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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 the 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 the open and close aperture Z-scan tech-

nique. SDNU-3 showed a significant enhancement in the two-photon absorption cross-section with magnitudes as high as about 700 GM (1 GM = 1.0×10^{50} cm⁴ s/photon) when excited with 800 nm light, which is the largest value based on a heteroacene system measured by using a Z-scan experiment so far. We attribute the outcome to sufficient electronic coupling between the strong charge transfer of quadrupolar substituents and the tetraazachrysene 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 band gap, organic p-conjugated compounds have been widely explored as NLO materials to enhance TPA absorption cross-sections.^[14–22] In particular, extended p-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 heteroatoms to replace the CH units in their skeleton, have attracted great attention due to their unique photo-physical and electronic properties as well as their highly-or-

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dered 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, 150 and 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-section 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 800 nm light. To further improve the TPA cross-sections of heteroacenes molecules, structural adjustment of both backbones and branched chains for the realization of more effective intramolecular charge transfer are highly desirable.

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 p-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 tetraazachrysenes 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 p-p 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 ($\phi = 75.3\%$), which is among the highest value reported for azaa-

cene 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

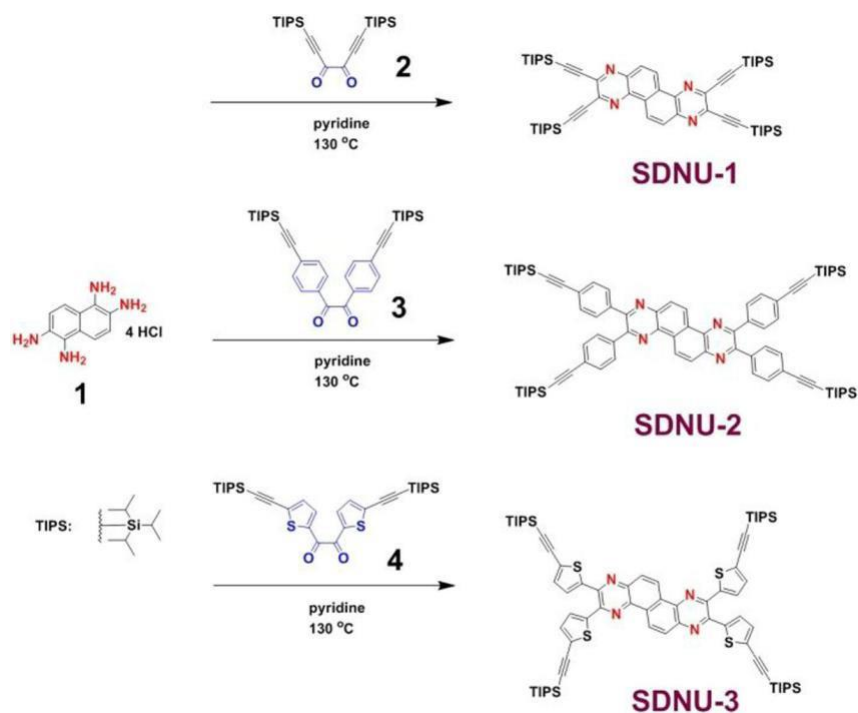
The synthetic procedures of SDNU-1, SDNU-2 and SDNU-3 are shown in Scheme 1. The precursors 1, 2 and 3 were prepared according to the previously-reported procedures with some modification.^[47–49] Compound 4 was prepared in 52 % yield through the palladium-catalyzed Stille-coupling reaction. All three target products were obtained by condensing diketones with diamines in pyridine solutions under reflux condition. The as-synthesized materials were fully characterized by ¹H and ¹³C 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 ¹H NMR spectra.

2.2. 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 ($a = 11.67 \text{ \AA}$, $b = 19.34 \text{ \AA}$, $c = 14.37 \text{ \AA}$, $a = 90.8^\circ$, $b = 107.8^\circ$, $\gamma = 90.8^\circ$) crystallized in the monoclinic space group P21/c with a big unit cell ($V = 3102.56 (3) \text{ \AA}^3$; 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 (Figure 1 a), where the acetylene, the pyrazine ring and the naphthalene group are in the same plane (Figure 1 b,c). 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 \AA) due to the steric hindrance of TIPS substituents (Figure S1).

2.3. Optical properties

The normalized optical absorption spectra of three compounds in dichloromethane (DCM) solutions are shown in Figure 2 and the corresponding data are summarized in Table S3. The UV-vis absorption spectra of SDNU-1 and SDNU-2 exhibit an appar-



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

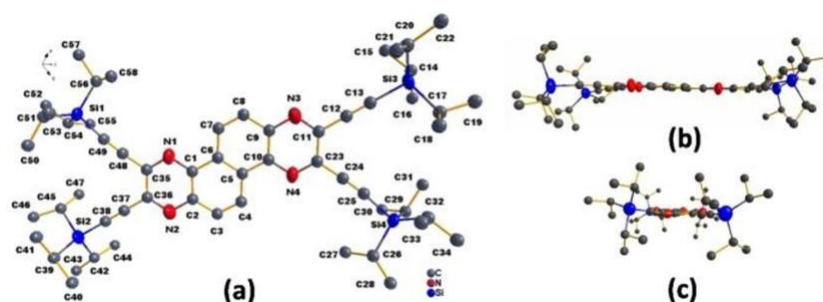


Figure 1. The crystal structure of SDNU-1.

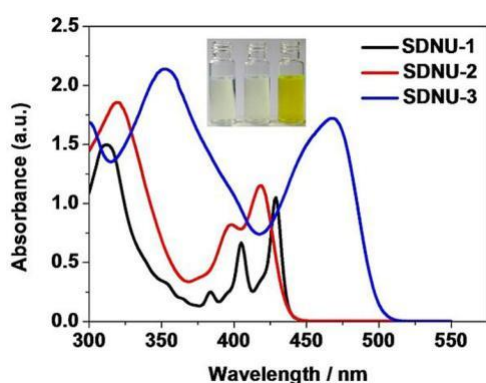


Figure 2. The absorption spectra of SDNU-1, SDNU-2 and SDNU-3 in di-chloromethane solution. Inset were the corresponding photograph of SDNU-1 (left), SDNU-2 (middle) and SDNU-3 (right).

ent 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 ($\epsilon = 1.43 \times 10^5 \text{ cm}^2 \text{ mol}^{-1}$), which is red-shifted by 40 nm and 50 nm relative to that of SDNU-1 (428 nm, $\epsilon = 1.01 \times 10^5 \text{ cm}^2 \text{ mol}^{-1}$) and SDNU-2 (418 nm, $\epsilon = 1.24 \times 10^5 \text{ cm}^2 \text{ mol}^{-1}$). The red shift suggests a considerable intramolecular charge-transfer transition absorption of peripheral thiophene units to the tetraazachry-sene 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 (F_f) of all three compounds in DCM solution were measured with quinine bisulfate ($F_f = 55\%$ 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 (Figure 3). The quantum yields of SDNU-1

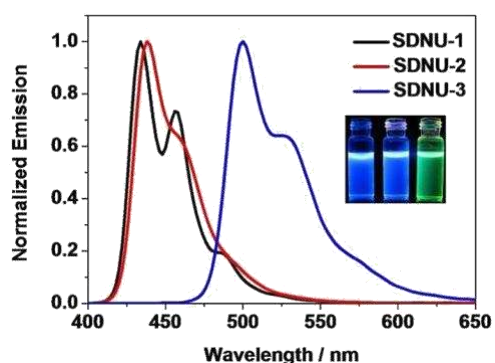


Figure 3. The fluorescence spectra of SDNU-1, SDNU-2 and SDNU-3 in di-chloromethane solution. Inset were the corresponding photograph of SDNU-1 (left), SDNU-2 (middle) and SDNU-3 (right).

(36.3 %) and SDNU-2(22.8 %) were found to be obviously higher than that of SDNU-3 (7.45 %). The introduction of four thieryl 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.

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

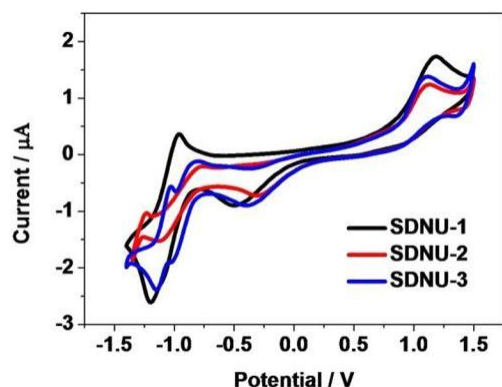


Figure 4. Cyclic voltammograms of three compounds.

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 @6.13 eV, @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 thieryl groups, it exhibited rela-

tively 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 Figure S2 and Table S4. From the optimized ground-state geometries (Figure S2), their HOMO electron densities mainly distribute on the aza-chrysenes cores as well as substituted moieties, while the LUMO ones are mainly located on the tetraazachrysenes 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 band gap results.

2.6. Solid-state fluorescence study

As shown in Figure 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 (F_s) 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–S33) reveal that the fluorescence decay times (t) 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 ($9.72 \times 10^7 \text{ s}^{-1}$), SDNU-1 ($25.11 \times 10^7 \text{ s}^{-1}$), SDNU-3 ($6.65 \times 10^7 \text{ s}^{-1}$); while the nonradiative decay rate increases with the order of SDNU-2 ($1.01 \times 10^7 \text{ s}^{-1}$), SDNU-1 ($0.08 \times 10^7 \text{ s}^{-1}$), SDNU-3 ($1.03 \times 10^7 \text{ s}^{-1}$), which is consistent with their solid-state fluorescence quantum yields.

Samples	λ_{em} [nm] ^[a]	F_s [%] ^[b]	t [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 F_s and t , $k_r = F_s/t$ and $k_{nr} = (1/F_s)/t$.

Molecular simulation was conducted to analyze the dihedral angle between the tetraazachrysene cores and peripheral sub-stituents for SDNU-1, SDNU-2 and SDNU-3. The as-obtained results (Figure S5) indicates that there is a tilt angle of 1.158 for SDNU-1, 40.18 for SDNU-2 and 29.68 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

The third-order nonlinear optical properties of SDNU-1, SDNU-2 and SDNU-3, were studied using opened and closed aperture Z-scan technique excited with 800 nm light and a repetition rate of 1 kHz. The resulting curves are shown in Figure 5 and Figure 6. The experimental data of nonlinear refractive index (n_2), TPA coefficient (b) and TPA cross-section value (d_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. Figure 5 a and 6 a showed the opened Z-scan

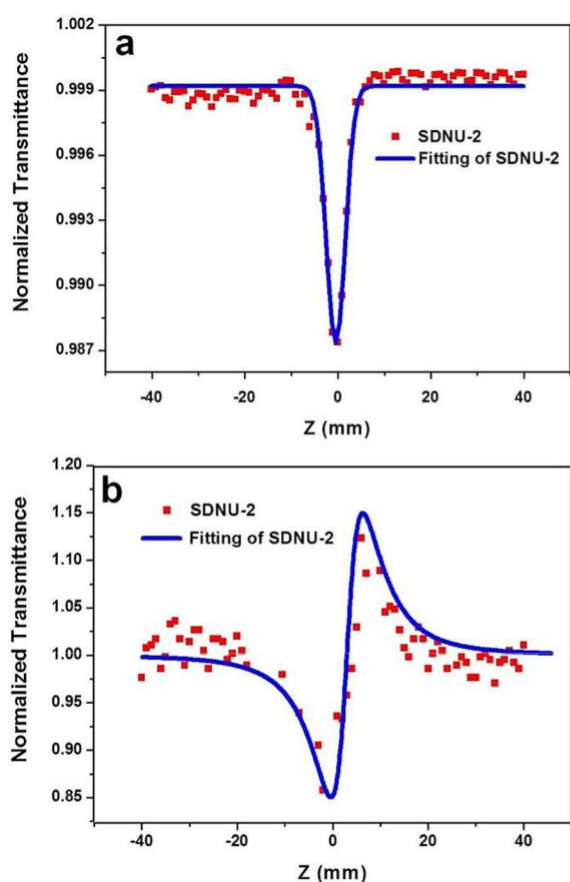


Figure 5. Opened and closed Z-scan curves of SDNU-2.

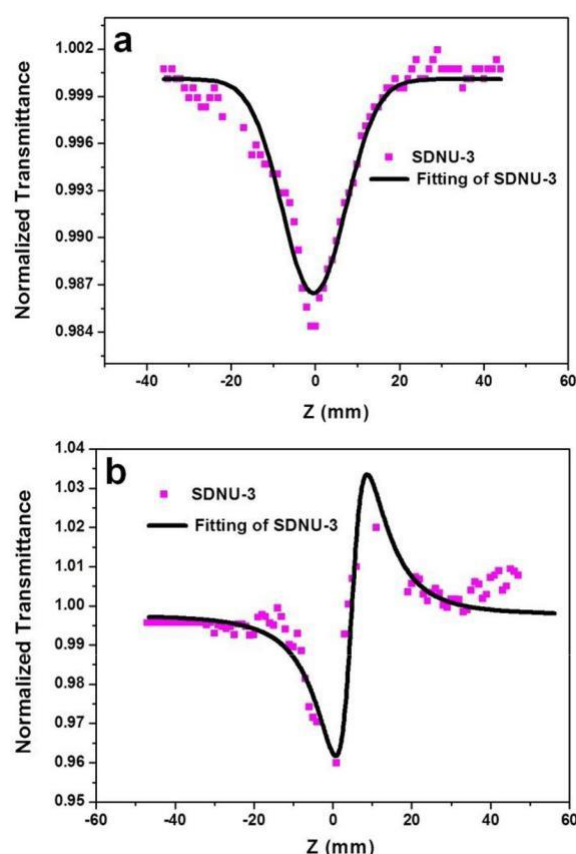


Figure 6. Opened and closed Z-scan curves of SDNU-3.

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

Samples	n_2 [$\text{cm}^2 \text{W}^{-1}, 10^{16}$]	b [$\text{cm W}^{-1}, 10^{12}$]	d_2^{\max} [GM]
SDNU-2	0.13	0.43	592
SDNU-3	0.12	0.51	702

curves of SDNU-2 and SDNU-3, and their nonlinear absorption coefficient (b) are 0.43×10^{12} and $0.51 \times 10^{12} \text{ cm W}^{-1}$, respectively. Figure 5 b and 6 b 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 $0.12 \times 10^{16} \text{ cm W}^{-1}$, respectively. Therefore, the calculated TPA cross-sections (d_2^{\max}) of SDNU-2 and SDNU-3 are 592 and 702 GM, respectively. SDNU-3 shows the highest TPA cross-section behavior 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-p-acceptor (d-p-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.

3. Conclusion

In conclusion, we have designed and synthesized three new 3,6,9,12-tetra-substituted tetraazachrysenes derivatives with various alkynyl and aryl groups. The HOMOs and LUMOs of all as-prepared tetraazachrysenes 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 an 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 was employed to characterize the two-photon absorption (TPA) properties of tetraazachrysenes derivatives, elucidating a TPA maximum of 700 GM in dichloromethane solution, which is the largest value among all heteroacenes measured by performing a Z-scan experiment at present. Currently, devices based on SDNU-2 and SDNU-3 are under investigation in our lab.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

Keywords: azaacenes · fluorescence quantum yields · synthesis · two-photon absorption

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