,3-*b*]acridine-7,14-diylidene) dimalononitrile (**QA-D**)

Under a N<sub>2</sub> atmosphere, **QA-1** (0.20 g, 0.31 mmol), TiCl<sub>4</sub> (0.17 g, 0.63 mmol), malononitrile (0.24 g, 3.72 mmol), triethylamine (3 mL) were added to 20 mL of dichloromethane and stirred for 24 h at room temperature. After removal of the solvent under reduced pressure, the crude product was purified by silica chromatography, eluting with (V (petroleum ether) / V (dichloromethane) = 1/3) to obtain dark green solid **QA-D** (0.19 g, 82%). M.p.: 173.1-176.4  $\square$ . <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ 8.67 (s, 1H), 8.51 (dd, J = 8.0, 1.6 Hz, 1H), 7.69 (ddd, J = 8.6, 7.0, 1.6 Hz, 1H), 7.45 (d, J = 8.8 Hz, 1H), 7.21 (t, J = 7.4 Hz, 1H), 4.79-4.23 (m, 2H), 1.81 (s, 1H), 1.62 (dt, J = 15.3, 7.6 Hz, 2H), 1.52–1.42 (m, 2H), 1.41-1.19 (m, 17H), 0.89 (t, J = 6.9 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  155.09, 139.29, 134.39, 133.61, 127.24, 122.82, 121.94, 117.55, 117.16, 116.76, 114.49, 111.63, 70.30, 49.23, 31.93, 29.70, 29.65, 29.62, 29.58, 29.37, 29.30, 27.05, 26.84, 22.70, 14.12. HRMS (ESI) m/z calcd for C<sub>50</sub>H<sub>61</sub>N<sub>6</sub><sup>+</sup> (M+H)<sup>+</sup> 745.49522, found 745.49554.

#### 2.2.8

2,2'-(5,12-didodecyl-2,9-diphenyl-5,12-dihydroquinolino[2,3-*b*]acridine-7,14-diylidene)dimal ononitrile (**QA-E**)

The synthetic procedures were almost the same as that of **QA-D**, except that compound **QA-A** (0.50 g, 0.62 mmol). The crude product was purified by silica gel column chromatography (V (petroleum ether) /V (dichloromethane) = 1/2) to give the dark green solid **QA-E** (0.40 g, 72%). M.p.: 202.1-204 $\square$ . <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ 8.75 (d, J = 2.0 Hz, 1H), 8.64 (d, J = 11.5 Hz, 1H), 8.02 (dd, J = 9.0, 2.0 Hz, 1H), 7.74 (d, J = 7.3 Hz, 2H), 7.58 (d, J = 9.0 Hz, 1H), 7.51 (t, J = 7.7 Hz, 2H), 7.40 (t, J = 7.4 Hz, 1H), 4.59-4.15 (m, 2H), 1.68 (dt, J = 15.1, 7.6 Hz, 2H), 1.58 (d, J = 14.6 Hz, 1H), 1.56-1.46 (m, 2H), 1.46 (s, 16H),

0.89 (t, J = 6.9 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  154.93, 139.04, 138.37, 135.04, 133.48, 133.32, 129.23, 127.90, 127.09, 125.11, 122.80, 117.63, 117.34, 117.19, 115.08, 111.75, 70.17, 49.21, 31.92, 29.71, 29.66, 29.62, 29.60, 29.37, 29.33, 27.16, 26.85, 22.69, 14.12. HRMS (ESI) m/z calcd for C<sub>62</sub>H<sub>69</sub>N<sub>6</sub><sup>+</sup> (M+H)<sup>+</sup> 897.55782, found 897.55707. 2.2.9

2,2'-(2,9-bis(4'-(diphenylamino)-[1,1'-biphenyl]-4-yl)-5,12-didodecyl-5,12-dihydroquinolino[ 2,3-*b*]acridine-7,14-diylidene)dimalononitrile (**QA-F**)

The synthetic procedures were almost the same as that of **QA-D**, except that compound **QA-B** (0.20 g, 0.16 mmol). The crude product was purified by silica gel column chromatography (V (petroleum ether) /V (dichloromethane) = 1/2) to give the dark green solid **QA-F** (0.14 g, 65%). M.p.: 230.1-234 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.78 (d, J = 1.8 Hz, 1H), 8.68–8.61 (m, 1H), 8.09–7.98 (m, 1H), 7.77 (t, J = 9.9 Hz, 2H), 7.75 (s, 2H), 7.58 (d, J = 9.1 Hz, 1H), 7.55–7.47 (m, 2H), 7.29 (dd, J = 13.9, 6.4 Hz, 5H), 7.17 (d, J = 7.7 Hz, 5H), 7.06 (dd, J = 20.0, 12.8 Hz, 2H), 4.59–4.23 (m, 2H), 1.69 (dt, J = 15.0, 7.6 Hz, 2H), 1.62–1.47 (m, 5H), 1.44–1.13 (m, 16H), 1.01–0.75 (m, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  147.63, 129.35, 127.62, 127.38, 127.32, 124.63, 123.69, 123.12, 31.94, 29.72, 29.67, 29.61, 29.39, 29.35, 26.86, 22.71, 14.13. HRMS (ESI) m/z calcd for C<sub>98</sub>H<sub>94</sub>N<sub>8</sub><sup>+</sup> (M)<sup>+</sup> 1382.75960, found 1382.75940.

# **3 Results and discussion**

#### 3.1 Synthesis and structure

The synthetic procedure of M-1, Z-1, Z-2 were shown in Scheme S1. The synthetic routes for the compounds QA-1, QA-A, QA-B, QA-C, QA-D, QA-E and QA-F were shown in Scheme 1. The synthesis of quinacridone derivatives was started from a commercially available quinacridone precursor. The N-alkylation of quinacridone gave **QA-1**. Then the bromination of QA-1 with N-bromosuccinimide (NBS) provided compound QA-2 in good yield. Suzuki coupling reaction of bis(pinacolato)diboron with QA-2 and 4-bromotriphenylamine respectively gave compounds QA-3 and M-1. Then Suzuki coupling reaction of bromoiodobenzene with M-1 gave compound Z-1 and Ullmann coupling reaction of bromoiodobenzene with carbazole gave compound Z-2. In the next step, QA-A, QA-B and

**QA-C** were obtained Suzuki coupling reaction of bromobenzene, **Z-1** and **Z-2** with **QA-2**, respectively. Finally, by Knoevenagel reaction, **QA-1**, **QA-A** and **QA-B** reacted with malononitrile to obtain the target products **QA-D**, **QA-E** and **QA-F**, respectively. All intermediates and target compounds were confirmed by stan-dard spectroscopic methods.

3.2 Photophysical properties

The UV-Vis absorption spectra of compounds (QA-1 and QA-A-F) in  $CH_2Cl_2$  (ca. 10<sup>-5</sup> M) solution were shown in Fig. 1, and the absorption data were listed in Table 1. In the UV-Vis spectra in Fig. 1, seven QA derivatives have multiple absorption peaks. The absorption peak around 220-320 nm belongs to the n- $\pi^*$  transition of the electrons on the heterocycle and the  $\pi$ - $\pi^*$  transition of the molecule at 450-650 nm. These absorption peaks are attributed to the electron transfer of the electron donating group in the QA molecule to the electron-withdrawing carbonyl group (C=O) or dicyandivinyl group. The maximum absorption peaks of QA-1, QA-A, QA-B, and QA-C are located at 520 nm, 532 nm, 536 nm, and 533 nm, respectively. Compared with QA-1, the maximum absorption peaks of the compounds with electron donors are significantly red shifted due to intramolecular charge transfer between electron donors and acceptors.

Compared with QA-1, the maximum absorption peaks of QA-A, QA-B and QA-C have a larger red shift. Similarly, compared with QA-D, the maximum absorption peaks of QA-E and QA-F have a larger red shift. These phenomena are caused by the introduction of electron donors such as triphenylamine and carbazole, the increase of conjugate system of material molecules, and the easier transition of off-domain electrons from low-energy state to high-energy state. The absorption peaks of QA-D, QA-E and QA-F appeared at 650 nm, which was due to the introduction of strong electron-absorbing group of dicyanoethylene into quinacridone. QA-F has the largest absorption wavelength and the smallest band gap ( $E_{gap} = 1.79 \text{ eV}$ ) in seven target compounds. The introduction of electron-donating groups and strong electron-withdrawing groups (DCN) can reduce the HOMO and LUMO band gap, which is beneficial to intramolecular charge transfer, resulting in a significant red shift in the UV absorption spectrum<sup>30</sup>.

The luminescence spectra have a consistent variation with the absorption spectra, as showed in Fig. 2. The fluorescence quantum yields ( $\Phi_{PL}$ ) of the compounds QA-A, QA-B,

and **QA-C** were 0.39, 0.03, and 0.48, respectively, which are lower than those of the compound QA-1 ( $\Phi_{PL} = 0.96$ ). It may be that the free rotation of the phenyl group leads to the weakening of fluorescence. It could also be the result of the charge separation from intramolecular charge transfer with the stronger electron donating group. QA-B molecule contains more freely rotating phenyl groups, so the fluorescence quantum yield is minimal., The fluorescence quantum yield of QA-C ( $\Phi_{PL}$  =0.48) is higher than that of QA-A ( $\Phi_{PL}$ =0.39), because the steric hindrance of carbazole limits the free rotation of phenyl group. In addition, the increase of Stokes shift of the compounds introduced to electron-donating groups further proves the existence of non-radiative transition. The red emission peaks ( $\lambda_{em}$ ) of QA-A, QA-B and QA-C are 546.5, 555, and 549 nm, respectively, which show a significant red shift compared with QA-1 ( $\lambda_{em} = 531.5$  nm). The fluorescence of QA-D, QA-E and QA-F is quenched in solvents of different polarities introducing DCN group. The reason for fluorescence quenching is that the steric hindrance between DCN group and quinacridone distorts the structure of the molecule, destroys the planar configuration of the molecule and turns it into a butterfly-shaped molecule, resulting in the non-radiative transition of the excited state in the molecule<sup>31</sup>. The solvatochromic effect is an important method to study the polarity of a compound. The fluorescence emission spectra of QA-1, QA-A, QA-B and QA-C in different polar solvents are shown in Fig 3. It can be seen from the figure that the peak shape and peak position of QA-A and QA-C do not change significantly with the increase of solvent polarity. This indicates that the introduction of phenyl group and carbazole has little effect on the polarity of the compounds. However, QA-B exhibited fluorescent properties in the non-polar solvent toluene and CHCl<sub>3</sub>, and exhibited fluorescence quenching in the polar solvents CH<sub>3</sub>CN and DMSO. This phenomenon indicates that the introduction of triphenylamine into the QA parent enhances molecular non-polarity.



Figure. 1 UV-vis absorption spectra of quinacridone derivatives in the dilute solution (1  $$\times\,10^{-5}\,M$  in  $CH_2Cl_2)$ 

Comnd	$\frac{1}{2}$ (mm) $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ (mm)		Ф	) (nm)	Stokes shift
Compa	$\Lambda_{max}$ (IIIII)	Aonset (IIIII)	$\Psi_{ ext{PL}}$	$\Lambda_{em}$ (IIIII)	(nm)
QA-1	487 , 520	545	0.96	531.5	146.5
QA-A	496 , 532	552	0.39	546.5	161.5
QA-B	500 , 536	561	0.03	555	170
QA-C	497 , 533	556	0.48	549	164
QA-D	470 , 635	674	-	-	-
QA-E	493 , 650	687	-	-	-
QA-F	477 , 658	692	-	-	-

Table 1. The photophysical data of the quinacridone derivatives

<sup>a</sup> The lowest-energy absorption edge of the absorption spectra.



Figure 2. Fluorescence spectra of quinacridone derivatives in the dilute solution

 $(2 \times 10-7 \text{ M in CH}_2\text{Cl}_2)$ 



Figure 3. Fluorescence spectra of quinacridone derivatives in various solvents (2  $\times$  10  $^{-7}$ 

M)

3.3 Electrochemical properties

The effect of substituents on the electrochemical properties of target compounds was further studied by cyclic voltammetry using a standard three-electrode system (with platinum carbon as the working electrode, platinum wire as the auxiliary electrode, Ag/AgCl electrode as the reference electrode, and ferrocene as the internal standard) as the electrolytic cell, tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as a supporting electrolyte, CH<sub>2</sub>Cl<sub>2</sub> as solvent, concentration being  $1.0 \times 10^{-3}$  M, and scanning speed being 100 mV/s. The cyclic voltammograms of seven target compounds were shown in Fig 4, and the specific data were listed in Table 2.

According to the cyclic voltammetry curve of the compounds, the initial oxidation potential was obtained and the HOMO energy level was calculated. The LUMO energy level was obtained by the HOMO value plus the band gap  $E_{gap}^{32}$ , and the data was shown in Table 2. The HOMO/LUMO energy levels of QA-1 and QA-A~F were calculated as -5.78/-3.50eV, -5.77/-3.52eV, -5.61/-3.40eV, -5.65/ -3.42eV, -5.87/-4.03eV, -5.85/-4.05eV and -5.65/-3.86eV, respectively showed from Fig. 4. When the carbonyl group is substituted by DCN group, the oxidation potential of compounds **OA-D**, **OA-E**, **OA-F** increases, and the LUMO level decreases significantly, so it's easier to get electronics, compared with that of compound QA-1, QA-A, QA-B. It indicates that the introduction of donor and acceptor can effectively reduce the band gap between HOMO and LUMO of the other compounds, which is beneficial to ICT. Comparing the DFT-calculated HOMO/LUMO level in Table 5, we can find that the value of the CV test is inconsistent with the theoretically calculated value. However, the decrease trend of QA-1 and QA-A~F is consistent, thus, theoretical calculation verify the experimental value of cyclic voltammetry, and have a good guiding value for the design of compound.

Correct d	E <sup>ox</sup> <sub>onset</sub> ( eV )	$E_{gap}^{a}(eV)$	Electrochemical (eV)		
Compa			HOMO <sup>b</sup>	LUMO <sup>c</sup>	
QA-1	0.68	2.28	-5.78	-3.50	
QA-A	0.67	2.25	-5.77	-3.52	
QA-B	0.51	2.21	-5.61	-3.40	

 Table 2. Cyclic voltammetric data of the quinacridone derivatives

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QA-C	0.55	2.23	-5.65	-3.42		
QA-D	0.77	1.84	-5.87	-4.03		
QA-E	0.75	1.80	-5.85	-4.05		
QA-F	0.55	1.79	-5.65	-3.86		

 $^a$  Band gap estimated from  $\lambda_{onset},\,E_{gap}=1240/\lambda_{onset}.$ 

<sup>b</sup>  $E_{HOMO} = -(E_{onset}^{ox} + 5.1) \text{ eV.}$  <sup>c</sup>  $E_{LUMO} = E_{HOMO} + E_{gap}$ .



Figure 4. Cyclic voltammograms of quinacridone derivatives are measured in  $CH_2Cl_2$ 

#### 3.4 Nonlinear optical properties

The third-order NLO properties of all compounds were determined by an open/closed-aperture Z-scan technique. The solvent was  $CHCl_3$ , the concentration was 1 mg/mL, the laser pulse energy used was 0.4  $\mu$ J, the wavelength was 1030 nm, the pulse width was 190 fs, and focal length was 250 mm. The non-linearity of pure  $CHCl_3$  was also measured under the identical conditions and found to negligible nonlinear response.

Fig.5 shown the normalized signal measured by the QA derivatives under open-cell conditions. It was used to describe the absorption process of third-order nonlinear optics. The black circle was the experimental data, and the red line was the curve after fitting. All compounds exhibited a symmetric anti-saturation absorption curve with respect to the focus (Z=0), and the sample had the lowest transmission intensity at the focal position.

When nonlinear absorption exists, open-cell curves and closed-cell curves can be obtained, and the data measured by the closed-cell is divided by the open-hole data to obtain a single nonlinear refractive property. It can be seen from Fig. 6 that all the patterns have the shape of the peak after the valley, indicating that the nonlinear refractive index  $n_2>0$ , which is the self-focusing phenomenon, the difference between the peak and the valley ( $\Delta T_{p-v}$ ) and the third-order non- The linear refractive index  $n_2$  (m<sup>2</sup>/W) is related.

Nonlinear refractive index <sup>33</sup>:

$$n_2 = \frac{\lambda \Delta T_{p-\nu}}{0.812\pi (1-S)^{0.25} I_0 L_{eff}}$$
(3.4.1)

where S is the linear transmittance of the small aperture pupil,  $\Delta T_{p-v}$  is the peak-to-valley difference of the sample, and  $n_0$  is the linear refractive index of the solvent (CHCl<sub>3</sub>  $n_0 = 1.4476$ ). The nonlinear optical coefficients  $n_2$  and  $\beta$  are obtained by calculation, and the effective third-order nonlinear polarizability of the compound is calculated according to the following equation (esu)  $\chi^{(3)}$ ,  $\chi^{(3)}_R$ ,  $\chi^{(3)}_I$  <sup>34-36</sup>.

$$\left|\chi^{(3)}\right| = \sqrt{\left|\chi^{(3)}_{R}\right|^{2} + \left|\chi^{(3)}_{I}\right|^{2}}$$
 (3.4.2)

$$\chi_R^{(3)} = \frac{n_0^2 C n_2}{80\pi} \tag{3.4.3}$$

$$\chi_{I}^{(3)} = \frac{9 \times 10^{8} n_{0}^{2} \varepsilon_{0} c^{2} \beta}{4\pi \omega}$$
(3.4.4)

By the third-order nonlinear polarization coefficient  $\chi^{(3)}$ , the second-order hyperpolarizability  $\gamma$ of the sample can be obtained by the following formula:

$$\gamma = \chi^{(3)} / N \left[ (n_0^2 + 2) / 3 \right]^4$$
 (3.4.5)

where N is the molecular density of the solute,  $N=N_Ac$ , and c is the molar concentration of the sample solution. The third-order nonlinear parameters obtained by the corresponding calculations were summarized in Table 3.





Figure 5. Normalized open-aperture Z-scan curves of the quinacridone derivatives solutions. The open circles and solid lines represent the experimental data and theoretical fitting curves, respectively



Figure 6. Normalized close-aperture Z-scan curves of the quinacridone derivatives solutions. The open circles and solid lines represent the experimental data and theoretical fitting curves, respectively.

According to the data in Table 3, the third-order nonlinear performance exhibited by this series of compounds is roughly the same as the expected value of the initial design of the compound,

and the nonlinear absorption coefficient  $\beta$  are between 1.23-3.09×10<sup>-13</sup> m/W. The order nonlinear polarizability  $\chi^{(3)}$  are between 4.38-13.26×10<sup>-12</sup> esu. And the molecular second-order hyperpolarizability  $\gamma$  are between 1.21-5.32  $\times$  10<sup>-33</sup> esu. For the convenience of comparison, the opening curves of QA-1 and QA-A~F were placed in the same picture as shown in Fig. 7. The depth of the opening was from QA-F > QA-E > QA-B > QA-D > QA-C > QA-A > QA-1. It can be seen from Fig. 7 that triphenylamine is acted as a strong electron donor to promote ICT, which is very beneficial to improve the third-order nonlinear performance of materials. When the DCN group with strong electron absorption is introduced into the conjugated system, the electron mobility of the molecule is improved. The delocalization degree of  $\pi$  electron and dipole torch of molecule increase, which reduce the transition energy of electron from ground state to excited state. The  $\gamma$  of **QA-F** in the third-order nonlinear performance ( $\gamma = 5.32 \times 10^{-33}$  esu) is nearly 4 times higher than the  $\gamma$  of **QA-1**, and is nealy 7823 times higher than the  $\gamma$  of urea ( $\gamma = 0.68 \times 10^{-36}$ esu). Compound QA-F has the most excellent third-order nonlinear properties in these compounds. It is attributed to the strong power supply of triphenylamine group and the strong electricity absorption of DCN, which reduce the transition energy from ground state to excited state. The energy level of the HOMO orbit can be increased by the electron donor group, and the energy level of the LUMO orbit can be decreased by the electron acceptor group. Thus, the band gap  $E_{gap}$  of the molecule can be reduced and the nonlinear optical response of the material can be enhanced.

Compd	$\boldsymbol{\beta} \text{ (m/W)} \\ \times 10^{-13}$	$n_2 (m^2/W) \times 10^{-17}$	$\chi_{\rm R}^{(3)}$ (esu) ×10 <sup>-13</sup>	$\chi_{\rm I}^{(3)}$ (esu) ×10 <sup>-12</sup>	$\chi^{(3)}(esu)$ ×10 <sup>-12</sup>	$\gamma$ (esu) $\times 10^{-33}$
QA-1	1.23	1.20	9.67	4.29	4.38	1.21
QA-A	1.36	1.27	9.10	5.90	5.97	2.35
QA-B	1.73	1.11	8.94	7.41	7.46	3.55
QA-C	1.42	1.20	9.07	6.51	6.58	2.52
QA-D	1.54	1.13	9.08	6.62	6.68	2.82
QA-E	1.85	1.19	8.76	7.94	8.00	3.58
QA-F	3.09	1.07	8.65	13.23	12.26	5.32

Table 3. Third-order NLO parameters of quinacridone derivatives in CHCl<sub>3</sub>

Samula	<b>β</b> (m/W)	$n_2 ({ m m}^2/{ m W})$	$\chi^{(3)}(esu)$	γ(esu)	Deference
Sample	×10 <sup>-13</sup>	×10 <sup>-17</sup>	×10 <sup>-12</sup>	×10 <sup>-33</sup>	Reference
QA-1	1.23	1.20	4.38	1.21	This work
QA-A	1.36	1.27	5.97	2.35	This work
QA-B	1.73	1.11	7.46	3.55	This work
QA-C	1.42	1.20	6.58	2.52	This work
QA-D	1.54	1.13	6.68	2.82	This work
QA-E	1.85	1.19	8.00	3.58	This work
QA-F	3.09	1.07	12.26	5.32	This work
	202.6	0.07	0.35		[37]
Fe N	28.5	0.16	-	-	[38]
	100	-	-	4.68 <sup>a</sup>	[39]
HOOC	338.6	0.08	0.53	0.02 <sup>a</sup>	[40]
	250	0.06	8.80	-	[41]
Graphene	-	-	-	32	[42]

# Table 4. The NLO properties of organic and inorganic NLO materials

<sup>a</sup>.  $\gamma$  was calculated by using solvatochromic data.



Figure 7. Normalized open-aperture Z-scan curves of quinacridone derivatives

## 3.5 Theoretical calculation

In order to gain a deep insight into the relationship between the molecular structure and properties of the synthesized target compounds, density functional theory (DFT) calculations were performed. DFT calculations were performed on the B3LYP/6-31G (d) level <sup>43-46</sup>. The structure optimization of the seven target compounds was shown in Fig. 8. It can be seen from Fig. 8 that **QA-1**, **QA-A**, **QA-B** and **QA-C** have excellent molecular planarity. DCN groups form a large steric hindrance effect with ortho hydrogen, which makes the center of quinacridone twist into a "V" structure at the upper and lower sides in the molecular structure of **QA-D**, **QA-E** and **QA-F**. The "V" structure of the molecule weakens  $\pi$ - $\pi$  stacking between molecules and makes the compounds have better solubility in solvents.



Figure 8. Optimized geometries of D-A-D quinacridone derivatives at the B3LYP/6-31G(d) level

Compd	HOMO ( eV )	LUMO ( eV )	$E_{gap} \left( eV \right)$
QA-1	-5.21	-2.11	3.10
QA-A	-5.18	-2.13	3.05
QA-B	-4.88	-2.16	2.72
QA-C	-5.33	-2.28	3.04
QA-D	-5.65	-3.20	2.45
QA-E	-5.59	-3.15	2.44
QA-F	-4.98	-3.16	1.81

# Table 5. DFT-calculated HOMO and LUMO energies

It is found that the distribution of HOMO and LUMO of QA-B and QA-F compounds are quite different from that of other compounds by DFT calculation and simulation. The HOMO is mainly distributed on the electron donor triphenylamine, while that of LUMO is on the electron acceptor quinacridone. The phenomenon of several other compounds is not obvious. The reason is that the triphenylamine group has a large electron supply capacity, and the quinacridone structure has a large electron absorption capacity. The formation of "D-A-D" type electronic push-pull structure in the molecule is conducive to the delocalization of  $\pi$ electrons in the conjugated system. The triphenylaniline groups at both ends of the molecular structure of **QA-B** and **QA-F** have more electron supplying ability than benzene ring, so the difference between distribution in HOMO and in LUMO is greater than that in QA-A and **QA-E.** This phenomenon is conducive to the delocalization of  $\pi$  electrons in the conjugated system. Therefore, the second-order hyperpolarizability  $(\gamma)$  of compounds QA-B and QA-F are higher than those of compounds QA-A and QA-E. In terms of molecular design of nonlinear optical materials, triphenylamine is a better electron donor group than benzene ring. In addition, the three benzene rings of triphenylamine in compound **QA-B** have larger degree of freedom of rotation, so the angle between triphenylamine and quinacridone is smaller. This is beneficial to the delocalization of  $\pi$  electron from triphenylamine to quinacridone, and to the improvement of the nonlinear response of the material. The angle between carbazole group and quinacridone in QA-C compound is larger because two benzene rings connected together are not conducive to rotation. The difficulty of  $\pi$  electron delocalization from carbazole to quinacridone increases, which is not conducive to the third-order nonlinear response of materials. This is consistent with the third-order nonlinear performance test results. The  $\gamma$  of **QA-B** compound is larger than that of **QA-C**. Compared with carbazole, triphenylamine is a better electron donor group. On the other hand, when the quinacridone structure of compounds **QA-E** and **QA-F** is connected to DCN group, the ability of electron absorption is enhanced, and the dipole moment of the molecule is increased. It is advantageous for  $\pi$  electron to be delocalized from the electron donor group at both ends to the electron acceptor group in the middle. Compared with compound QA-B, the  $\gamma$  of compound QA-F increases obviously. Similarly, the  $\gamma$  of compound QA-E is significantly

higher than that of compound **QA-A**. In conclusion, reducing the angle between the electron donating groups at both ends of the molecule and quinacridone, enhancing the electron donating ability of the electron donating groups at both ends of the molecule and the electron absorbing ability of quinacridone structure are conducive to enhancing the third-order nonlinear response of the material.



Figure 9. DFT-calculated frontier molecular orbitals of the quinacridone derivatives 4 Conclusion

Seven derivatives of D-A-D quinacridone were designed and synthesized. The relationship between molecular structure and nonlinear optical properties was studied by cyclic voltammetry, DFT calculation and Z-scan. The results show that the molecular structure of D-A-D type push-pull structure can enhance the nonlinear optical response of the material when the two sides of quinacridone are connected with electron donor groups. It is beneficial to improve the nonlinear optical response of the material by enhancing the power supply performance of the electronic groups on both sides of the molecule and adding DCN groups to enhance the electronic absorption performance of quinacridone, reducing the angle between the electronic group and quinacridone. Among the seven target compounds, **QA-F** has excellent third-order nonlinear properties, and its  $\gamma$  ( $\gamma$ =5.32×10<sup>-33</sup> esu) is 4.38 times that of

**QA-1** ( $\gamma$ =1.21×10<sup>-33</sup> esu). It provides a new idea for the molecular design and study on the relationship between structure and properties of D-A-D organic nonlinear optical materials.

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# Study on new quinacridone derivatives with enhanced third-order

# nonlinear optical properties

- A series of new quinacridone derivatives were synthesized. •
- Increasing the electron absorption ability of quinacridone structure is helpful to improve the • nonlinear response of materials.
- Introducing dicyanoethylene group can reduce the band gap of the molecule and promote • intramolecular charge transfer.

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#### **Declaration of interests**

 $\checkmark$  The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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