



# Self-assembled triphenylamine-hexaazatriphenylene two-photon absorption dyes

Tsutomu Ishi-i<sup>a,\*</sup>, Shogo Amemori<sup>a</sup>, Chie Okamura<sup>a</sup>, Kaori Yanaga<sup>a</sup>, Rempei Kuwahara<sup>b</sup>, Shuntaro Mataka<sup>c</sup>, Kenji Kamada<sup>d,\*</sup>

<sup>a</sup> Department of Biochemistry and Applied Chemistry, Kurume National College of Technology, 1-1-1 Komorino, Kurume 830-8555, Japan

<sup>b</sup> Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasuga-koh-en, Kasuga 816-8580, Japan

<sup>c</sup> Institute for Materials Chemistry and Engineering, Kyushu University, 6-1 Kasuga-koh-en, Kasuga 816-8580, Japan

<sup>d</sup> Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

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## ABSTRACT

This paper reports the self-assembling and two-photon absorption natures of donor–acceptor molecules, tri(phenanthro)hexaazatriphenylene (TPHAT-C) and tri(phenanthrolino)hexaazatriphenylene (TPHAT-N), bearing six electron-donating moieties. In the <sup>1</sup>H NMR spectra, a line-broadening effect, arising from self-assembled aggregation was observed. Several hundred nanometer scale aggregates were detected in dynamic light scattering. The one-dimensional aggregation of the TPHAT molecules was indicated by the concentration dependence in UV/vis one-photon absorption and one-photon excited fluorescence spectroscopies. An enhancement of the two-photon absorption cross-section was observed in the self-assembled TPHAT system. The order of the two-photon absorption nature is in agreement with the order of the aggregative nature.

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## 1. Introduction

Supramolecular self-assembly of organic  $\pi$ -conjugated molecules, has been of much interest in view of the potential applications to electronics, optoelectronics, and photonics.<sup>1</sup> For example, in organic light-emitting diodes, field-effect transistors, and photovoltaics, self-assembled  $\pi$ -conjugated molecules have been widely used as donor and acceptor functional materials.<sup>2–4</sup> Furthermore, interest in self-assembling donor–acceptor conjugated molecules as attractive new targets for ambipolar functional materials has grown.<sup>5</sup>

Donor–acceptor substituted  $\pi$ -conjugated structures have also been developed in the field of two-photon absorption materials,<sup>6–12</sup> which have a wide range of potential applications, including optical power limitation,<sup>13</sup> microfabrication,<sup>14</sup> three-dimensional optical data storage,<sup>15</sup> two-photon laser scanning fluorescence imaging,<sup>16</sup> and photodynamic therapy.<sup>17</sup> Donor–acceptor substitution can enhance the two-photon absorption activity of molecules<sup>6,9,11,18</sup> through an increase in the transition dipole moment<sup>11,19</sup> or the dipole moment difference between the ground and excited states. Various types of conjugated systems incorporating donor and acceptor moieties have been studied to enhance the two-photon absorption cross-section, and the resultant structure–property

relationships have been discussed.<sup>6–9</sup> Two-photon absorption cross-sections can also be enhanced by intermolecular interactions, such as intercalation<sup>20</sup> and self-assembling to form dimers and aggregates.<sup>21–30</sup> For self-assembled systems, the two-photon absorption properties of porphyrins,<sup>21,27</sup> pseudoisocyanines,<sup>22</sup> squaryliums,<sup>23</sup> [(aminostyryl)styryl]anthracenes,<sup>24</sup> and tetraphenylethylenes<sup>29</sup> have been reported; however, the variety of systems is still limited. In this paper, we report new self-assembled systems with donor–acceptor moieties within the molecular structures and the corresponding two-photon absorption properties. The new systems have structural cores of tri(phenanthro)hexaazatriphenylene (TPHAT-C) or tri(phenanthrolino)hexaazatriphenylene (TPHAT-N), and each core demonstrates both electron-accepting and self-assembling characters.<sup>31</sup> Six triphenylamine (TPA)-based, electron-donating groups were introduced at the periphery of the TPHAT-C and TPHAT-N cores to form donor–acceptor conjugated molecules with self-assembling abilities (Chart 1). Combinations of the TPA groups with the TPHAT-C and TPHAT-N cores resulted in TPHAT-C-TPA and TPHAT-N-TPA molecules, respectively. The  $\pi$ -electron expanded TPHAT-C-ETPA, bearing an ethylene spacer, was also designed as a superior self-assembling molecule. The TPHAT-C-TPA-<sup>t</sup>Bu molecule, containing bulky *tert*-butyl groups, was prepared as non-aggregative reference. The aggregative nature of the TPHAT-C and TPHAT-N derivatives were studied by MALDI-TOF mass spectrometry, and <sup>1</sup>H NMR, dynamic light scattering, one-photon absorption, and one-photon excited fluorescence spectroscopies, and

\* Corresponding authors. Tel.: +81 942 35 9404; fax: +81 942 35 9400; e-mail addresses: [ishi-i@kurume-nct.ac.jp](mailto:ishi-i@kurume-nct.ac.jp) (T. Ishi-i), [k.kamada@aist.go.jp](mailto:k.kamada@aist.go.jp) (K. Kamada).

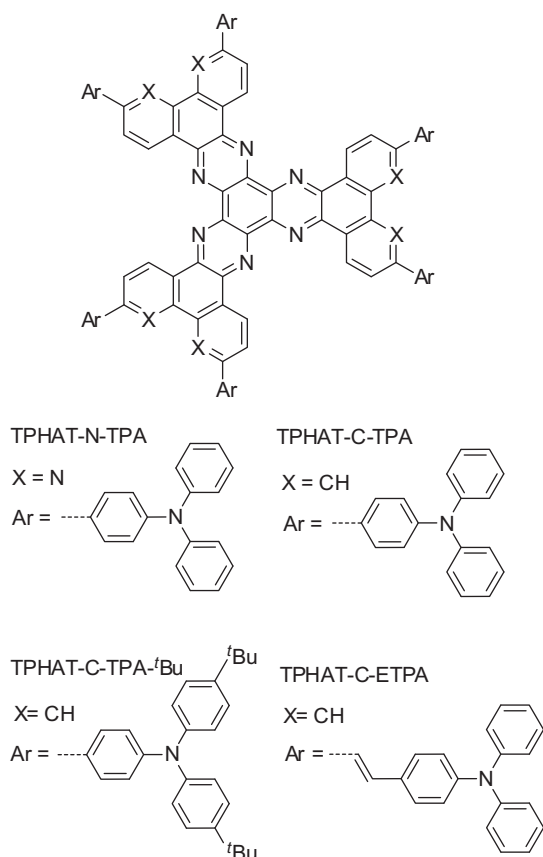


Chart 1. Hexaazatriphenylenes TPHAT-N and TPHAT-Cs.

the two-photon absorption cross-sections were measured by the femtosecond Z-scan method.

## 2. Results and discussion

### 2.1. Preparation

Key synthetic intermediates, 2,9-bis(diphenylaminophenyl)-1,10-phenanthroline-5,6-dione (**3**) and 3,4-disubstituted 9,10-phenanthrenequinone **5a–c** were obtained from cross-coupling reactions of the corresponding dibromide **1**<sup>31b</sup> and **4**,<sup>32</sup> respectively, mediated by a palladium(0) catalyst (Scheme 1). The obtained **3** and **5a–c** were condensed with hexaaminobenzene **9**<sup>33</sup> to produce the desired TPHATs (Scheme 1). The obtained TPHAT-N-TPA, TPHAT-C-TPA, TPHAT-C-TPA-*t*Bu, and TPHAT-C-ETPA were identified using spectroscopic methods and elemental analysis.

In the <sup>1</sup>H NMR spectra at room temperature, a line-broadening effect arising from aggregation was observed in halogenated solvents, such as chloroform-*d*<sub>1</sub> and 1,1,2,2-tetrachloroethane-*d*<sub>2</sub>. At higher temperatures (120 °C) in 1,1,2,2-tetrachloroethane-*d*<sub>2</sub>, the broad peaks of the phenanthrene-fused system TPHAT-C-TPA became sharp due to aggregate dissociation (Fig. S2, Supplementary data). The resulting spectra provided eight aromatic proton signals from the phenanthrene rings and TPA moieties; from this, the structure of TPHAT-C-TPA could be assigned. In contrast, the broad peaks from the phenanthroline-fused systems TPHAT-N-TPA and the  $\pi$ -electron expanded system TPHAT-C-ETPA still appeared even at the higher temperature, indicating the highly aggregative nature of these compounds (Figs. S1, S4, Supplementary data). In TPHAT-C-TPA-*t*Bu, the proton signals are sharp even at room temperature, because the steric hindrance of the *tert*-butyl groups disturbs aggregation (Fig. S3, Supplementary data).

### 2.2. Spectral properties and aggregative nature

Direct evidence for the aggregation of TPHAT-N-TPA, TPHAT-C-TPA, and TPHAT-C-ETPA was obtained from MALDI-TOF mass spectrometry, in which aggregate species can be detected up to the tetramer (Figs. S6–S8, Supplementary data). For example, in addition to the parent ion of TPHAT-N-TPA (*m/z* 2149), significant peaks are seen at several multiples of the parent ion, up to *m/z* 8596, and these indicate assembly of four molecules.

In dynamic light scattering, several hundred nanometer scale aggregates were detected in TPHAT-N-TPA (90 nm), TPHAT-C-TPA (530 nm), and TPHAT-C-ETPA (300 nm) in toluene solution (0.2 mM). In TPHAT-C-TPA-*t*Bu, such aggregate species could not be detected under the same conditions (Fig. S9, Supplementary data).

The one-dimensional aggregation of the TPHAT-N and TPHAT-C molecules is indicated by concentration dependence in UV/vis one-photon absorption spectroscopy (Fig. 1). The UV/vis spectra of TPHAT-C-TPA in toluene show the longest absorption band at around 470 nm, which can be assigned to the charge-transfer transition from the TPA chromophore to the TPHAT-C chromophore (Fig. 1(b)). The intensity of the absorption band increased with decreasing concentration, indicating a dynamic exchange from the aggregate species with a weak absorption band to the monomer species with a strong absorption band. This trend is similar to that for the previously reported one-dimensional  $\pi$ -stacked TPHAT-N/TPHAT-C molecules with an *H*-type parallel stacking mode.<sup>31</sup> The concentration dependence for the TPHAT-N-TPA was less than for the TPHAT-C-TPA (Fig. 1(a,b)), indicating the superior aggregative nature of the phenanthroline-fused TPHAT-N system.<sup>31b</sup> For TPHAT-C-ETPA, the spectra were almost unchanged, irrespective of the concentration, and the weak absorption band that appeared as a shoulder at around 500 nm was observed even at the more dilute concentration of 0.001 mM (Fig. 1(c)). The enhanced aggregation could be attributed to the expansion of the  $\pi$ -electron system by introduction of the additional ethylene  $\pi$ -spacer between the TPHAT-C core and the TPA moieties. In contrast, in TPHAT-C-TPA-*t*Bu a strong absorption band was observed at around 485 nm even at higher concentrations (1.0 mM), indicating a non-aggregative nature (Fig. 1(d)). As a summary of the foregoing results, one can conclude that the order of the aggregative nature increased in the order TPHAT-C-TPA-*t*Bu < TPHAT-C-TPA < TPHAT-N-TPA < TPHAT-C-ETPA.

The aggregation of the TPHAT molecules is reflected in the one-photon excited fluorescence spectra. As a result of the aggregation, a bathochromic shift of the emission band was observed along with a reduction in the emission intensity (Fig. 2). A moderate 18 nm bathochromic shift and a moderate 0.50 fluorescence quantum yield ( $\Phi_{\text{FL}}$ ) are produced in the TPHAT-C-TPA system (Fig. 2(b)). In the enhanced aggregation system, the bathochromic shift increases to 43 nm in TPHAT-N-TPA and 76 nm in TPHAT-C-ETPA, and the  $\Phi_{\text{FL}}$  values are reduced to 0.02 in TPHAT-N-TPA and 0.03 in TPHAT-C-ETPA (Fig. 2(a,c)). In contrast, a small bathochromic shift of 5 nm and a large fluorescence quantum yield ( $\Phi_{\text{FL}}$ ) of 0.91 are produced in the non-aggregative TPHAT-C-TPA-*t*Bu system (Fig. 2(d)).

The aggregate structure can be visualized by atomic force microscopy (AFM, Fig. 3). The aggregated toluene solution (0.01 mM) of TPHAT-C-TPA was casted on freshly cleaved mica. The AFM image indicates a nanoscale fibrous structure with a height of ca. 3.4 nm, which is comparable to the molecular size of TPHAT-C-TPA.

### 2.3. Two-photon absorption nature

The two-photon absorption cross-sections ( $\delta$ ) were determined by the open-aperture Z-scan method with a femtosecond Ti:sapphire laser as a light source (Figs. S10–S15, Supplementary data). The shorter wavelength region of the two-photon absorption spectra

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