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Synthesis, Photophysical Properties and Two Photon Absorption Study of Tetraazachrysene-based N-heteroacenes

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Abstract: *Three novel N-heteroacene molecules (**SDNU-1**, **SDNU-2** and **SDNU-**3) based on tetraazachrysene units as cores have been designed, synthesized and fully characterized. Their photophysical, electrochemical and fluorescence properties were investigated, and they exhibited blue to green emission in solid state. Interestingly, **SDNU-2** exhibited high solid photoluminescence quantum efficiencies (75.3%), which is the highest value of N-heteroacenes derivatives to date. Two-photon absorption studies have been conducted by using open and close aperture Z-san technique. **SDNU-3** showed a significant enhancement in the two-photon absorption cross-section with magnitudes as high as ~700 GM (1 GM = 1 × 10^{-50} cm^4 s/photon) when excited with 800 nm light, which is the largest value based on heteroacene system measured by Z-scan experiment so far. We attribute the outcome to sufficient electronic coupling between the strong charge transfer of quadrupolar substituents and the trtraazachrysene core. Our result would provide a new guideline to design novel efficient two-photon materials based on N-heteroacene cores.*

1. Introduction

Two photon (TPA) process is a nonlinear optical (NLO) phenomenon, and the efficiency of this process can be evaluated by accessing TPA, where one molecule can absorb two photons with identical or different frequencies in order to excite a molecule from one state (usually the ground state) to a higher energy state.[1] Organic molecules with high two-photon absorption properties have attracted many scientists' attention due to their potential applications in three-dimensional (3D) fluorescence imaging, lasing up-conversion, optical power limitation, photodynamic therapy and 3D optical data storage.[2-13] Benefiting from their diverse advantages including well-defined structural diversity, flexibility and functionality, fast response, and variable bandgap, organic π-conjugated compounds have been widely explored as NLO materials to enhance TPA absorption cross-sections.[14-22] In particular, extended π-conjugated systems with the symmetrical substitution of electron-donating and electron-accepting units have been regarded as efficient TPA molecules to exhibit larger TPA absorption cross-sections compared to the corresponding unsubstituted counterparts, indicating that the efficient intramolecular charge transfer (ICT), [23, 24] caused by the donating and withdrawing abilities of electron donor and acceptor, plays an important role in increasing their TPA cross-sections values.[25-27] Efforts to further increase the nonlinearity are usually focused on enlarging the conjugation length or increasing the strength of donors or acceptors or both.[28] As a result, the nonlinearity properties of the whole chromophores could be well tuned.

In the past decades, heteroacenes, a type of acenes with one or more heteroatomsto replace the CH units in their skeleton, have attracted great attention due to their unique photophysical and electronic properties as well as their highly-ordered structures in the solid state, which endows them wide applications in organic electronics such as photovoltaic effect, energy transfer, organic light-emitting diodes, TPA absorption and so on.[29-34] For example, the TPA cross-section of fluorescein,[35] Rhodamine B,[36] and Rhodamine 6G [37]have been reported to be 36, 150and 134 GM, respectively. Recently, Yu group[38] reported that three donor-acceptor ladder-type heteroacene molecules exhibited intense intramolecular charge-transfer and displayed obvious two-photon absorption behaviors with TPA cross-sections of 64, 72, and 83 GM (chloroform, 800 nm), respectively. In order to further increase the TPA cross-section value, Yu group prepared new ladder-type oligomers[39], consisting of thienoacene derivatives as the donor and perylene diimide (**PDI**)as the acceptor. They found that these compounds could display the highest TPA cross-section value of 125 GM. However, all currently-reported TPA cross-sections values based on heteroacenes are relatively small compared with other organic TPA materials such as triphenylamine derivatives (a TPA cross-section of 790 GM)[40] and some other conjugated compounds[41]excited with 800nm light. To further improve the TPA cross-sections of heteroacenes molecules, structural

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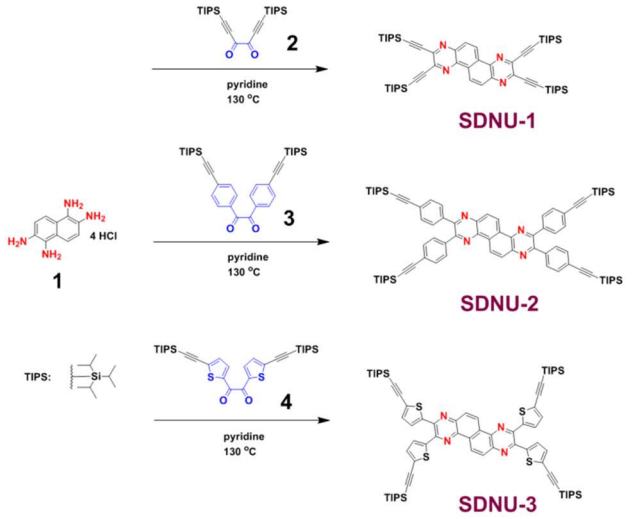
adjustment of both backbones and branched chains for the realization of more effective intramolecular charge transfer are highly desirable.



Scheme 1. Synthetic procedures of **SDNU-1**, **SDNU-2** and **SDNU-3.**

As one family member of heteroacenes, N-heteroacenes (or azaacenes, nitrogen-contained analogues of acenes) have been widely demonstrated as promising n-type semiconductors in optoelectrical devices. [29,30,42] Especially, azaacenes-based donor-acceptor molecules with various functions are very promising[43] because their unique electronic/optical properties as well as interesting intermolecular self-assembly motifs can show the ideal TPA absorption ability. Especially, the high electron-polarizability held by the large delocalized π-conjugated systems can be further enhanced by the push–pull electronic characteristics. [44-46] The combination of these factors are in favor of realizing a series of molecules with significant TPA cross-section ability. Unfortunately, such NLO properties based on azaacenes are scarcely available and rarely investigated. Recently, our group synthesized novel TPA materials through the combination of pyrazine species and triphenylamine unit[28] and we demonstrated that the maximum TPA cross-section value can reach 211 GM in dichloromethane solution with 800 nm excitation. These results convince us that azaacenes could have great potential applications in highly efficient NLO materials.

Herein, continuing our research on functional azaacenes compounds,[31] we report the synthesis and characterization of three new N-heteroacene with tetraazachrysene units as their backbone (**SDNU-1**, **SDNU-2** and **SDNU-3**). Four spherical triisopropylsilyl (TIPS) groups are attached onto the backbone, which guarantees that the as-synthesized N-heteroacene is stable and easily soluble in organic solvents by decreasing π-π interactions via steric hindrance. Interestingly, we found that the solid-state emission of all three compounds varied by changing the linking substituents, and **SDNU-2** exhibited an intriguing intense solid-state fluorescence quantum yield (φ = 75.3%), which is among the highest value reported for azaacene materials so far. The investigation on the nonlinear optical (NLO) properties revealed that **SDNU-3** exhibited a TPA cross section of 702 GM through open aperture z-scan measurement, which is the largest value based on heteroacenes measured by Z-scan experiment.

2. Results and discussion

2.1. Synthesis and characterization

The synthetic procedures of **SDNU-1**, **SDNU-2** and **SDNU-3** are shown in Scheme 1. The precursors **1, 2** and **3** were prepared according to the previously-reported procedures with some modification.[47-49] Compound **4** was prepared in 52% yield through the palladium-catalyzed Stille-coupling reaction. All three target products were obtained by condensing diketones with diamines in pyridine solutions under reflux condition. The as-synthesized materials were fully characterized by ^{1}H and ^{13}C NMR, Fourier Transform infrared spectroscopy (FT-IR), and matrix assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF-MS). All the original data have been provided in supporting information (SI). All final compounds have shown good solubility in common organic solvents such as chloroform, dichloromethane, and *o*-dichlorobenzene (*O*-DCB) at room temperature. Also, all final molecules display excellent thermal stability with the decomposition temperature (T_d, 5% weight loss) larger than 400 °C under nitrogen atmosphere. Note that heating the solids of all three compounds in air at 200 °C for two hours did not lead to detectable changes as indicated by ^{1}H NMR spectra.

2.2. Crystal structure of SDNU-1

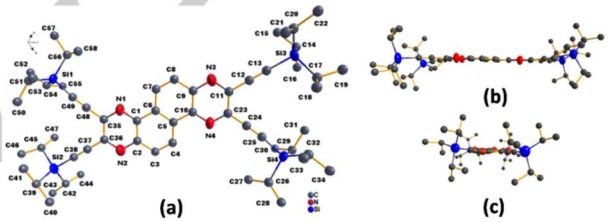


Figure 1. The crystal structure of **SDNU-1**.

The crystals of **SDNU-1** suitable for Single Crystal X-ray crystallographic diffraction (SCXRD) was obtained by slow diffusion of methanol into tetrahydrofuran (THF) solution. The structure analysis of **SDNU-1** (a = 11.67 Å, b = 19.34 Å, c = 14.37 Å, α= 90 °C, β= 107°C, γ= 90°C) crystallized in the monoclinic space group P21/c with a big unit cell (V = 3102.56 (3) Å3; CCDC number: 1858979; details of the unit cell parameters are provided in Table S1 and S2). As expected, the configuration of the conjugated backbone is nearly planar (Fig. 1a), where the acetylene, the pyrazine ring and the naphthalene group are in the same plane (Fig. 1b, 1c). As far as we know, **SDNU-1** is the first simplest ladder-type N-heteroacene, whose structure has been confirmed by single crystal.[50] **SDNU-1** forms one-dimensional herringbone packing motif, but does not show too much overlap of the backbone (plane distance of 5.27 Å) due to the steric hindrance of TIPS substituents (Fig. S1).

2.3. Optical properties

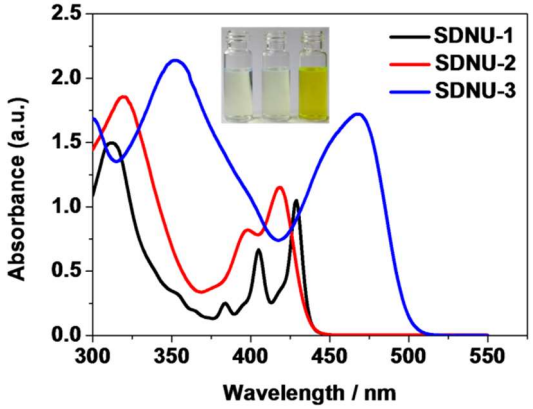


Figure 2. The absorption spectra of **SDNU-1, SDNU-2 and SDNU-3** in dichloromethane solution. Inset were the corresponding photograph of **SDNU-1** (left), **SDNU-2** (middle) and **SDNU-3** (right).

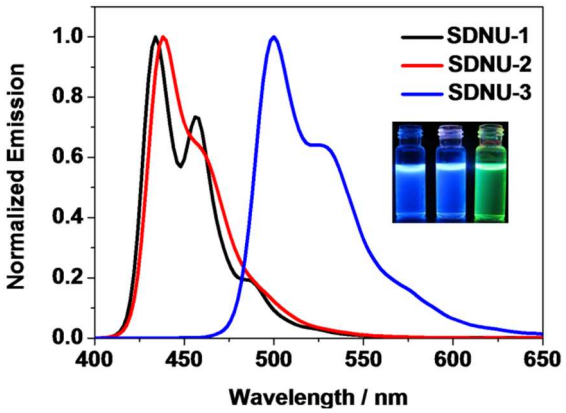


Figure 3. The fluorescence spectra of **SDNU-1, SDNU-2** and **SDNU-3** in dichloromethane solution. Inset were the corresponding photograph of **SDNU-1** (left), **SDNU-2** (middle) and **SDNU-3** (right).

The normalized optical absorption spectra of three compounds in dichloromethane (DCM) solutions are shown in Fig. 2 and the corresponding data are summarized in Table S3. The UV-vis absorption spectra of **SDNU-1** and **SDNU-2** exhibit an apparent bathochromic shift and relatively lower molar extinction coefficients relative to that of **SDNU-3**. The longest wavelength absorption of **SDNU-3** occurs at 468 nm (ε = 1.43× 10^5 cm^2mol^{-1}), which is red-shifted by 40 nm and 50 nm relative to that of **SDNU-1** (428 nm, ε = 1.01 × 10^5 cm^2mol^{-1}) and **SDNU-2** (418 nm, ε = 1.24 × 10^5 cm^2mol^{-1}). The red shift suggests a considerable intramolecular charge-transfer transition absorption of peripheral thiophene units to the tetraazachrysene core in **SDNU-3**. Moreover, the absorption spectra of **SDNU-1** and **SDNU-2** do not show any significant change by switching the solvent from low polar solvent DCM to high polar solvent N,N-dimethylformamide (DMF), suggesting the poor efficiency of intramolecular charge-transfer in the ground state.

The fluorescence quantum yields (Φ_f) of all three compounds in DCM solution were measured with quinine bisulfate (Φ_f = 55% in 0.1 M H_2SO_4) as a standard and are summarized in Table S3. Upon irradiation with UV light, the solutions of **SDNU-1** and **SDNU-2** in DCM exhibited a moderate blue fluorescence while the solution of **SDNU-3** in DCM showed a weak green fluorescence (Fig. 3). The quantum yields of **SDNU-1** (36.3%) and **SDNU-2**(22.8%) were found to be obviously higher than that of **SDNU-3** (7.45%). The introduction of four thienyl groups resulted in a remarkable effect on the absorption and emission spectra, which is probably due to the different structures between in the excited state and in ground state.

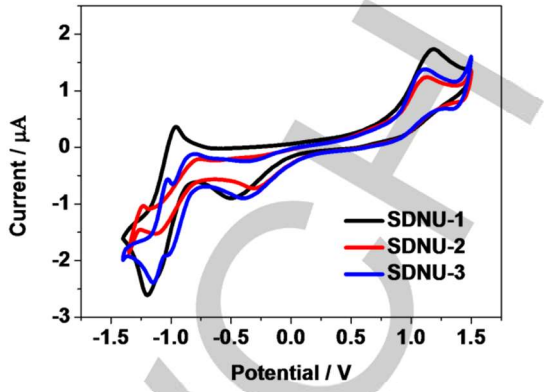


Figure 4. Cyclic voltammograms of three compounds.

2.4. Cyclic voltammetry

The cyclic voltammetry (CV) is employed to investigate the electrochemical properties of **SDNU-1**, **SDNU-2** and **SDNU-3** for highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels. The as-obtained CV curves are shown in Figure 4 and the resulting data are summarized in Table S3. In the cathodic scan, the initial onset oxidation potentials of the chromophores were found to occur at − 1.11 V, − 1.18 V and − 1.22 V (vs Ag/AgCl), which corresponded to LUMO levels of − 3.30 eV, − 3.23 eV and − 3.19 eV, respectively, according to the empirical equation $E_{LUMO} = -[q(E_{red}–E_{Fc/Fc+}) + 4.8)]$.[51] The HOMO energy levels of three compounds were calculated to be − 6.13eV, − 6.06 eV and − 5.67 eV, respectively, according to the equation $E_{HOMO} = -(E_{LUMO} + E_g^{opt})$ eV.[17] Because **SDNU-3** possesses the stronger electron-donating effect from thienyl groups, it exhibited relatively higher HOMO level in comparison with those of **SDNU-1** and **SDNU-2** with ethynyl and phenyl unit as the peripheral groups. All the electronic energy levels could be further illustrated by the density functional theory (DFT) calculations using B3LYP functional and 6-31G (d) basis set as discussed below.

2.5. Molecular simulations

To get further insight into geometrical configurations and electronic structures of **SDNU-1**, **SDNU-2** and **SDNU-3**, TD-DFT calculations at the B3LYP/ 6-31G(d)[52] level were performed. The results are illustrated in Fig. S2 and Table S4. From the optimized ground-state geometries (Fig. S2), their HOMO electron densities mainly distribute on the aza-chrysene cores as well as substituted moieties, while the LUMO ones are mainly located on the tetraazachrysene cores. The DFT calculated LUMO levels for **SDNU-1**, **SDNU-2** and **SDNU-**3 are − 2.99, − 2.87 and − 2.97 eV, and HOMO levels are − 6.10, − 5.82 and − 5.57 eV (Table S4), which are consistent with the experimental data. Moreover, the HOMO–LUMO energy gaps (E_g^{cal}) of **SDNU-1**, **SDNU-2** and **SDNU-3** range from 2.60 to 3.11 eV (Table S4), which are consistent with their optical bandgap results.

2.6. Solid-state fluorescence study

As shown in Fig. S3, **SDNU-1** exhibits solid-state fluorescence emission at 456 nm along with a shoulder peak at 487 nm, while **SDNU-2**/**SDNU-3** emits a strong peak at 481/559 nm. The solid fluorescence quantum yields (Φs) of **SDNU-1**, **SDNU-2** and **SDNU-3** are 8.75%, 75.3% and 6.09%, respectively (Table 1). To the best of our knowledge, 75.3% is the highest value of solid-state fluorescence quantum yields in azaacenes derivatives. Furthermore, time-resolved fluorescence spectra (Figure S31-33) reveal that the fluorescence decay times (τ) of **SDNU-1**, **SDNU-2** and **SDNU-3** (Table 1) are 0.90, 3.00 and 0.91 ns, respectively. We also estimated the radiative and nonradiative decay rates of **SDNU-1**, **SDNU-2** and **SDNU-3**, and found that the radiative decay rate decreases with the trend of **SDNU**-2 ($9.72 \times 10^7\ s^{-1}$), **SDNU-1** ($25.11 \times 10^7\ s^{-1}$), **SDNU-3** ($6.65 \times 10^7\ s^{-1}$); while the nonradiative decay rate increases with the order of **SDNU-2** ($1.01 \times 10^7\ s^{-1}$), **SDNU-1**($0.08 \times 10^7\ s^{-1}$), **SDNU-3** ($1.03 \times 10^7\ s^{-1}$), which is consistent with their solid-state fluorescence quantum yields.

Molecular simulation was conducted to analyze the dihedral angle between the tetraazachrysene cores and peripheral substituents for **SDNU-1**, **SDNU-2** and **SDNU-3**. The as-obtained results (Fig. S5) indicates that there is a tilt angle of 1.15° for **SDNU-1**, 40.1° for **SDNU-2** and 29.6° for **SDNU-3**, suggesting that the trend of increasing steric hindrance is **SDNU-1**, **SDNU-3**, and **SDNU-2**. Generally, molecules with higher stereo-hindrance effect will be beneficial for their fluorescence efficiency because of the relatively loose solid-state stacking pattern.[53]

2.7. Two-Photon Absorption Investigation

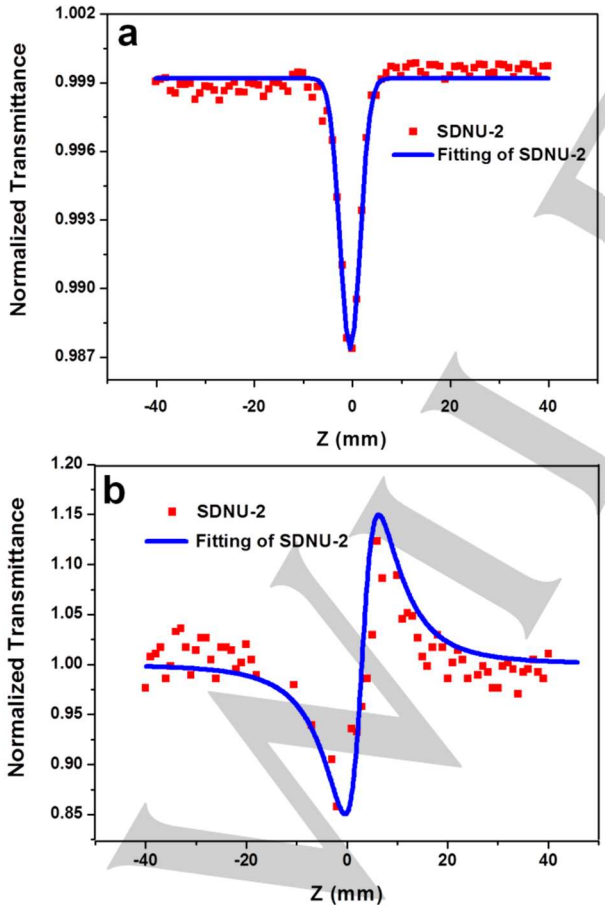


Figure 5. Opened and closed Z-scan curves of **SDNU-2**.

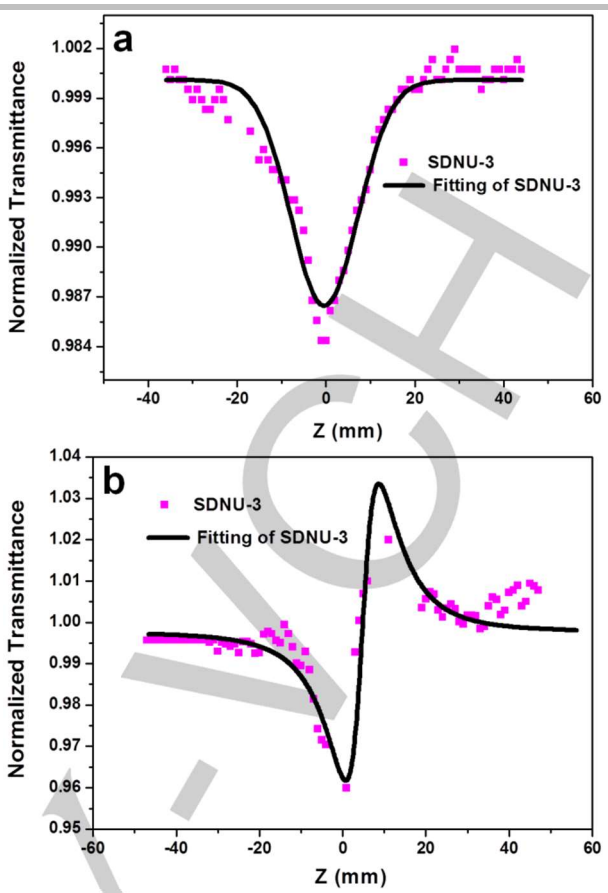


Figure 6. Opened and closed Z-scan curves of **SDNU-3**.

The third-order nonlinear optical properties of **SDNU-1**, **SDNU-2** and **SDNU-3**, were studied using opened and closed aperture Z-san technique excited with 800 nm light and a repetition rate of 1 kHz. The resulting curves are shown in Fig. 5 and 6. The experimental data of nonlinear refractive index (n_2), TPA coefficient (β) and TPA cross-section value (δ_2^{max}) are summarized in Table 2. All three compounds were measured at dichloromethane solution (5×10^{-3} M). Note that dichloromethane does not show any two-photon absorption activity under the experimental conditions. Due to the weak electron-donating ability of (triisopropylsilyl)acetylene segment, **SDNU-1** exhibited negligible third-order nonlinear optical properties. Fig. 5a and 6a showed the opened Z-scan curves of **SDNU-2** and **SDNU-3**, and their nonlinear absorption coefficient (β) are 0.43×10^{-12} and 0.51×10^{-12} cmW^{-1}, respectively. Fig. 5b and 6b showed the closed Z-scan curves and their nonlinear refractive coefficient (n_2) of **SDNU-2** and **SDNU-3** are 0.13×10^{-16} and 0.12×10^{-16} cmW^{-1}, respectively. Therefore, the calculated TPA cross-sections (δ_2^{max}) of **SDNU-2** and **SDNU-3** are 592 and 702 GM, respectively. **SDNU-3** shows the highest TPA cross-section bahavior among all azaacene derivatives. The TPA cross-section is strongly associated with the charge transfer character of the material. The relative electron-rich thienyl group of **SDNU-3** demonstrated the enhanced intramolecular charge-transfer (ICT) states. So we attribute the outcome to sufficient electronic coupling between the strong charge transfer of quadrupolar substituents and the tetraazachrysene core. The results indicate that the ladder-type azaacene derivatives can enhance the TPA cross-section.

The TPA cross-section value of **SDNU-3** is parallel to those of donor-π-acceptor (D-π-A) type compounds excited with 800 nm light.[40] However, their TPA cross-sections are relatively small compared with those of other organic TPA materials, such as porphyrin derivatives[41], which showed a TPA cross-section of 3500 GM excited with 800 nm light. Thus, reasonable molecular design of both the backbones and branched chains based on azaacenes may be required to obtain the enhanced two-photon absorption cross-sections.

Table 1. Optical properties of three compounds.

Samples	$\lambda_{em\ (nm)}$ [a]	Φ_s (%)[b]	τ (ns)	$k_r(10^7\ s^{-1})$[c]	$k_{nr}(10^7\ s^{-1})$
SDNU-1	456	8.75	0.90	9.72	1.01
SDNU-2	481	75.3	3.00	25.11	0.08
SDNU-3	559	6.09	0.91	6.65	1.03

[a]The solid emission. [b] absolute fluorescence quantum yield [c] Rate constants for radiative (k_r) and nonradiative decay (k_{nr}) were calculated from the Φ_s and τ, $k_r = \Phi_s/\tau$ and $k_{nr} = (1 - \Phi_s)/\tau$.

Table 2. The calculated nonlinear refractive index, nonlinear coefficient and TPA cross-section for **SDNU-2** and **SDNU-3.**

Samples	n_2 (cm^2W^{-1}, 10^{-16})	β (cmW^{-1} 10^{-12})	δ_2^{max} (GM)
SDNU-2	0.13	0.43	592
SDNU-3	0.12	0.51	702

3. Conclusion

In conclusion, we have designed and synthesized three new 3,6,9,12-tetrasubstituted tetraazachrysene derivatives with various alkynyl and aryl groups. The HOMOs and LUMOs of all as-prepared tetraazachrysene derivatives are easily affected by the different substituents because significant orbital coefficients are located on the tetraazachrysenes attached by these substituents. Their photophysical, electrochemistry and fluorescence properties were fully investigated, and these materials exhibited blue to green emission in solution and obviously enhanced emission in the solid state. Interestingly, **SDNU-2** displayed a high fluorescence quantum efficiency of 75.3%, which is the highest value of azaacene derivatives to date. The Z-scan method is employed to characterize the two-photon absorption (TPA) properties of tetraazachrysene derivatives, elucidating a TPA δ maximum of ~700 GM in dichloromethane solution, which is the largest value among all heteroacenes, measured by Z-scan experiment at present. Currently, the devices based on **SDNU-2** and **SDNU-3** are under investigation in our lab.

Conflict of interest

There are no conflicts to declare.

Acknowledgements

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Keywords: Azaacenes •Two Photon Absorption • Fluorescence quantum yields • Synthesis

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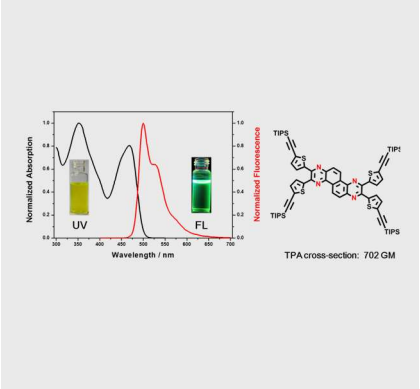
Through the condensation reaction between 1,2,5,6-naphthalenetetraamine and triisopropylsilyl (TIPS) substituted diketones, three novel azaacenes coded as **SDNU-1, SDNU-2 and SDNU-3**, have been designed and synthesized. The as-prepared compounds exhibited distinctive nonlinear optical properties.



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