Triphenylamine-modified quinoxaline derivatives as two-photon photoinitiators

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Two new chromophores, triphenylamine-modified quinoxaline (**TPAQ**) and benzoquinoxaline (**TPABQ**), were synthesized, and their linear spectroscopy and two-photon absorption properties were investigated. For comparison, 4-ethoxyphenyl-substituted quinoxaline (**EOQ**) and benzoquinoxaline (**EOBQ**) were prepared. The results showed that **TPAQ** possesses a high fluorescence quantum yield and a high δ_{2PA} value of >160 GM in the laser light wavelength range of 780–820 nm, and is superior to most common benzil-type compounds as a photoinitiator in two-photon initiated polymerization.

Introduction

Materials displaying two-photon absorption (2PA) properties have extensively been studied in recent years due to their promising applications in materials science and the biological imaging area, such as 3D microfabrication,[1–4] photodynamic therapy,[5] two-photon microscopy,[6–9] optical power limiting,[10,11] three-dimensional optical data storage[12–14] and two-photon laser scanning fluorescence therapy.[5,8,9] Two-photon induced polymerization has also attracted great attention for its stronger 3D fabrication capability and higher resolution than the traditional UV light lithographic technique.[2] In the past decade, the two-photon induced polymerization microfabrication technique has made great progress in resolution improvement and fabrication speed, and various kinds of complicated 3D-structures have been fabricated for practical uses.[15–21] In this fabrication technique, the most commonly used resins are commercially available negative-tone photoresist resins containing conventional ultraviolet initiators. However, such initiators have only very low two-photon sensitivities because of their small two-photon absorption cross sections (δ_{2PA} values are at a level of a few tens GM).[22] Normally, the induced polymerization fabrication process of a resin using photoinitiators with small 2PA cross sections need high laser powers, which would likely lead to damage of the resulting 3D-structures. In order to avoid this problem, two main measures are taken to improve the two-photon sensitivity of a resin. One is to optimize resin components; the other is to develop new photoinitiators with higher sensitivities. New photoinitiators may be obtained by (a) designing novel chromophores with large two-photon absorption cross sections; and (b) modifying the molecular structures of existing photoinitiators (*e.g.*, by introducing radical stabilizing groups or enlarging parent conjugate systems). Apparently, the latter is the simplest way to obtain new two-photon induced polymerization initiators.

In this paper, we report a simple, convenient method for improving two-photon absorption cross sections of benzil-type compounds that are among the most common photoinitiators in UV light. By both translating the parent benzil to quinoxaline or benzoquinoxaline and introducing electron-rich moieties (4-ethoxyphenyl or triphenylamine moiety) into the system, we obtained a new series of two-photon absorption chromophores, **EOQ**, **EOBQ**, **TPAQ** and **TPABQ** (shown in Fig. 1). Further, their photophysical properties and two-photon induced polymerization as photoinitiators were investigated.

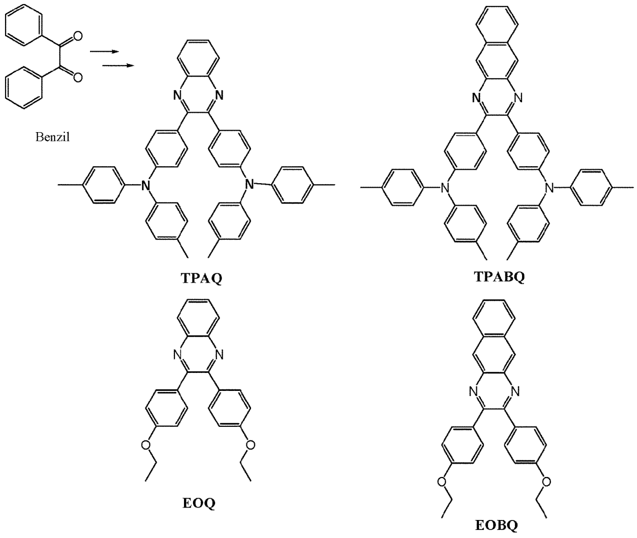

Fig. 1 Chemical structures of the target compounds.

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Experimental

General procedures

All reagents and solvents were purchased from commercial sources. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker DMX-400 NMR Spectrometer using tetramethylsilane as the internal standard. Mass spectra were recorded on a Micromass GCT-MS spectrometer or a Bruker BIFLEX III Mass Spectrometer. UV–visible spectra were recorded at a concentration of 1×10^{-5} M on a UV 3100PC Scanning Spectrophotometer (Shimadzu, Japan). Infrared spectra were recorded on a FT/IR-410 spectrophotometer (JASCO Corp.).

Fluorescence spectra were recorded at a concentration of 1×10^{-6} M on a RF5300PC spectrofluorophotometer (Shimadzu, Japan). The one-photon excited fluorescence lifetimes were recorded at a concentration of 1×10^{-5} M on a single photon count fluorescence spectrometer (F900, Edinburgh Instrument Co. UK). Elemental analyses were carried out on a Carlo-Erba 1160 elemental analyzer. Two-photon induced fluorescence (TPIF) measurements were performed with a mode-locked Ti-sapphire laser.

Synthesis of materials

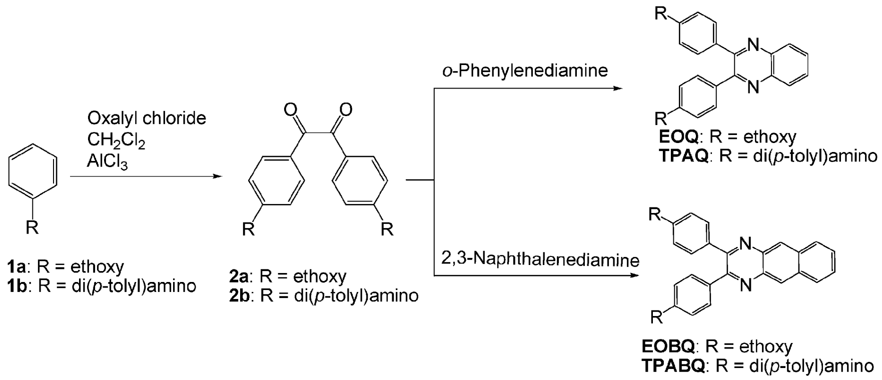
The target compounds, **TPAQ**, **TPABQ**, **EOQ** and **EOBQ**, were synthesized in two steps with high yields as illustrated in Scheme 1. The intermediate compounds **2** were obtained by the Friedel–Crafts reaction of the starting materials **1** with oxalyl chloride in isolated yields of 89% for **2a** and 61% for **2b**. Then **2** underwent a condensation cyclization with *o*-phenylenediamine or 2,3-naphthalenediamine to provide the target compounds **EOQ**, **TPAQ**, **EOBQ** and **TPABQ** in high yields.

4,4′-Diethoxybenzil (2a). To a suspension of anhydrous aluminium chloride (1.335 g, 0.01 mol) in dichloromethane (50 mL) was added oxalyl chloride (0.646 g, 5 mmol) in one portion, and then ethoxybenzene (**1a**) (1.35 g, 12 mmol) over 5 min. The reaction mixture was heated at reflux for 6 h. After cooling, the mixture was quenched with crushed ice (50 g) mixed with concentrated hydrochloric acid (10 mL). The organic phase was separated, and the aqueous phase was extracted with dichloromethane (20 mL). The combined organic phases were washed with water (2 × 50 mL) and brine (2 × 50 mL), and dried over anhydrous Na_2SO_4. The solvent was removed in vacuum and the residue purified by column chromatography on silica gel with dichloromethane–petroleum ether (1 : 1, v/v), providing the product as a white solid in 89% yield (1.23 g); mp 148–149 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (d, H, J = 8.96 Hz), 6.96 (d, 4H, J = 8.96 Hz), 4.13 (q, 4H, J = 7.00 Hz), 1.55 (t, 6H, J = 7.00 Hz). MS (MALDI-TOF): m/z 298.12 (M^+).

4,4′-Bis[di(*p*-tolyl)amino]benzil (2b). This compound was prepared from 4,4′-dimethyltriphenylamine (**1b**) and oxalyl chloride according to the same procedure as that for **2a** to give an orange–red solid of the product in 61% yield; mp 106–107 °C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.62 (d, 4H, J = 8.76 Hz), 7.20 (d, 8H, J = 8.16 Hz), 7.09 (d, 8H, J = 8.16 Hz), 6.75 (d, 4H, J = 8.76 Hz), 2.29 (s, 12H). MS (MALDI-TOF): m/z 600.28 (M^+).

2,3-Bis(4-ethoxyphenyl)quinoxaline (EOQ). A suspension of **2a** (167 mg, 0.6 mmol) in AcOH (10 mL) was heated until the material was fully dissolved. To this solution was added *o*-phenylenediamine (63 mg, 0.6 mmol) in one portion, and the reaction mixture was heated at reflux for 10 h. After cooling, the precipitate was collected by suction filtration and further purified by column chromatography on silica gel using a solvent mixture of dichloromethane–petroleum ether (1 : 1, v/v), providing the product as a white solid in 95% yield (199 mg); mp 151–152 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.21 (dd, 2H, J_1 = 6.27 Hz, J_2 = 3.43 Hz), 7.75 (dd, 2H, J_1 = 6.27 Hz, J_2 = 3.43 Hz), 7.49 (d, 4H, J = 8.68 Hz), 6.87 (d, 4H, J = 8.68 Hz), 4.06 (q, 4H, J = 6.96 Hz), 1.43 (t, 6H, J = 6.96 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.60, 153.1, 141.0, 131.5, 131.3, 129.5, 129.0, 114.3, 63.5, 14.8. MS (MALDI-TOF): m/z 370.2 (M^+). Anal. calc. for $C_{22}H_{22}N_2O_2$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.60; H, 5.97; N, 7.26%.

2,3-Bis(4-ethoxyphenyl)benzoquinoxaline (EOBQ). This compound was prepared from **2a** and 2,3-naphthalenediamine according to the same procedure as that for **EOQ** to give the product as a yellow solid in 85% yield; mp 171–172 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.67 (s, 2H), 8.09 (dd, 2H, J_1 = 6.44 Hz, J_2 = 3.23 Hz), 7.54 (d, 4H, J = 8.74 Hz), 7.56–7.52 (m, 2H), 6.88 (d, 4H, J = 8.74 Hz), 4.09 (q, 4H, J = 6.98 Hz), 1.44 (t, 6H, J = 6.98 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.7, 153.8, 137.9, 133.8, 131.6, 131.3, 128.4,



Scheme 1 Synthetic route to the target compounds.

127.1, 126.4, 114.2, 63.5, 14.73. MS (MALDI-TOF): *m*/*z* 420.2 (M^+). Anal. calc. for $C_{22}H_{22}N_2O_2$: C, 79.98; H, 5.75; N, 6.66. Found: C, 79.62; H, 5.69; N, 6.91%.

2,3-Bis[4-(di-*p*-tolylamino)phenyl]quinoxaline (TPAQ). This compound was prepared from **2b** and *o*-phenylenediamine according to the same procedure as that for **EOQ** to give the product as a yellow solid in 91% yield; mp 239–241 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.20–8.10 (m, overlapped, 2H), 7.72 (dd, 2H, J_1 = 6.42 Hz, J_2 = 3.36 Hz), 7.34 (d, 4H, J = 8.56 Hz), 7.03 (d, 8H, J = 8.28 Hz), 6.97 (d, 8H, J = 8.28 Hz), 6.90 (d, 4H, J = 9.04 Hz), 2.33 (s, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.2, 149.0, 144.8, 140.7, 133.2, 131.2, 130.7, 130.0, 129.6, 128.8, 125.3, 120.8, 20.9. MS (MALDI-TOF): *m*/*z* 672.3 (M^+). Anal. calc. for $C_{48}H_{40}N_4$: C, 85.68; H, 5.99; N, 8.33. Found: C, 85.70; H, 6.09; N, 8.31%.

2,3-Bis[4-(di-*p*-tolylamino)phenyl]benzoquinoxaline (TPABQ). This compound was prepared from **2b** and 2,3-naphthalenediamine according to the same procedure as that for **EOQ** to give the product as a yellow solid in 87% yield; mp 273–275 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.66 (s, 2H), 8.08 (dd, 2H, J_1 = 6.45 Hz, J_2 = 3.23 Hz), 7.53 (dd, 2H, J_1 = 6.45 Hz, J_2 = 3.23 Hz), 7.46 (d, 4H, J = 8.72 Hz), 7.11 (d, 8H, J = 8.39 Hz), 7.06 (d, 8H, J = 8.39 Hz), 6.99 (d, 4H, J = 8.72 Hz), 2.34 (s, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.1, 149.0, 144.7, 138.0, 133.8, 131.6, 130.7, 129.9, 128.4, 127.0, 126.3, 125.3, 120.7, 20.8. MS (MALDI-TOF): *m*/*z* 722.5 (M^+). Anal. calc. for $C_{22}H_{22}N_2O_2$: C, 86.39; H, 5.86; N, 7.75. Found: C, 85.99; H, 5.75; N, 7.60%.

Measurements of fluorescence quantum yields

The quantum yields of the materials were measured by using Coumarin 307 as the standard according to a known procedure.[23] Absorbance was limited to equal or less than 0.1. The quantum yield was calculated by the following equation:

$$Q_{YS} = Q_{YR}\frac{I_S A_R n_S^2}{I_R A_S n_R^2}$$

where Q_{YS} is the quantum yield, A_S the absorbency and I_S fluorescence area of the tested compound, respectively; Q_{YR} (0.58) is the quantum yield of Coumarin 307 in acetonitrile solution,[24] A_R the absorbency and I_R fluorescence area of coumarin 307, respectively; and n_S and n_R are the refractive index of toluene and acetonitrile, respectively.

Measurements of two-photon absorption cross sections

2PA spectra were obtained by the two-photon-induced excited fluorescence (TPEF) method reported by Xu *et al.*[25] TPEF spectra were recorded on SD2000 spectrometer (Ocean Optical) with the excitation by a mode-locked Ti-sapphire femtosecond laser (Tsunami, Spectra-Physics), where oscillating wavelength, pulse width and repetition rate were 780 nm, 80 fs and 82 MHz, respectively. It is assumed that fluorescence quantum yields after two-photon excitation are the same as those after one-photon excitation. 2PA cross sections are obtained by calibration against fluorescein in aqueous 0.1 M NaOH solution (pH = 11) for the femtosecond measurements.

Two-photon induced polymerization

Two-photon induced polymerization (TPP) experiments were performed with the irradiation of 80 fs pulses from a mode-locked Ti-sapphire femtosecond laser (Tsunami, Spectra-Physics) with a repetition rate of 80 MHz at 800 nm. The photoresist resin was prepared by mixing methyl acrylic acid (MAA) as monomer, DEP-6A as cross-linker, and a dye as photoinitiator. In the control experiment, commercially available benzil was used as initiator. The lasing source was tightly focused by a 100 × 100 oil-immersion objective lens with a high numerical aperture (N.A. = 1.40, Olympus). The focal point was focused on the liquid photopolymerisable resin which was placed on a cover glass above the *xyz*-step motorized stage controlled by a computer. After laser fabrication, the unpolymerized resin was washed out with ethanol. The images of fabricated lines were observed using a field-emission scanning electron microscope (FE-SEM, JOEL, JSM-6330F).

Results and discussion

Photophysical properties

Photophysical properties of the target compounds (**EOQ**, **EOBQ**, **TPAQ** and **TPABQ**) were studied in $CHCl_3$ solution and the data are summarized in Table 1.

Linear spectroscopy

From Table 1 and Fig. 2, we can see that all the target compounds show an intense absorption band with absorption maxima being located in the range of 350–470 nm. As expected, a red shift in the absorption maximum occurred from **EOQ** to **EOBQ** or from **TPAQ** to **TPABQ** due to the conjugation expansion in the benzoquinoxaline system as compared to the quinoxaline one. On the other hand, the red-shift from **EOQ** to **TPAQ** or from **EOBQ** to **TPABQ** indicated that triphenylamine moiety provides the molecule with a larger degree of conjugation than does the alkoxyaryl group. Thus, the maximum emission wavelength in $CHCl_3$ from **EOQ** to **TPABQ** could be red-shifted by 134 nm. The absorption maxima of **EOBQ** and **TPAQ** appeared at 405 and 419 nm, respectively, indicating that the half of wavelength of their two-photon absorption maxima is around 400 nm. In contrast, the absorption maximum of benzil is located at 290 nm. Therefore, the absorption maximum of benzil can be adjusted to about 400 nm by modification to enlarge its conjugated system.

The fluorescence quantum yields of the target compounds were determined (Table 1). The quinoxaline-type compounds exhibited significantly higher fluorescence quantum yields than the benzoquinoxaline-type ones, indicating that the benzoquinoxaline is a relatively weak π-acceptor. Moreover, the triphenylamine-modified species showed higher fluorescence quantum yields than the corresponding ethoxyphenyl-modified ones. This may be attributed to the stronger electron-donating ability of the triphenylamine moiety than that of the alkoxyaryl group. It is noteworthy that the conjugation length of the molecules does not produce a significant effect on the radiative lifetimes of these chromophores for the one-photon excited fluorescence lifetime of the excited state.

Table 1 Linear and nonlinear optical properties of the target compounds in $CHCl_3$

Compound	λ_{abs}/nm	λ_{em}/nm	δ(GM)	η (%)	τ_r/ns
EOQ	290/371	439	15	11.6	0.91
EOBQ	330/405	483	25	4.5	ND
TPAQ	307/419	555	163	14.6	4.99
TPABQ	304/464	573	159	9.8	3.86

λ_{abs} and λ_{em} are absorption and emission maxima, respectively; δ is the largest 2PA cross section in the measured range; η is the fluorescence quantum yield; and τ_r is the radioactive lifetime.

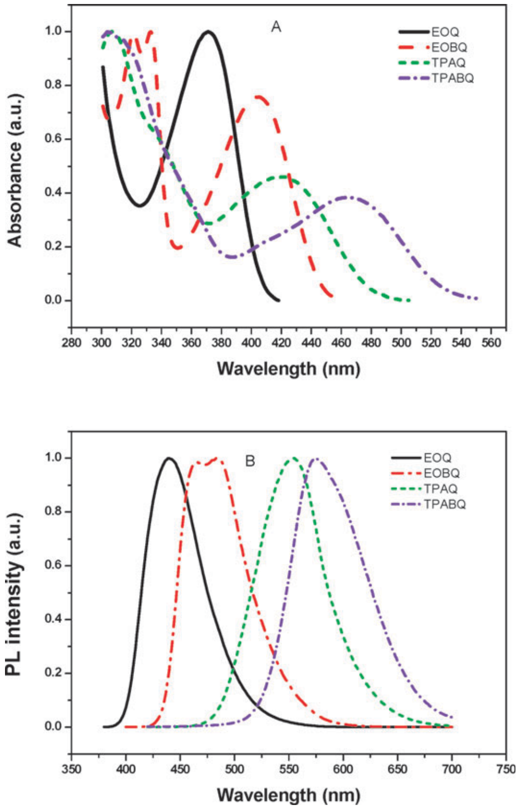


Fig. 2 Normalized absorption spectra (A) and normalized fluorescence spectra (B) of the target compounds in $CHCl_3$.

Two-photon absorption cross-section measurements

2PA cross sections (δ_{2PA} values) of the target compounds were measured to understand their 2PA behaviors using a two-photon fluorescence method (Table 1), and their 2PA spectra are presented in Fig. 3. It was found that chromophores **EOQ**, **EOBQ**, **TPABQ** and **TPAQ** exhibited a 2PA cross-section maximum of around 15, 25, 70 and 160 GM, respectively, in the wavelength range of 780–820 nm where laser light is widely used for two-photon microfabrication. The results suggested that the modification of quinoxaline or benzoquinoxaline by a triphenylamine group is very favorable for enhancing its δ_{2PA} value. Interestingly, **TPABQ** with a larger conjugation system, gives a far lower δ_{2PA} value in the wavelength range of 780–820 nm as compared to **TPAQ**, indicating that an appropriate π-conjugation degree of the π-acceptor part is essential for providing high 2PA cross sections. **TPAQ** should be a promising candidate for photoinitiators.

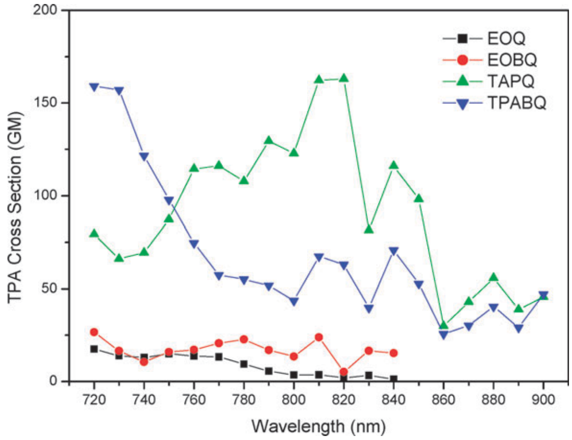


Fig. 3 Two-photon excitation spectra of the target compounds in $CHCl_3$.

Two-photon photopolymerization

Two-photon initiating polymerization (TPP) experiments were performed to understand the TPP behavior of chromophores. Usually, the threshold energy of polymerization is evaluated as the lowest average laser power leading to polymer lines being produced by the translating resin.[26] Here, the polymerization

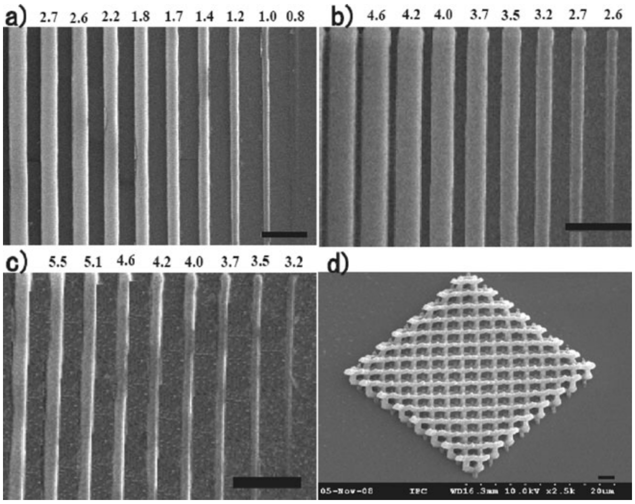


Fig. 4 SEM images of **TPAQ** (a), **TPABQ** (b) and benzil (c) after polymerization. The laser powers used to fabricate lines are shown on the SEM images in the power range of 0.8–5.5 mW. The scan speed is 10 m s^{-1}. (d) SEM image of a photonic crystal using **TPAQ** as photoinitiator (0.5%), MMA (48%) and DPE-6A (51.5%). The scale bar is 2 μm.

threshold is defined as the average power, before being induced into the objective lens, below which the polymer line can not be fabricated using a linear scan speed of 10 μm s^{-1}. The threshold of the resin using **TPAQ**, **TPABQ** and benzil as radical photoinitiators, is 0.8, 2.6 and 3.2 mW, respectively. We measured the widths of radical polymer lines at an exposure power of 3.2 mW. The polymerization rate for the resin using **TPAQ**, **TPABQ** and benzil as photoinitiators at a power of 3.2 mW can be calculated as 5.96, 3.89 and 0.66 μm^3 s^{-1}, respectively, according to ref. 26. TPP experiments showed that the chromophore **TPAQ** as photoinitiator is far better than the common photoinitiator benzil. We can successfully fabricate a diamond photonic crystal structure using a resin containing 48% MMA, 51.5% DPE-6A and 0.5% **TPAQ** as photoinitiator (SEM image shown in Fig. 4(d)).

Conclusions

Two triphenylamine-modified quinoxaline (**TPAQ**) and benzoquinoxaline (**TPABQ**) chromophores were designed and synthesized, and their two-photon absorption and photophysical properties were investigated. The chromophore **TPAQ** exhibited a high δ_{2PA} value of >160 GM at 780–820 nm, which demonstrated a significant improvement relative to benzil-type photoinitiators. Two-photon initiating polymerization experiments showed that the resin using **TPAQ** as photoinitiator provides a much lower threshold than that using benzil. This strategy for the modification of common UV photoinitiators should promote a rapid development of new 2PA photoinitiators.

Acknowledgements

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