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New quinacridone derivatives: Synthesis, photophysical and third-order nonlinear optical properties

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Abstract: A series of quinacridone third-order nonlinear optical chromophores containing phenyl, 4-methoxyphenyl and *N*,*N*-bis(4-methoxyphenyl)aniline groups were designed and synthesized. The optical properties, electrical properties, theoretical calculations and Z-Scan of the compounds were measured and analyzed to investigate the relationship between structure and third-order NLO properties. The experimental results showed that the introduction of electron-donating groups at the N-position of quinacridone decreases the energy gap (E_{gap}) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the molecule, and promotes intramolecular charge transfer (ICT). Quinacridone derivatives containing *N*, *N*-bis (4-methoxyphenyl) aniline have good third-order nonlinear optical properties, with the nonlinear absorption coefficient (β) value of 1.4319×10⁻¹³ and the second-order superpolarizability (γ) of 2.6849×10⁻³³ esu .

Keywords: Third-order NLO; Quinacridone; Z-Scan technology; ICT

1. Introduction

In recent years, with the development of nonlinear optical materials in the fields of microscopy^[1], optical storage micromachining^{[2][3]}, three-dimensional data storage^{[4][5]}, optical power limitation^{[6][7][8]} and laser conversion^[9], etc., the synthesis of new organic compounds with superior third-order nonlinear optical properties has attracted people's attention. The polarization of organic third-order nonlinear optical materials, originating from the delocalization of π electrons in the main chain, showed strong photoelectric coupling characteristics: the charge is easy to move, and the time required for the polarization of the dielectric particles to generate electric dipoles is relatively short. Compounds containing large π organic conjugated system ^{[10][11][12][13]} have good electrochemical properties, photochemical properties^{[14][15]}, good mechanical and processing properties. In order to obtain a third-order nonlinear optical material with a higher the second-order superpolarizability γ value, the molecular structure need to be reasonably modified to give the molecules a large delocalization, a large absorption wavelength, a small E_{gap}, and a large molecular dipole moment. Therefore, the organic conjugated compound containing the delocalized large π structure may preferably be a third-order nonlinear optical material.

Quinacridone is a strong electron acceptor with a highly delocalized conjugated system. When it is connected to an electron donating unit, it will lower E_{gap} and promote ICT, showing excellent NLO performance. ^[16] However, the rigid coplanar structure of quinacridone increases the intermolecular π - π stacking, resulting in extremely poor solubility, which reduces the third-order NLO performance.^[17] Although the addition of different

nitrogen-containing electron donors to the benzene ring of the quinacridone structure has been studied^[18], the introduction of different electron donors at their N-position has not been studied, and we expect such designs to have better performance. Thus, a different electron donor can be inserted at the N-position of the quinacridone to form a donor-acceptor-donor (D-A-D) chromophore. The relationship between D, π and A has been studied by Filip Bureš et al.^[19], but the relationship between our quinacridone derivatives and third-order nonlinear optical properties has not been verified. This system is not only expected to change the planar structure of the quinacridone core, but also to increase the degree of conjugation of π electrons.^{[20][21]}.

In this paper, we designed and synthesized a series of quinacridone-based derivatives by coupling bromobenzene, *p*-methoxybromobenzene, 4-bromo-*N*,*N*-bis (4-methoxyphenyl) aniline with the parent quinacridone molecule (Scheme 1). Structurally, the quinacridone core tends to be planar^{[17][18]}, however, after the introduction of the electron donating groups, all compounds have core distortion and improved solubilities. In addition, the effects of different structures of quinacridone derivatives on optical properties, electrochemical properties and third-order nonlinear optical properties were discussed, and further verified using semi-empirical (ZINDO)^{[22][23]} and density functional theory (DFT)^{[24][25]}.

2. Experimental section

2.1. Materials

Unless otherwise indicated, all chemicals, solvents and starting materials are used as purchased without further purification.

2.2. Instruments

The ¹H nuclear magnetic-resonance (¹H MNR) spectra was recorded on a Varian XL-200 spectrometer with tetramethylsilane (TMS) (Bruker, SwissConfederation) as the internal standard. MS spectra were recorded on an AB SCIEX 5800 MALDI TOF/TOFTM. The melting points were obtained using a Microscopic digital melting point instrument X-4 (Beijng tech, China) under N₂ at a heating rate of 10 $\Box \cdot \min^{-1}$. The Ultraviolet-visible (UV-vis) absorption spectra of the synthesized compounds were recorded on a UV-1800 UV-visible spectrophotometer (Shimadzu, Japan) with a quartz cuvette (path length 1 cm). The fluorescence spectra were obtained with a RF-6000 PC (Shimadzu, Japan). Cyclic voltammetry(CV) was performed on an IVIUM V63126 instrument (Ivium Technologies, Netherlands) with a scan rate of 100 mV·s⁻¹. A three-electrode configuration was used for the measurements, with a platinum disk as the working electrode, a platinum wire as the counter electrode, and an Ag/Ag⁺ electrode as the reference electrode.

2.3. Synthesis

2.3.1. 5,12-Biphenyl-5,12-dihydroquinolino[2,3-*b*]acridine-7,14-dione (1)

5,12-Dihydroquinolino[2,3-*b*]acridine-7,14-dione (0.20 g,0.064 mmol), cesium carbonate (0.83 g, 0.26 mmol), CuI (0.012 g, 0.006 mmol), iodobenzeneand (0.52 g, 0.26 mmol), and 2,2,6,6-tetramethylheptane-3,5-dione (0.024 g, 0.012 mmol) were placed in a 50 mL three-neck flask, purged with three nitrogen/vacuum cycles, and under nitrogen atmosphere added *N*,*N*-dimethylformamide (DMF) 20 mL. The mixture was heated at reflux for 24 h and then cooled to room temperature. The resulting mixture was poured into saturated 50 mL salt water and filtered. The crude product was purified by column chromatography eluting with

EA/CH₂Cl₂ (1/200), yielding the product **1** as a orange solid (0.16 g, 54%), m.p. >400 \Box . ¹H NMR (500 MHz ,CDCl₃) δ 8.55 (s, 1H), 8.25 (s, 1H), 7.88-7.79 (m, 4H), 7.78-7.71 (m, 1H), 7.51-7.41 (m, 3H), 7.02 (d, *J* = 8.8 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 179.18, 144.32, 137.80, 137.68, 136.35, 131.69, 130.80, 129.37, 127.39, 124.76, 123.00, 119.43, 117.52, 115.88, 115.62, 113.35, 111.08. HRMS (ESI) m/z calcd for C₃₂H₂₁N₂O₂⁺ (M+H)⁺ 465.15975, found 465.15945.

2.3.2. 5,12-Bis(4-methoxyphenyl)-5,12-dihydroquinolino[2,3-b]acridine-7,14-dione(2)

The synthetic procedure was basically the same as that of **1**, except that compound iodobenzene was replaced with 4-bromoanisole (0.60 g, 0.26 mmol), *N*,*N*-dimethylformamide was replaced by *N*,*N*- dimethylacetamide, and the reaction time was extended to 48 h. The crude product was purified by column chromatography eluting with EA/CH₂Cl₂ (1/40), yielding the product **2** as an orange solid (0.21 g, 62%), m.p. >400 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.58 - 8.34 (m, 1H), 8.21- 8.13 (m, 1H), 7.73-7.60 (m, 1H), 7.40-7.23 (m, 6H), 6.98 (d, *J* = 8.8 Hz, 1H), 4.04 (s, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 179.23, 179.23, 160.67, 144.43, 144.43, 137.99, 137.40, 135.41, 130.59, 130.59, 130.38, 127.34, 124.99, 122.23, 119.78, 117.34, 116.67, 116.61, 115.69. HRMS (ESI) m/z calcd for C₃₄H₂₅N₂O₄⁺ (M+H)⁺ 525.18088, found 525.18088.

2.3.2. 4-Bromo-N,N-bis(4-methoxyphenyl)aniline (T-1)

4-Bromoaniline (2.00 g, 11.63 mmol), *p*-iodoanisole (8.16 g, 34.87 mmol), KOH (5.22 g, 93.05 mmol), CuCl (0.12 g, 1.16 mmol), and 1,10-phenanthroline monohydrate (0.42 g, 2.33 mmol) were placed in a 100 mL three-neck flask, purged with three nitrogen/vacuum cycles, and under nitrogen atmosphere added methylbenzene 40 mL. The mixture was heated at reflux for 24 h and then cooled to room temperature. The solvent was removed by distillation under reduced pressure. The crude product was purified by column chromatography eluting with PE/CH₂Cl₂ (4/1), yielding the product **T-1** as a light yellow solid (3.98 g, 89%), ¹H NMR (500 MHz, CDCl₃) δ 7.26-7.23 (m, 1H), 7.04 (d, *J* = 9.0 Hz, 1H), 6.86-6.77 (m, 1H), 3.81 (s, 2H).

2.3.3

5,12-Bis(4-(bis(4-methoxyphenyl)amino)phenyl)-5,12-dihydroquinolino[2,3-*b*]acridine-7,14dione (**3**)

The synthetic procedure was basically the same as that of **1**, except that compound iodobenzene was replaced with 4-bromo-*N*,*N*-bis(4-methoxyphenyl)aniline (0.980 g, 0.260 mmol), *N*,*N*-dimethylformamide was replaced by *N*,*N*- dimethylacetamide, and the reaction time was extended to 48 h. The crude product was purified by column chromatography eluting with EA/CH₂Cl₂ (1/40), yielding the product **3** as an orange solid (0.22 g, 60%), m.p. >400°C.¹H NMR (500 MHz, CDCl₃) δ 8.52 (dd, *J* = 8.1, 1.5 Hz, 1H), 8.27 (s, 1H), 7.58 (ddd, *J* = 8.6, 6.9, 1.6 Hz, 1H), 7.35-7.28 (m, 5H), 7.29-7.22 (m, 1H), 7.18-7.13 (m, 4H), 7.03-6.98 (m, 1H), 6.98 (s, 5H), 3.91-3.80 (m, 7H). ¹³C NMR (126 MHz, CDCl₃) δ 179.58, 159.56, 159.22, 149.77, 146.99, 144.60, 138.08, 135.83, 129.90, 129.76, 129.65, 127.48, 125.86, 125.15, 124.45, 123.14, 122.56, 119.76, 117.60, 116.01, 115.71, 113.44. HRMS (ESI) m/z calcd for $C_{60}H_{46}N_4O_6^+$ (M+H)⁺ 919.34, found 919.3471.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic routes for the compounds 1, 2 and 3 are shown in Scheme 1. Among them, 1, 2 and 3 are new compounds. Synthesis of quinacridone derivatives starting from a commercially available quinacridone precursor, three target compounds were obtained by Ullmann coupling reaction in which the target compounds 2 and 3 were reacted in N,N-dimethylformamide solvent for 24 hours. The yield was only 15%, but the solvent was changed to N,N-dimethylacetamide, and the reaction time was extended to 48 hours to obtain a yield of 60%. All of target compounds were fully characterized by NMR and High-resolution mass spectrometry.



Scheme 1 The synthesis procedure of the quinacridone derivatives

3.2. Photophysical properties

3.2.1. Ultraviolet-visible absorption spectroscopy

To reveal the effect of different electron-donating groups on the charge transfer absorption properties of the three compounds, the UV-visible spectra of the three compounds were measured in CH_2Cl_2 , as shown in **Figure 1**. The data are summarized in **Table 1** below. The **Figure 1** shows the ultraviolet absorption range of the target compound at 220-650nm, where the absorption at 450-550 nm is the characteristic absorption band of quinacridone.

From Figure 1 two prominent characteristic absorption bands can be observed. One of the characteristic absorption bands lies between 220-320 nm, which is attributed to the $n-\pi^*$ transition of the electrons on the heterocyclic ring and the π - π^* transition of the molecule. Another characteristic absorption band is between 450-550 nm, which is generated by the transfer of electrons from the donor (N-R) in the molecule to the acceptor (C=O). The stronger the electron-donating ability of the group introduced in quinacridone, the stronger the electron-transporting ability inside the molecule, which in turn causes red shift. ^[26] The maximum absorption peaks of compounds 1 to 3 are located at 509 nm, 511 nm, and 515 nm. Compared with the maximum absorption peak of compound 1, the maximum absorption peaks of 2 and 3 are red-shifted by 2 nm and 6 nm, respectively. This is due to the higher electron-donating properties of *p*-methoxyphenyl and *N*, *N*-bis (4-methoxyphenyl) aniline introduced in 2 and 3.



Figure 1. UV-vis absorption spectra of the quinacridone derivatives in the dilute

solution $(1 \times 10^{-5} \text{ M in CH}_2\text{Cl}_2)$

Compound	λ_{max} (nm) λ	onset ^a (nm)	$\Phi_{PL}{}^b$	$\lambda_{em}(nm)$	Stokes shift (nm)
1	291,476,509	529	0.98	522	137
2	318,481,511	539	0.81	562	177
3	292,485,515	541	-	-	-

Table 1. The photophysical data of the quinacridone derivatives

^a The lowest-energy absorption edge of the absorption spectra. ^b Tested in CH₂Cl₂ solution, calculation methods and standards in Reference [27].

3.2.2. Fluorescence spectrum

Figure 2 shows the fluorescence spectrum (concentration of 2 x 10^{-6} M) of a D-A-D type quinacridone derivative in toluene and CH₂Cl₂ using an excitation wavelength of $\lambda = 475$ nm. Fluorescence data are shown in Table 1 and Table 2. Compound 1, 2 solution was

yellow-green, while compound **3** shown orange-red color. Among the tested compounds, **1** is a planar structure, which is beneficial to the occurrence of radiation transition, so its fluorescence quantum yield (Φ_{PL}) in toluene and CH₂Cl₂ is as high as 0.94 and 0.98. A substance with high fluorescence efficiency, the molecules of which are mostly in a planar configuration and have a certain rigidity^[28]. However, compound **3** due to the introduction of the *N*,*N*-bis(4-methoxyphenyl)aniline group, the spatial structure of the entire molecule is distorted, resulting in a greatly reduced Φ_{PL} (0.35) in toluene and fluorescence quenching in CH₂Cl₂. The emission peak position of compound **2** is significantly red-shifted compared to **1**, but the luminous efficiency in toluene and CH₂Cl₂ is lower Φ_{PL} of 0.75 and 0.85, probably due to ICT and the competing non-radiative process with fluorescence due to -OCH₃ groups, which facilitates the absorption of energy from the compound to high energy orbit.



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

the test solvent is toluene, b: the test solvent is CH₂Cl₂).

Compound	λ_{abs} (nm)	$\lambda_{em}(nm)$	$\Phi_{ ext{PL}}$
1	509	513	0.94
2	511	516	0.75
3	515	524	0.35

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Figure 3 shows the fluorescence emission spectra of three compounds in different polar solvents. The fluorescence emission spectra of the compounds **1** and **2** are not affected by the polarity of the solvent, but the emission peak of the solvent in the solvent toluene showed a slight blue shift. For compound 3, it shows fluorescence quenching or slight fluorescence in common solvents (such as dichloromethane, DMSO, chloroform, acetonitrile, etc.). This is because the introduction of *N*, *N*-bis (4-methoxyphenyl) aniline group destroys the planar configuration of the molecule^[28], resulting in a non-radiative transition of the excited state. Compound 3 has fluorescence in toluene, mainly because the toluene solvent inhibits the non-radiative transition of the molecule.



Figure 3. Fluorescence spectra of the quinacridone derivatives in various solvents .

3.3. Electrochemical properties

In order to further investigate the effect of substituent changes on the molecular properties of the target compound, electrochemical analysis was performed 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 (TBAPF₆) is a supporting electrolyte. The sample to be tested and the electrolyte are dissolved in dichloromethane, wherein the TBAPF₆ concentration is 0.1 M and the concentration of the analyte is 1×10^{-3} M, and the scanning speed is 100 mV/s. The cyclic voltammetry curves of the three target compounds are shown in **Figure 4**, and the specific data are listed in **Table 3**. When calculating the HOMO and LUMO energy levels of

the compounds, the initial oxidation potential is obtained according to the cyclic voltammetry curve of the organic compounds, and the HOMO energy level is calculated. The LUMO energy level is added by the HOMO value plus the band gap. The $E_{gap}^{[29]}$ value is available, and the data is shown in **Table 3**.

It can be seen from **Table 3** that the HOMO / LUMO energy levels can calculated to be -6.198/-3.854 eV, -6.101/-3.800 eV, -5.804/-3.512 eV for **1**, **2** and **3** respectively. The introduction of an electron donor can reduce the oxidation initiation potential of the molecule, increase the HOMO level, facilitate the injection of holes, and increase the hole mobility of the material ^[30]. When the N-position of quinacridone introduces a strong electron-donating N,N-bis(4-methoxyphenyl)aniline group, the HOMO level is significantly improved, and the E_{gap} between HOMO and LUMO is lowered, making electrons more prone to transition, which is beneficial to ICT.

	<u> </u>		Electrochemical (eV)		
Compound	E ^{ox} onset (V)	$\mathbf{E_{gap}}^{a}(eV)$	HOMO ^b	LUMO ^c	
1	1.098	2.344	-6.198	-3.854	
2	1.001	2.301	-6.101	-3.800	
3	0.704	2.292	-5.804	-3.512	

Table 3. CV data of the quinacridone derivatives.

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

 $\label{eq:entropy} ^{b} E_{HOMO} = -(E_{onset}^{ox} ~+5.1) ~eV. ~^{c} E_{LUMO} = ~E_{onset}^{ox} ~+ E_{gap}.$



Figure 4. CV curves of the quinacridone derivatives are measured in CH₂Cl₂.

3.4. Nonlinear optical properties

In order to study the relationship between the structure of the compound and the third-order nonlinear optical properties, the Z-scan curve of the three target compounds (1~3) at 1030 nm was tested by Z-scan technique^[31].

The sample was firstly prepared into a chloroform solution at a concentration of 1 mg/mL and placed in a sample cell having a thickness of 2 mm. The laser pulse energy used in the experiment was 0.4 uJ^[32], the wavelength was 1030 nm, the pulse width was 190 fs, and the focal length was 250 mm. Similarly, the solvent chloroform was also measured under the same experimental conditions and found to have no nonlinear absorption, so the effect of the nonlinear optical effect of the solvent on the test can be ignored.

The closed-cell curve of the target compound 1~3 are shown in Figure 5. As can be seen

from the figure, the closed-loop curve shows a large peak-to-valley structure, indicating that the nonlinear refractive index $n_2^{[33]}$ of the compound is greater than zero, for self-focusing phenomenon.

The opening curve of the target compound 1~3 are shown in **Figure 6**. The opening curve of the compound 1~3 are valley-like, so these compounds are all anti-saturation absorption. The $\chi^{(3)}$ and γ of the compound 1~3 were calculated by the calculation method in Reference^[34]. The specific data is shown in **Table 4**.



Figure 5. 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



Figure 6. 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.

According to the data in **Table 4**, 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 (β) were between $1.3271 \sim 1.4319 \times 10^{-13}$ esu. The third-order nonlinear polarizability $\chi^{(3)}$ were between $5.5418 \sim 6.9312 \times 10^{-12}$ esu, and the second-order hyperpolarizability (γ) were between $1.5457 \sim 2.6849 \times 10^{-33}$ esu. The γ values of 1,5-diaminopurine^[35] and sulfonation in the naphthalimide derivatives^[36] reported in the literature are 5.1271×10^{-34} esu, 3.1541×10^{-34} esu. And the highest of our synthesis **3** can reach 2.6849×10^{-33} esu, the reason for the above phenomenon is attributed to the fused

heterocyclic structure of quinacridone, especially because the molecule contains electrons and these structures have a carbonyl group (C= O) of the withdrawal group and electron-inducing groups (N-R), and these structures have higher electron transport capabilities and electron delocalization. For the convenience of comparison, the opening curve of 1 - 3 are placed in the same picture as shown in Figure 7. The depth of the opening is from 3 > 2 > 1. As can be seen from **Table 4**, the γ value of **3** ($\gamma = 2.6849 \times 10^{-33}$ esu) is increased by 1.74 times than the γ value of 1 (1.54570 × 10⁻³³ esu). 3 exhibits better third-order nonlinear performance, which is attributed to the stronger chargeability of the N,N-bis(4-methoxyphenyl)aniline group, which enhances the HOMO level. As strong electron donor, 8 N,N-bis(4-methoxyphenyl)aniline group has stronger power supply than phenyl and methoxyphenyl groups, and promotes ICT, which is also very beneficial for improving the third-order nonlinear performance of materials.

Compound	$\boldsymbol{\beta} \text{ (m/W)} \\ \times 10^{-13}$	$n_2 (m^2/W) \times 10^{-17}$	$\boldsymbol{\chi}^{(3)} \mathbf{R}(esu)$ ×10 ⁻¹³	$\chi^{(3)}$ I(esu) ×10 ⁻¹²	$\chi^{(3)}$ (esu) $\times 10^{-12}$	γ (esu) $\times 10^{-33}$
1	1.3271	1.1742	9.5482	5.4589	5.5418	1.5457
2	1.3764	1.1728	9.7538	5.9457	6.0252	1.8842
3	1.4319	1.1586	9.2370	6.8694	6.9312	2.6849

Table 4. Third-order NLO parameters of the quinacridone derivatives in CHCl₃



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

3.5. Theoretical calculation

To further explained the relationship between the molecular structure and properties of the synthesized target compounds, we performed a DFT calculation. The structural optimization of the three target compounds synthesized were shown in Figure 8. The structure of the compound was simulated by Gaussian. The quinacridone derivatives 1 and 2 have good molecular planarity. Due to the large steric hindrance of the *N*,*N*-bis(4-methoxyphenyl)aniline group and the quinacridone precursor, the 3 molecular structure forms a certain distortion, which weakens the strong π - π stacking between molecules, so 3 has better solubility.



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

Generally, for organic third-order nonlinear optical materials with excellent performance, HOMO is mostly located in the donor region, and LUMO is located in the acceptor portion, which is more beneficial to the transport of molecules from the donor to the acceptor, while the molecular energy charge transfer is often associated with third-order nonlinear performance of organic materials. The DFT theoretical calculations (**Figure 9**) shown that for the compounds 1 and 2, both the LUMO and HOMO orbitals fall on the quinacridone parent ring. While compound 3 introduces a N,N-bis(4-methoxyphenyl)aniline group as a donor at the N-position of the quinacridone, the LUMO orbital mainly falls on the quinacridone HOMO orbital falls the parent ring, and the on N,N-bis(4-methoxyphenyl)aniline group. Compound **3** has a significant improvement in the HOMO level of the introduction of the benzene ring (1) at the N-position of the quinacridone.

This indicated that *N*,*N*-bis(4-methoxyphenyl)aniline group has a stronger electron donating ability than the phenyl ring. By introducing a *N*,*N*-bis(4-methoxyphenyl)aniline group as a donor at the N-position of quinacridone, the HOMO level of **3** is increased the most, so the compound **3** $E_{gap}(3.0064 \text{ eV})$ is the smallest (the theoretical calculation data is shown in Table **5**. Therefore, the introduction of a strong electron donating *N*,*N*-bis(4-methoxyphenyl)aniline group facilitates ICT and exhibits better third-order nonlinear optical performance. Comparing the CV HOMO/LUMO level, we can find that the value of the CV test is inconsistent with the theoretically calculated value. However, the decrease trend of compounds 1 to 3 is consistent, so theoretical calculations have a good guiding value for the design of compounds.

Jakob Wudarczyk and Klaus Müllen et al. found that the enhancement of the molecular dipole moment can also reflect the enhancement of third-order nonlinear optical performance^[37]. In the molecular design, it was found through theoretical calculation that *N*, *N*-bis(4-methoxyphenyl)aniline group also played a role in improving the molecular dipole moment (see Table 5). A quinacridone derivative in which the N-position is substituted by a phenyl ring has a molecular dipole moment of 0.0012 debye. Once a *N*,*N*-bis(4-methoxyphenyl)aniline group is introduced, the molecular dipole moment can be increased to 0.5655 debye. The second-order hyperpolarizability (γ) of the third-order nonlinear optical material is theoretically calculated in combination with the semi-empirical ZINDO method. Theoretical calculations and experimental data are not numerically identical, because the calculations are data obtained without solvents and gases. However, the trend of nonlinear performance of the compounds presented by the data is completely consistent, that

is, the γ value: 3>2>1. From the theoretical calculation data, it can be found that the low E_{gap} and the large dipole moment are favorable for the third-order nonlinear optical performance. This may be due to the introduction of the *N*,*N*-bis(4-methoxyphenyl)aniline group, which causes distortion of the entire molecular structure, thereby reducing the π - π accumulation between the molecules, and making the electron flow in the molecule smoother.



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

Table 5. DFT-calculated (B3LYP/6-31G G(d)*) HOMO and LUMO energies, dipole

moment, Second-order hyperpolarizability.

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Compd.	HOMO (eV)	LUMO (eV)	E _{gap} (eV)	dipole moment (Debye)	γ (esu) $\times 10^{-33}$		
1	-5.1337	-1.9722	3.1615	0.0012	0.2606		
2	-4.9955	-1.8895	3.1060	0.0010	0.3026		
3	-4.8216	-1.8152	3.0064	0.5655	0.8995		

4. Conclusions

In summary, we have reported three quinacridone derivatives with D-A-D push-pull structure synthesized and characterized by UV, FL, NMR and HRMS spectroscopy. Theoretical and experimental studies have shown that the introduction of a N,N-bis(4-methoxyphenyl)aniline donor group at the N-position of quinacridone significantly enhances the HOMO level and reduces E_{gap} , which facilitates charge transfer within the molecule. The third-order NLO properties exhibited are the best among all chromophores. The third-order NLO magnetic susceptibility ($\chi^{(3)}$) of the compound is 6.9312×10^{-12} esu, while the second-order hyperpolarizability of the molecule γ is 2.6849×10^{-33} esu. The chromophore **3** exhibits significant third-order NLO performance, which is in line with our structural design strategy. The results have clearly shown that quinacridone derivatives have great potential applications in third-order nonlinear optical materials.

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New quinacridone derivatives: Synthesis, photophysical and

third-order nonlinear optical properties

- A series of new D-A-D structure quinacridone derivatives have been synthesized. •
- The N-position electron-substituted quinacridone exhibited good third-order NLO.
- N, N-bis (4-methoxyphenyl) aniline group will enhance third-order NLO ٠ response.

Declaration of interests

 \boxtimes 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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