Tetrahedron 69 (2013) 29–37

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Self-assembled triphenylamine-hexaazatriphenylene two-photon absorption dyes

Tsutomu Ishi-i [a,*], Shogo Amemori [a], Chie Okamura [a], Kaori Yanaga [a], Rempei Kuwahara [b], Shuntaro Mataka [c], Kenji Kamada [d,*]

[a] Department of Biochemistry and Applied Chemistry, Kurume National College of Technology, 1-1-1 Komorino, Kurume 830-8555, Japan
[b] Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasuga-koh-en, Kasuga 816-8580, Japan
[c] Institute for Materials Chemistry and Engineering, Kyushu University, 6-1 Kasuga-koh-en, Kasuga 816-8580, Japan
[d] Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

ARTICLE INFO

Article history:
Received 10 August 2012
Received in revised form 22 October 2012
Accepted 25 October 2012
Available online 2 November 2012

Keywords:
Two-photon absorption
Self-assembly
Supramolecules
Donor–acceptor
Hexaazatriphenylenes

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 ^{1}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.

1. Introduction

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

Donor–acceptor substituted π-conjugated structures have also been developed in the field of two-photon absorption materials,[6–12] which have a wide range of potential applications, including optical power limitation,[13] microfabrication,[14] three-dimensional optical data storage,[15] two-photon laser scanning fluorescence imaging,[16] and photodynamic therapy.[17] Donor–acceptor substitution can enhance the two-photon absorption activity of molecules[6,9,11,18] through an increase in the transition dipole moment[11,19] 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.[6–9] Two-photon absorption cross-sections can also be enhanced by intermolecular interactions, such as intercalation[20] and self-assembling to form dimers and aggregates.[21–30] For self-assembled systems, the two-photon absorption properties of porphyrins,[21,27] pseudoisocyanines,[22] squaryliums,[23] [(aminostyryl)styryl]anthracenes,[24] and tetraphenylethylenes[29] have been reported; however, the variety of systems is still limited. In this paper, we report new self-assembled systems with donor–accepter 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.[31] 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 π-electron expanded TPHAT-C-ETPA, bearing an ethylene spacer, was also designed as a superior self-assembling molecule. The TPHAT-C-TPA-^{t}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 ^{1}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 (T. Ishi-i), k.kamada@aist.go.jp (K. Kamada).

0040-4020/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2012.10.070

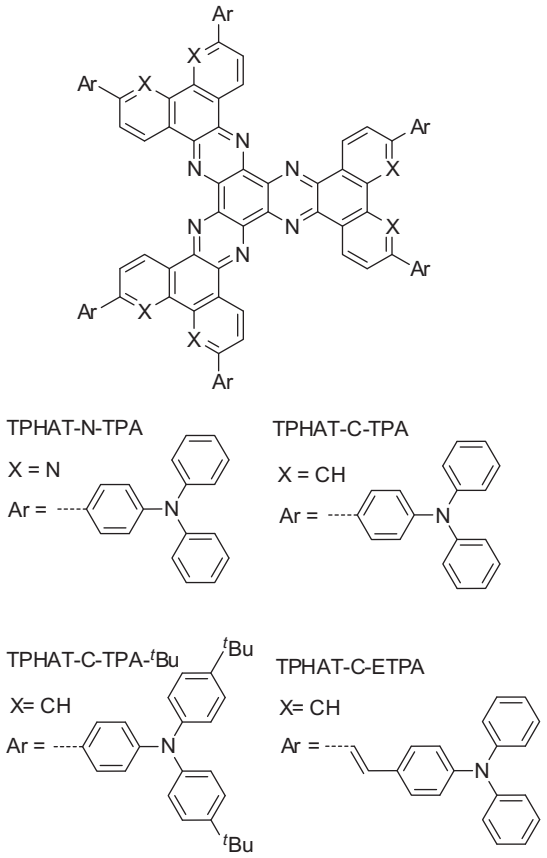


Chart 1. Hexaazatriphenylenes TPHAT-N and TPHAT-Cs.

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**[31b] and **4**,[32] respectively, mediated by a palladium(0) catalyst (Scheme 1). The obtained **3** and **5a**–**c** were condensed with hexaaminobenzene **9**[33] 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 ^{1}H NMR spectra at room temperature, a line-broadening effect arising from aggregation was observed in halogenated solvents, such as chloroform-d_1 and 1,1,2,2-tetrachloroethane-d_2. At higher temperatures (120 °C) in 1,1,2,2-tetrachloroethane-d_2, 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 π-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).

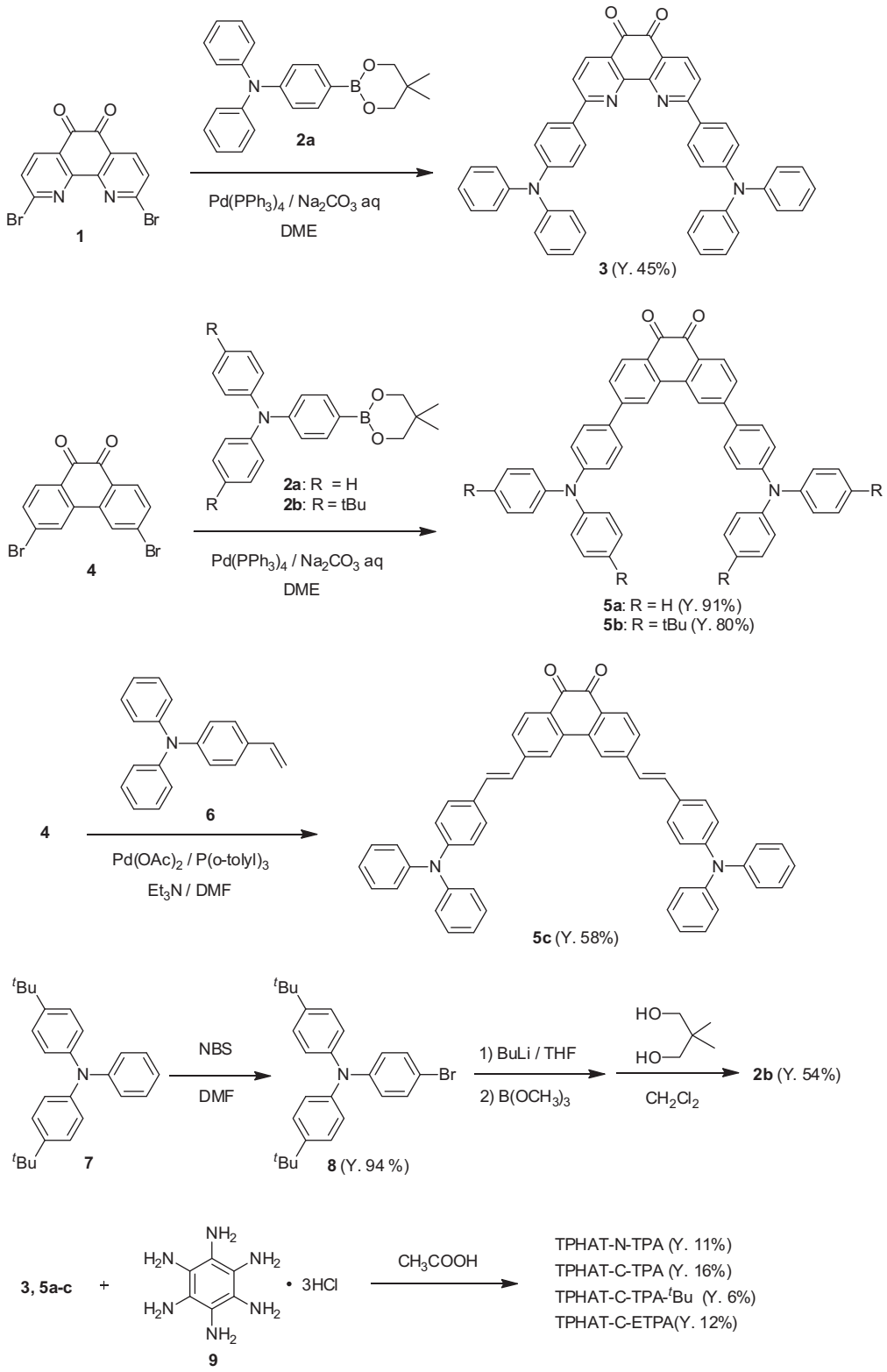
The one-dimensional aggregation of the TPHAT-N and TPHAT-C molecules is indicated by concentration dependence in UV/vis one-photon absorption spectroscopy (Fig. 1). The UV/vis spectra of TPHAT-C-TPA in toluene show the longest absorption band at around 470 nm, which can be assigned to the charge-transfer 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 π-stacked TPHAT-N/TPHAT-C molecules with an *H*-type parallel stacking mode.[31] 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.[31b] 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 π-electron system by introduction of the additional ethylene π-spacer between the TPHAT-C core and the TPA moieties. In contrast, in THPAT-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 (Φ_{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 Φ_{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 (Φ_{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 (δ) 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



Scheme 1. Preparation of hexaazatriphenylenes TPHAT-N and TPHAT-Cs.

overlaps with the tails of the one-photon absorption spectra, resulting in a saturable absorption phenomenon. The saturable absorption was corrected to precisely examine the two-photon absorption cross-sections.[34] The corrected two-photon absorption spectra indicated an absorption band from 850 to 870 nm, which is located at nearly double of the charge-transfer transition from the one-photon spectra (Fig. 4(a)). However, the two-photon absorption maxima were observed at higher transition energies than the one-photon absorption maxima (Fig. 1). This blue shift is due probably to intensity borrowing of the one-photon excited state from a strongly allowed two-photon excited state close to it through the vibronic coupling[12q,35] or direct transition to the low-laying two-photon allowed excited state just

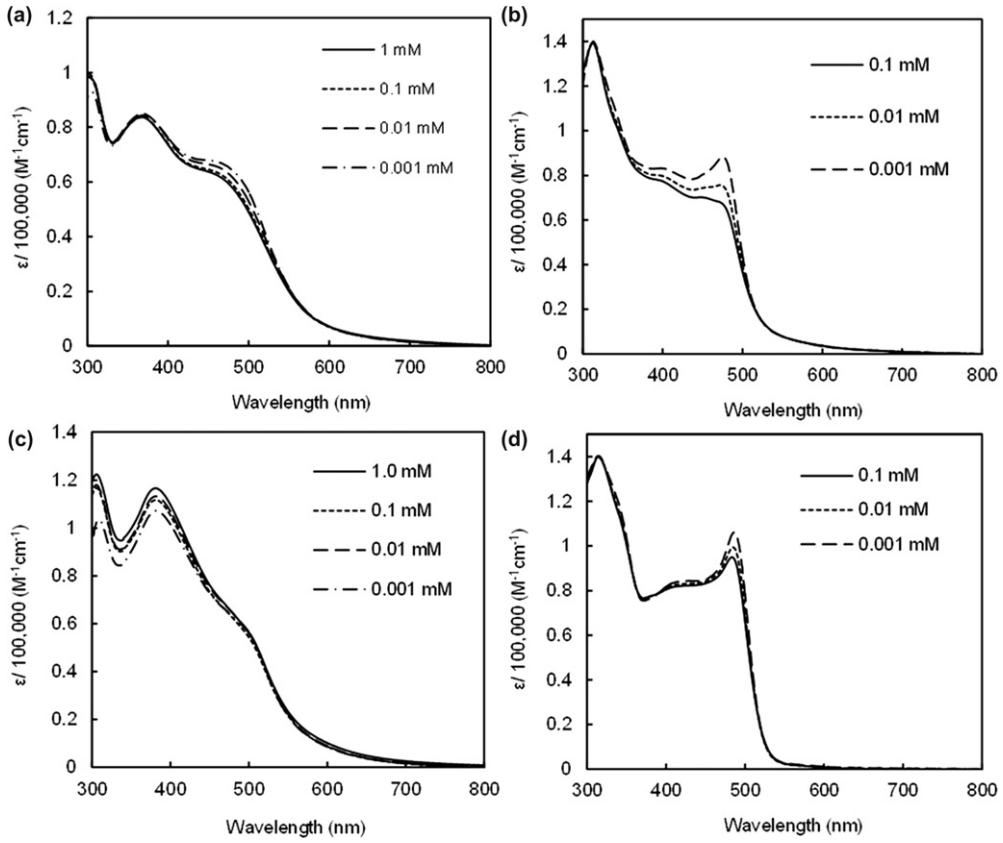


Fig. 1. UV/vis one-photon absorption spectra of (a) TPHAT-N-TPA, (b) TPHAT-C-TPA, (c) TPHAT-C-ETPA, and (d) TPHAT-C-TPA-^{t}Bu in toluene at room temperature.

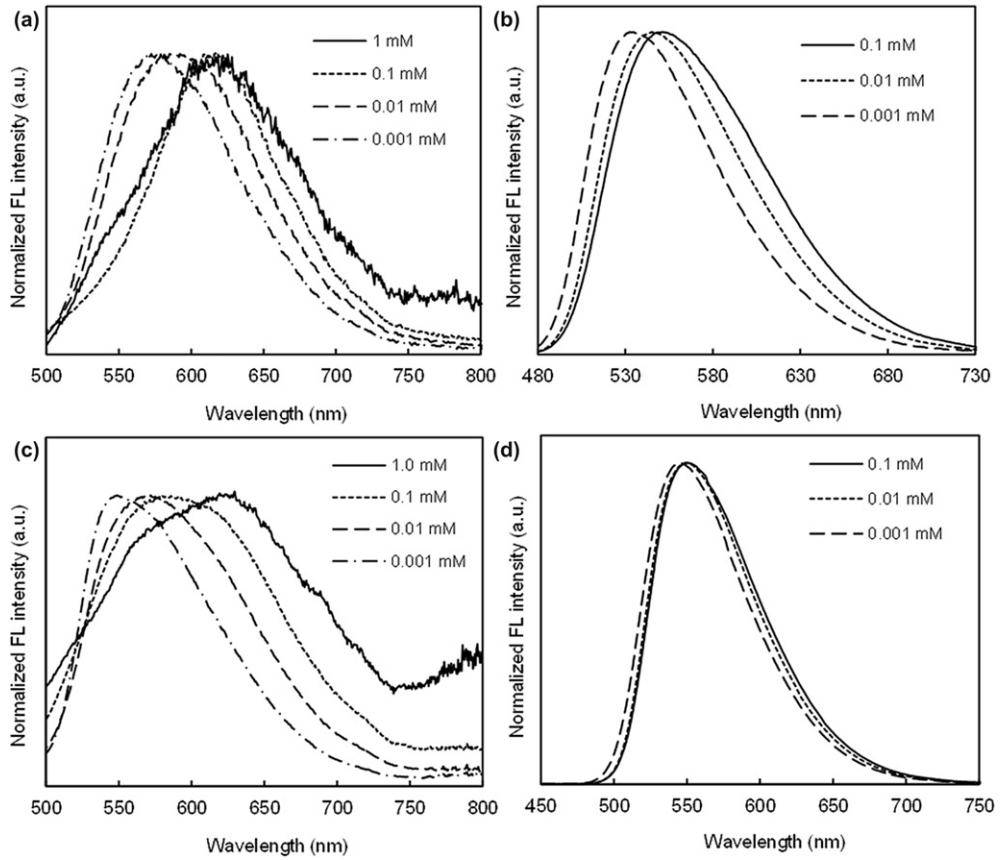


Fig. 2. One-photon excited fluorescence spectra of (a) TPHAT-N-TPA (ex. 450 nm), (b) TPHAT-C-TPA (ex. 450 nm), (c) TPHAT-C-ETPA (ex. 460 nm), and (d) TPHAT-C-^{t}Bu (ex. 400 nm) in toluene at room temperature.

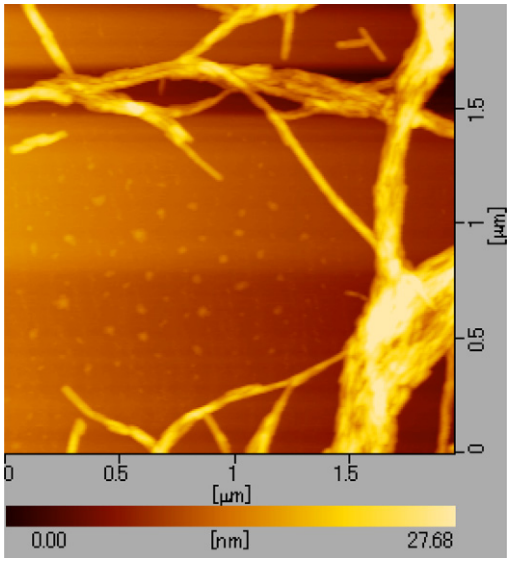


Fig. 3. Atomic force microscopy image of TPHAT-C-TPA. The sample was prepared by drop-casting on mica from a 0.01 mM toluene solution.

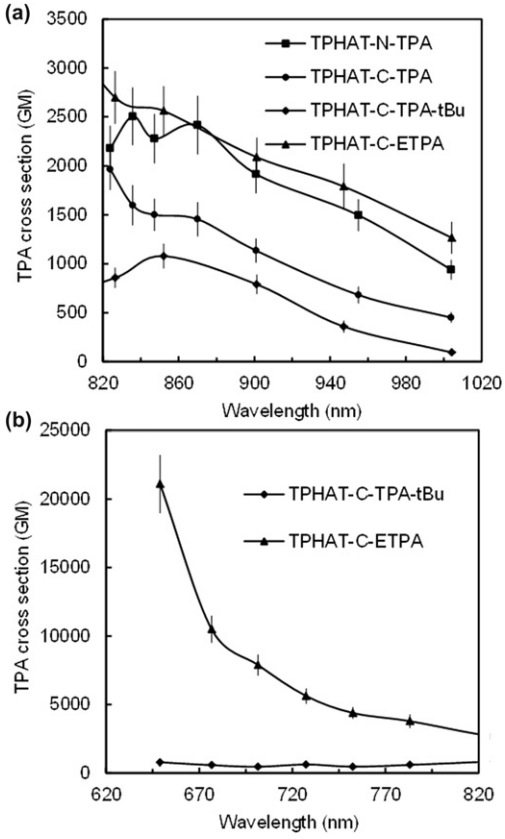


Fig. 4. Two-photon absorption spectra of TPHAT-N-TPA (0.6 mM), TPHAT-C-TPA (0.6 mM), TPHAT-C-ETPA (0.45 mM), and TPHAT-C-TPA-^{t}Bu (0.19 mM) in toluene in the range (a) 820–1020 nm and (b) 620–820 nm.

above the one-photon allowed state.[12g] Further studies are needed to distinguish the mechanisms.

An enhancement of the two-photon absorption cross-section was observed for the self-assembled TPHAT-C-TPA system to give a δ value of 1460 GM (at 870 nm), which is 1.4 times larger than the value for the non-aggregative TPHAT-C-TPA-^{t}Bu (1080 GM at 850 nm) system. The δ value increased with expansion of the π-electron system from TPHAT-C-TPA to TPHAT-C-ETPA (2560 GM at 850 nm). Compared to the phenanthrene-fused TPHAT-C-TPA system, the phenanthroline-fused TPHAT-N-TPA demonstrated a larger δ value (2420 GM at 870 nm). Thus, the order of the two-photon absorption nature was determined to be TPHAT-C-TPA-^{t}Bu<TPHAT-C-TPA<TPHAT-N-TPA<TPHAT-C-ETPA, which is in agreement with the aggregative nature. The enhancement of the two-photon absorption cross-section could be ascribed to the expansion of the π-electron system and/or the self-assembled aggregation of the TPHAT molecules. In previous studies, enhancement of the δ values was reported in some self-assembled *J*-type aggregate systems.[21–23] This enhancement can be explained by the strong increase in the transition dipole moment arising from the dipole coupling interactions of the *J*-type aggregates. A transition dipole coupling effect can also be expected in our TPHAT-based *H*-type aggregate system.

Two of the four compounds were examined at wavelengths shorter than 820 nm. In the spectral region, TPHAT-C-ETPA showed a significant increase in δ with decreasing wavelength, but TPHAT-C-TPA-^{t}Bu did not (Fig. 4(b)). The maximum δ value at 649 nm was almost nine times larger than that at 850 nm (Fig. S15, Supplementary data). This significant increase can be interpreted as resonance enhancement of the two-photon transition near the one-photon resonance,[18] because TPHAT-C-ETPA has a considerable one-photon absorption tail at these wavelengths (Fig. 1(c)), whereas there is no overlap with the one-photon absorption tail for TPHAT-C-TPA-^{t}Bu (Fig. 1(d)).

3. Conclusions

In conclusion, we created self-assembled two-photon absorption dyes based on a combination of an electron-accepting hexaazatriphenylene core and an electron-donating TPA moiety. The donor–acceptor molecules are self-assembled one-dimensionally to form *H*-type aggregates. The aggregative nature is enhanced significantly in a π-electron expanded system. The present self-assembled system provides moderate two-photon absorption cross-sections up to 2560 GM (for TPHAT-C-ETPA) in the 820–870 nm wavelength region, as well as a significant increase in the shorter wavelength region. Aggregation dependence on the two-photon absorption properties was observed in this *H*-type aggregate system, similar to the *J*-type aggregate systems previously reported. We believe that the present study provides useful information for the development of self-assembled two-photon absorption systems.

4. Experimental

4.1. General

All melting points are uncorrected. IR spectra were recorded on a JASCO FT/IR-470 plus Fourier transform infrared spectrometer, and measured as KBr pellets. ^{1}H and ^{13}C NMR spectra were determined in $CDCl_3$ and $CDCl_2CDCl_2$ with a JEOL JNM-AL 400 spectrometer. Residual solvent protons were used as internal standard and chemical shifts (δ) are given relative to tetramethylsilane (TMS). The coupling constants (*J*) are reported in hertz (Hz). Elemental analysis was performed at the Elemental Analytical Center, Kyushu University. Fast atom bombardment mass spectrometry (FAB-MS) spectra were recorded with a JEOL JMS-70 mass spectrometer with *m*-nitrobenzyl alcohol (NBA) as a matrix. Matrix assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed on a BRUKER AutoFLEX spectrometer using delayed extraction mode and with an

acceleration voltage of 20 keV. Samples were prepared from a solution of dichloromethane using dithranol as the matrix.

Gel permeation chromatography (GPC) was performed with a Japan Analytical Industry LC-908 using JAIGEL-1H column (20×600 mm) and JAIGEL-2H column (20×600 mm) eluting with chloroform (3.0 mL/min). Analytical TLC was carried out on silica gel coated on aluminum foil (Merck 60 F_{254}). Column chromatography was carried out on silica gel (KANTO 60N). THF was distilled from sodium and benzophenone under an argon atmosphere just before use. DMF was distilled from calcium hydride under reduced pressure just before use. 2,9-Dibromo-1,10-phenanthroline (**1**),[31b] 2,2-dimethyl-1,3-propanediol 4-(diphenylamino)phenylboronate (**2a**),[36] 3,6-dibromo-9,10-phenanthrenequinone (**4**),[32] 4-(diphenylamino)styrene (**6**),[12h] *N*,*N*-bis(4-*tert*-butylphenyl)aniline (**7**),[37] and hexaaminobenzene trihydrochloride (**9**)[33] were prepared according to methods reported previously.

4.2. 2,9-Bis[4-(diphenylamino)phenyl]-1,10-phenanthroline-5,6-dione (3)

To a mixture of **1** (552 mg, 1.5 mmol) and tetrakis(triphenylphosphine)palladium (0) (347 mg, 0.3 mmol) in deaerated DME (30 mL) were added **2a** (954 mg, 3.3 mmol) and deaerated aqueous 2 M sodium carbonate solution (15 mL) at 60 °C under an argon atmosphere and the resulting mixture was heated at 85 °C for 16 h. The reaction mixture was poured into water (150 mL) and extracted with dichloromethane (150 mL×2). The organic layer was washed with brine (400 mL) and water (400 mL×4), dried over anhydrous magnesium sulfate, and evaporated in vacuo to dryness. The residue was purified by silica gel column chromatography (KANTO 60N) eluting with dichloromethane to give **3** in 45% yield (471 mg, 0.68 mmol) as a violet solid. An analytical sample obtained by recrystallization from dichloromethane/hexane. Mp 137–138 °C; IR (KBr, cm^{-1}) 1667 ($\nu_{C=O}$), 1568, 1549, 1489, 1326, 1283, 1177, 827, 753, 696; ^1H NMR ($CDCl_3$) δ 7.11 (t, J=7.4 Hz, 4H, ArH), 7.14–7.23 (m, 12H, ArH), 7.31 (t, J=7.4 Hz, 8H, ArH), 7.90 (d, J=8.4 Hz, 2H, ArH), 8.20 (d, J=8.6 Hz, 4H, ArH), 8.47 (d, J=8.4 Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 120.3, 122.0, 124.1, 125.4, 125.9, 129.0, 129.5, 130.6, 137.6, 146.9, 150.7, 153.1, 162.2, 178.8; MALDI-TOF-MS m/z (positive, dithranol) 696.26 (M^+, calcd for $C_{48}H_{32}N_4O_2$ 696.25). Anal. Calcd for $C_{48}H_{32}N_4O_2 \cdot 0.3CH_2Cl_2$ (696.79): C, 80.32; H, 4.55; N, 7.76. Found: C, 80.05; H, 4.24; N, 7.69.

4.3. 3,6-Bis[4-(diphenylamino)phenyl]-9,10-phenanthrenequinone (5a)

According to a method similar to the preparation of **3**, **5a** was obtained in 91% yield (630 mg, 0.907 mmol) from **4** (366 mg, 1.0 mol), **2a** (636 mg, 2.2 mol), tetrakis(triphenylphosphine)palladium (0) (231 mg, 0.2 mmol), deaerated DME(20 mL), and deaerated aqueous 2 M sodium carbonate solution (10 mL). The crude product was purified by silica gel column chromatography (KANTO 60N) eluting with dichloromethane. An analytical sample was obtained by recrystallization from dichloromethane/hexane. Brown solid; mp 284–285 °C; IR (KBr, cm^{-1}) 3060, 3034, 1662 ($\nu_{C=O}$), 1588, 1512, 1489, 1323, 1294, 1268, 1193, 1180, 925, 825, 753, 696; ^1H NMR ($CDCl_3$) δ 7.10 (t, J=7.2 Hz, 4H, ArH), 7.16–7.20 (m, 12H, ArH), 7.31 (t, J=7.2 Hz, 8H, ArH), 7.59 (d, J=8.8 Hz, 4H, ArH), 7.66 (dd, J=1.6, 8.4 Hz, 2H, ArH), 8.24 (d, J=1.6 Hz, 2H, ArH), 8.26 (d, J=8.4 Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 121.7, 122.8, 123.8, 125.1, 127.4, 128.1, 129.4, 129.5, 131.2, 132.3, 136.2, 147.2, 148.1, 149.0, 180.0; FAB-MS (positive, NBA) m/z 695 [$(M+1)^+$]. Anal. Calcd for $C_{50}H_{34}N_2O_2 \cdot 0.1CH_2Cl_2$ (694.82): C, 85.56; H, 4.90; N, 3.98. Found: C, 85.32; H, 4.86; N, 3.99.

4.4. 3,6-Bis[4-bis(4-*tert*-butylphenyl)aminophenyl]-9,10-phenanthrenequinone (5b)

According to a method similar to the preparation of **3**, **5b** was obtained in 80% yield (516 mg, 0.56 mmol) from **4** (256 mg, 0.7 mmol), **2b** (723 mg, 1.54 mol), tetrakis(triphenylphosphine) palladium (0) (162 mg, 0.14 mmol), deaerated DME (14 mL), and deaerated aqueous 2 M sodium carbonate solution (7 mL). The crude product was purified by silica gel column chromatography (KANTO 60N) eluting with dichloromethane. An analytical sample was obtained by recrystallization from dichloromethane/hexane. Violet solid; mp 368–369 °C; IR (KBr, cm^{-1}) 3035, 2962, 2903, 2867, 1671 ($\nu_{C=O}$), 1589, 1509, 1323, 1298, 1281, 1267, 1188, 825; ^1H NMR ($CDCl_3$) δ 1.33 (s, 36H, CH_3), 7.10 (d, J=8.8 Hz, 8H, ArH), 7.15 (d, J=8.8 Hz, 4H, ArH), 7.32 (d, J=8.8 Hz, 8H, ArH), 7.57 (d, J=8.8 Hz, 4H, ArH), 7.65 (dd, J=1.2, 7.8 Hz, 2H, ArH), 8.23 (d, J=1.2 Hz, 2H, ArH), 8.25 (d, J=7.8 Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 31.4, 34.4, 121.5, 121.8, 124.8, 126.3, 127.3, 127.9, 129.3, 131.2, 131.3, 136.3, 144.4, 146.8, 148.2, 149.4, 180.1; FAB-MS (positive, NBA) m/z 920 [$(M+1)^+$]. Anal. Calcd for $C_{66}H_{66}N_2O_2 \cdot 0.7CH_2Cl_2$ (919.24): C, 81.86; H, 6.94; N, 2.86. Found: C, 81.77; H, 6.87; N, 2.91.

4.5. 3,6-Bis{2-[4-(diphenylamino)phenyl]ethenyl}-9,10-phenanthrenequinone (5c)

To a suspension of **4** (915 mg, 2.5 mmol), **6** (1.60 g, 5.9 mmol), and triethylamine (2.8 mL, 20 mmol) in dry DMF (20 mL) was added a solution of palladium acetate (45 mg, 0.20 mmol) and tri(*o*-tolyl) phosphine (122 mg, 0.40 mmol) in dry DMF (5 mL) at 100 °C under an argon atmosphere, and the mixture was allowed to stand at 100 °C for 4.5 h. After the reaction mixture was cooled to 0 °C, it was quenched with aqueous 1 N hydrochloric acid solution and extracted with dichloromethane (250 mL×2). The organic layer was washed with brine (400 mL×8), dried over anhydrous magnesium sulfate, and evaporated in vacuo to dryness. The residue was purified by silica gel column chromatography (KANTO 60N) eluting with dichloromethane/methanol (299:1, v/v) to give **5c** in 58% yield (1.68 g, 1.44 mmol): violet solid; mp 165–167 °C; IR (KBr, cm^{-1}) 3058, 3027, 1666 ($\nu_{C=O}$), 1580, 1507, 1486, 1280, 1236, 1172, 956, 923, 830, 750, 693; ^1H NMR ($CDCl_3$) δ 7.05–7.17 (m, 18 H, ArH and olefinic H), 7.30 (t, J=8.3 Hz, 8H, ArH), 7.33 (d, J=16.1 Hz, 2H, olefinic H), 7.46 (d, J=8.8 Hz, 4H, ArH), 7.61 (dd, J=1.0, 8.3 Hz, 2H, ArH), 8.09 (d, J=1.0 Hz, 2H, ArH), 8.19 (d, J=8.3 Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 122.0, 122.6, 123.6, 125.0, 125.1, 126.3, 128.1, 129.4, 129.7, 129.8, 131.0, 132.9, 136.1, 145.2, 147.2, 148.6, 179.7; FAB-MS (positive, NBA) m/z 747 [$(M+1)^+$]. Anal. Calcd for $C_{54}H_{38}N_2O_2 \cdot 0.2CH_2Cl_2$ (746.89): C, 85.22; H, 5.07; N, 3.67. Found: C, 85.48; H, 5.04; N, 3.75.

4.6. 3,6,13,16,23,26-Hexakis[4-(diphenylamino)pheny]-tri-1,10-phenanthrolino[5,6-*b*:5′,6′-*h*:5″,6″-*n*]-1,4,5,8,9,12-hexaazatriphenylene (TPHAT-N-TPA)

A mixture of **2** (447 mg, 0.64 mmol), hexaaminobenzene trihydrochloride (65 mg, 0.235 mmol) in deaerated acetic acid (10 mL) was heated at the refluxing temperature for 17 h under an argon atmosphere. After the reaction mixture was cooled to room temperature, it was poured into water (150 mL), and extracted with dichloromethane (150 mL×2). The organic layer was treated with aqueous 1 M sodium hydrogen carbonate solution (200 mL), washed with brine (200 mL) and water (200 mL×2), dried over anhydrous magnesium sulfate, and evaporated in vacuo to dryness. The residue was subjected to silica gel column chromatography (KANTO 60N) eluting with chloroform to give crude TPHAT-N-TPA. The crude product was purified by GPC eluting with chloroform to give TPHAT-N-TPA in 11% yield (53 mg, 0.025 mmol); dark brown solid; mp >350 °C; IR (KBr, cm^{-1}) 1577, 1488, 1369, 1315, 1282, 1217,

1176, 828, 753, 696; MALDI-TOF-MS (positive, dithranol) *m*/*z* 2148.79 (M^+, calcd for $C_{150}H_{96}N_{18}$ 2148.81). Anal. Calcd for $C_{150}H_{96}N_{18}\cdot 1.6CHCl_3$ (2150.49): C, 77.76; H, 4.20; N, 10.77. Found: C, 77.48; H, 4.49; N, 11.02.

4.7. 3,6,13,16,23,26-Hexakis[4-(diphenylamino)phenyl]-triphenanthro[9,10-*b*:9′,10′-*h*:9″,10″-*n*]-1,4,5,8,9,12-hexaazatriphenylene (TPHAT-C-TPA)

According to a method similar to the preparation of TPHAT-N-TPA, TPHAT-C-TPA was obtained in 16% yield (85 mg, 0.040 mmol) from hexaaminobenzene trihydrochloride (83 mg, 0.3 mmol), **5a** (521 mg, 0.75 mmol), and deaerated acetic acid (11.5 mL). The reaction mixture was purified by silica gel column chromatography (KANTO 60N) eluting with chloroform and GPC eluting with chloroform. Dark brown solid; mp >350 °C; IR (KBr, cm^{-1}) 3057, 3031, 1588, 1490, 1272, 820, 750, 693; ^{1}H NMR (1,1,2,2-tetrachloroetane-d_2 (1 mM), 120 °C) δ 7.12 (t, *J*=7.6 Hz, 12H ArH), 7.21 (d, *J*=8.0 Hz, 24H, ArH), 7.19–7.24 (br d, 12H, ArH), 7.35 (t, *J*=7.6 Hz, 24H, ArH), 7.64–7.74 (br d, 12H, ArH), 7.88–7.97 (br d, 6H, ArH), 8.47–8.57 (br s, 6H, ArH), 9.31–9.48 (br d, 6H, ArH); ^{13}C NMR (1,1,2,2-tetrachloroetane-d_2 (5 mM), 120 °C) δ 120.2, 123.5, 123.7, 125.1, 125.3, 126.2, 127.4, 128.2, 129.6, 129.7, 132.4, 134.6, 141.4, 141.7, 148.0, 148.1; MALDI-TOF-MS (positive, dithranol) *m*/*z* 2142.89 [M^+, calcd for $C_{150}H_{96}N_{18}$ 2142.84]. Anal. Calcd for $C_{156}H_{102}N_{12}\cdot 0.8CHCl_3$ (2144.56): C, 84.07; H, 4.63; N, 7.50. Found: C, 84.36; H, 4.80; N, 7.34.

4.8. 3,6,13,16,23,26-Hexakis{[4-bis(4-*tert*-butylphenyl)amino]phenyl}-triphenanthro[9,10-*b*:9′,10′-*h*:9″,10″-*n*]-1,4,5,8,9,12-hexaazatriphenylene (TPHAT-C-TPA-^{t}Bu)

According to a method similar to the preparation of TPHAT-N-TPA, TPHAT-C-TPA-^{t}Bu was obtained in 6% yield (28 mg, 0.010 mmol) from hexaaminobenzene trihydrochloride (56 mg, 0.20 mmol), **5b** (460 mg, 0.50 mmol), deaerated acetic acid (4 mL), and deaerated 1,1,2,2-tetrachloroethane (2 mL). The reaction mixture was purified by silica gel column chromatography (KANTO 60N) eluting with chloroform and GPC eluting with chloroform. Brown solid; IR (KBr, cm^{-1}) 3033, 2957, 2901, 2865, 1598, 1508, 1364, 1321, 1267, 824; ^{1}H NMR (1,1,2,2-tetrachloroetane-d_2 (1 mM), 120 °C) δ 1.44 (s, 108H, CH_3), 7.16 (d, *J*=8.7 Hz, 24H, ArH), 7.23 (d, *J*=8.3 Hz, 12H, ArH), 7.38 (d, *J*=8.7 Hz, 24H, ArH), 7.74 (d, *J*=8.3 Hz, 12H, ArH), 8.05 (d, *J*=7.8 Hz, 6H, ArH), 8.70 (s, 6H, ArH), 9.64 (d, *J*=7.8 Hz, 6H, ArH)); ^{13}C NMR (1,1,2,2-tetrachloroetane-d_2 (5 mM), 120 °C) δ 31.7, 34.5, 120.2, 123.0, 124.9, 126.3, 126.7, 127.6, 128.3, 129.2, 132.8, 133.9, 141.8, 142.3, 142.5, 145.3, 146.5, 148.5; MALDI-TOF-MS (positive, dithranol) *m*/*z* 2815.79 [M^+, calcd for $C_{204}H_{198}N_{12}$ 2815.59]. Anal. Calcd for $C_{204}H_{198}N_{12}\cdot 0.8CHCl_3$ (2817.84): C, 84.43; H, 6.88; N, 5.77. Found: C, 84.35; H, 6.87; N, 5.81.

4.9. 3,6,13,16,23,26-Hexakis{2-[4-(diphenylamino)phenyl]ethenyl}triphenanthro[9,10-*b*:9′,10′-*h*:9″,10″-*n*]-1,4,5,8,9,12-hexaazatriphenylene (TPHAT-C-ETPA)

According to a method similar to the preparation of TPHAT-N-TPA, TPHAT-C-ETPA was obtained in 12% yield (14 mg, 0.006 mmol) from hexaaminobenzene trihydrochloride (17 mg, 0.06 mmol), **5c** (112 mg, 0.15 mmol), deaerated acetic acid (1 mL), and deaerated 1,1,2,2-tetrachloroethane (0.5 mL). The reaction mixture was purified by silica gel column chromatography (KANTO 60N) eluting with chloroform/hexane (3:1, v/v) and GPC eluting with chloroform. Dark brown solid; mp >350 °C; IR (KBr, cm^{-1}) 3057, 3022, 1586, 1490, 1274, 830, 750, 693; MALDI-TOF-MS (positive, dithranol) *m*/*z* 2299.59 [M^+, calcd for $C_{168}H_{114}N_{12}$ 2298.93]. Anal. Calcd for $C_{168}H_{114}N_{12}\cdot 1.2CHCl_3$ (2300.78): C, 83.15; H, 4.75; N, 6.88. Found: C, 83.02; H, 4.77; N, 7.03.

4.10. 4-Bis(4-*tert*-butylphenyl)amino-1-bromobenzene (8)

To a suspension of **7** (1.25 g, 3.5 mmol) in DMF (14 mL) was added dropwise NBS (623 mg, 3.5 mmol) in DMF (1.4 mL) at 0 °C under an argon atmosphere and the mixture was stirred at room temperature for 1 h. The reaction mixture was quenched with water (15 mL). The formed precipitate was collected by filtration, and washed with water (100 mL) and methanol (10 mL) to give **8** in 94% (1.442 g, 3.3 mmol) as white powder. An analytical sample was obtained by recrystallization from methanol. Mp 158–159 °C; IR (KBr, cm^{-1}) 3037, 2960, 2900, 2864, 1580, 1509, 1485, 1323, 1295, 1284, 1271, 828, 817; ^{1}H NMR ($CDCl_3$) δ 1.31 (s, 18H, CH_3), 6.92 (d, *J*=8.8 Hz, 2H, ArH), 6.99 (d, *J*=8.8 Hz, 4H, ArH), 7.25 (d, *J*=8.8 Hz, 4H, ArH), 7.28 (d, *J*=8.8 Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 31.4, 34.3, 113.8, 124.0, 124.3, 126.1, 131.9, 144.7, 146.1, 147.4; FAB-MS (positive, NBA) *m*/*z* 435, 437 (M^+). Anal. Calcd for $C_{26}H_{30}BrN$ (436.43): C, 71.55; H, 6.93; N, 3.21. Found: C, 71.16; H, 6.94; N, 3.33.

4.11. 2,2-Dimethyl-1,3-propanediol 4-bis(4-*tert*-butylphenylamino)phenylboronate (2b)

To a suspension of **8** (1.658 g, 3.8 mmol) in dry THF (20 mL) was added dropwise 1.66 M butyllithium hexane solution (2.52 mL, 4.18 mmol) at −78 °C for 4 min under an argon atmosphere. After the mixture was allowed to stand at −78 °C for 1 h, a solution of trimethylborate (0.474 g, 4.56 mmol) in dry THF (4 mL) was added at −78 °C for 5 min. The mixture was allowed to stand at −78 °C for 30 min and warmed up to 0 °C. The reaction mixture was quenched with aqueous 1.2 N hydrochloric acid solution (3.6 mL) and water (40 mL) at 0 °C, and extract with ethyl acetate (100 mL×2). The organic layer was washed with brine (40 mL) and water (40 mL), dried over anhydrous magnesium sulfate, and evaporated in vacuum to dryness. The residue (1.50 g) was treated with 2,2-dimethyl-1,3-propanediol (0.542 g, 5.2 mmol) in dichloromethane (4 mL) under an argon atmosphere and the mixture was stirred at room temperature for 1 h. The reaction mixture was dried over anhydrous magnesium sulfate and evaporated in vacuum to dryness. The residue (1.90 g) was purified by silica gel column chromatography (KANTO 60N) eluting with hexane/dichloromethane, (1:9, v/v) to give **2b** in 54% yield (0.967 g, 2.06 mmol) as white solid. An analytical sample was obtained by recrystallization from dichloromethane. Mp 213–214 °C; IR (KBr, cm^{-1}) 3033, 2961, 2901, 2867, 1598, 1507, 1316 (ν_{BO}), 1275, 1135, 830; ^{1}H NMR ($CDCl_3$) δ 1.01 (s, 6H, CH_3), 1.31 (s, 18H, CH_3), 3.74 (s, 4H, CH_2), 7.00 (d, *J*=8.3 Hz, 2H, ArH), 7.02 (d, *J*=8.3 Hz, 4H, ArH), 7.24 (d, *J*=8.3 Hz, 4H, ArH), 7.63 (d, *J*=8.3 Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 21.9, 31.4, 31.9, 34.3, 72.3, 121.2, 124.4, 126.0, 134.7, 144.8, 145.9, 150.4; FAB-MS (positive, NBA) *m*/*z* 469 (M^+). Anal. Calcd for $C_{31}H_{40}BNO_2$ (469.47): C, 79.31; H, 8.59; N, 2.98. Found: C, 79.18; H, 8.57; N, 3.02.

4.12. UV/vis and fluorescence spectroscopy

UV/vis spectra were measured on a JASCO V-570 spectrophotometer in a 0.01 cm width quartz cell (1.0 mM), a 0.1 cm width quartz cell (0.1 mM), a 1.0 cm width quartz cell (0.01 mM), and 10.0 cm width quartz cell (0.001 mM). Fluorescence spectra were measured on a HITACHI F-4500 fluorescence spectrophotometer.

4.13. AFM observation

Atomic force microscopy (AFM) images were obtained on a SII SPA400 DFM (tapping mode). SI-DF 20 type tips were used. Samples were prepared by drop casting from 0.01 mM toluene solutions on freshly cleaved mica.

4.14. Dynamic light scattering

Dynamic light scattering was performed on Photal OTSUKA ELECTRONICS DLS-7000 with a 632 nm He–Ne laser source using a 12 mm width quarts cell.

4.15. Measurement of two-photon absorption

Two-photon absorption cross sections were measured from 649 to 1004 nm using the open-aperture Z-scan method[38] with an optical parametric amplifier (SpectraPhysics OPA-800) pumped by a femtosecond Ti:sapphire regenerative amplifier system operating at 1 kHz. The optical setup used for the Z-scan measurements is described elsewhere.[39] The laser beam was reshaped by passing through a small iris aperture to obtain a near Gaussian spatial profile. The pulse width of the laser beam was 110–130 fs in FWHM, which were measured by an autocorrelator with assuming a Gaussian temporal profile and used to calculate on-axis peak intensities at the focal point I_0. Sample solution was hold in a 2-mm quartz cuvette and used for the measurements.

Some examples of the open-aperture Z-scan traces of the compounds studied are shown in Figs. S1–S6. At each wavelength, the Z-scan measurements were repeated four times or more with different incident powers in the range of 0.01–0.40 mW, corresponding to I_0 of 3–140 GW cm^{-2} with Rayleigh ranges z_R of 5–10 mm depending on the wavelength and the optical setup. Each set of Z-scan traces with different I_0 was analyzed by global fitting procedure with theoretical model of transmittance of temporal and spatial Gaussian pulses through a TPA media with saturable absorption.[40] In the global fitting procedure, Rayleigh range z_R, TPA coefficient $\alpha^{(2)}$, and saturation intensity I_S were treated as global fitting parameters. The best fit curves are also shown in Fig. S1–S6 with solid curves. For TPHAT-C-TPA (Figs. S1 and S5), TPHT-N-TPA (Fig. S2), and TPHAT-C-ETPA (Figs. S3 and S6), saturable absorption was necessary to obtain reasonable curve fit, while it was not for TPHAT-C-^{t}Bu (Fig. S4).

With the $\alpha^{(2)}$ obtained from the curve fits, TPA cross section was calculated with the convention, $\sigma^{(2)}=h\nu\ \alpha^{(2)}/N$, where $h\nu$ is the photon energy of the incident laser pulse and N is the number density calculated from molar concentration of the sample solutions.

Acknowledgements

We thank Mr. Tomoyuki Ishikawa (Fukuoka Industrial Technology Center) for the MALDI-TOF mass spectrometry measurement. This work was partially supported by Tokuyama Science Foundation, Yoshida Foundation for the Promotion of Learning and Education, and by Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Culture, Sports, and Technology of Japan (No. 22550132).

Supplementary data

This material contains the details of open-aperture Z-scan traces, ^{1}H NMR spectra, MALDI-TOF-MS spectra, and dynamic light scattering. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2012.10.070. These data include MOL files and InChiKeys of the most important compounds described in this article.

References and notes

1. (a) Würthner, F. *Chem. Commun.* **2004**, 1564–2157; (b) Hoeben, F. J. M.; Jonkheijm, W.; Meijer, E. W.; Schenning, A. P. H. J. *Chem. Rev.* **2005**, *105*, 1491–1546; (c) Schenning, A. P. H. J.; Meijer, E. W. *Chem. Commun.* **2005**, 3245–3258; (d) Ajayaghosh, A.; Praveen, V. K. *Acc. Chem. Res.* **2007**, *40*, 644–656; (e) Elemans, J. A. A. W.; van Hameren, R.; Nolte, R. J. M.; Rowan, A. E. *Adv. Mater.* **2006**, *18*, 1251–1266; (f) Astruc, D.; Boisselier, E.; Ornelas, C. *Chem. Rev.* **2010**, *110*, 1857–1959; (g) Würthner, F.; Kaiser, T. E.; Saha-Möller, C. R. *Angew. Chem., Int. Ed.* **2011**, *50*, 3376–3410; (h) Magginia, L.; Bonifazi, D. *Chem. Soc. Rev.* **2012**, *41*, 211–241.
2. (a) Simpson, C. D.; Wu, J.; Watson, M. D.; Müllen, K. *J. Mater. Chem.* **2004**, *14*, 494–504; (b) Yamamoto, Y.; Fukushima, T.; Jin, W.; Kosaka, A.; Hara, T.; Nakamura, T.; Saeki, A.; Seki, S.; Tagawa, S.; Aida, T. *Adv. Mater.* **2006**, *18*, 1297–1300; (c) Wu, J.; Pisula, W.; Müllen, K. *Chem. Rev.* **2007**, *107*, 718–747; (d) Pisula, W.; Feng, X.; Müllen, K. *Adv. Mater.* **2010**, *22*, 3634–3649.
3. (a) Adam, D.; Schuhmacher, P.; Simmerer, J.; Häussling, L.; Siemensmeyer, K.; Etzbach, K. H.; Ringsdorf, H.; Haarer, D. *Nature* **1994**, *371*, 141–143; (b) Kato, T.; Mizoshita, N.; Kishimoto, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 38–68; (c) Shimizu, Y.; Oikaw, K.; Nakayama, K.; Guillon, D. *J. Mater. Chem.* **2007**, *17*, 4223–4229; (d) Kato, T.; Yasuda, T.; Kamikawa, Y.; Yoshio, M. *Chem. Commun.* **2009**, 729–739.
4. (a) Wu, W.; Liu, Y.; Zhu, D. *Chem. Soc. Rev.* **2010**, *39*, 1489–1502; (b) Kim, F. S.; Ren, G.; Jenekhe, S. A. *Chem. Mater.* **2011**, *23*, 682–732; (c) Operamolla, A.; Farinola, G. M. *Eur. J. Org. Chem.* **2011**, 423–450.
5. (a) Wu, J.; Watson, M. D.; Müllen, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 5329–5333; (b) Samorǒ, P.; Fechtenkötter, A.; Reuther, E.; Watson, M. D.; Severin, N.; Müllen, K.; Rabe, J. P. *Adv. Mater.* **2006**, *18*, 1317–1321; (c) Yasuda, T.; Shimizu, T.; Liu, F.; Ungar, G.; Kato, T. *J. Am. Chem. Soc.* **2011**, *133*, 13437–13444.
6. He, G. S.; Tan, L. S.; Zheng, Q.; Prasad, P. N. *Chem. Rev.* **2008**, *108*, 1245–1330.
7. Marder, R. *Chem. Commun.* **2006**, 131–134.
8. Pawlicki, M.; Collins, H. A.; Denning, R. G.; Anderson, H. L. *Angew. Chem., Int. Ed.* **2009**, *48*, 3244–3266.
9. Kim, H. M.; Cho, B. R. *Chem. Commun.* **2009**, 153–164.
10. (a) Hales, J. M.; Matichak, J.; Bredas, J. L.; Perry, J. W.; Mader, S. R. *Science* **2010**, *327*, 1485–1488; (b) Haque, S. A.; Nelson, J. *Science* **2010**, *327*, 1466–1467.
11. Albota, M.; Beljonne, D.; Brédas, J.-L.; Ehrlich, J. E.; Fu, J.-Y.; Heikal, A. A.; Hess, S. E.; Kogej, T.; Levin, M. D.; Marder, S. R.; McCord-Maughon, D.; Perry, J. W.; Röckel, H.; Rumi, M.; Subramaniam, G.; Webb, W. W.; Wu, X.-L.; Xu, C. *Science* **1998**, *281*, 1653–1656.
12. (a) Drobizhev, M.; Karotki, A.; Rebane, A.; Spangler, C. W. *Opt. Lett.* **2001**, *26*, 1081–1083; (b) Cho, B. R.; Son, K. H.; Lee, S. H.; Song, Y. S.; Lee, Y. K.; Jeon, S. J.; Choi, J. H.; Lee, H.; Cho, M. *J. Am. Chem. Soc.* **2001**, *123*, 10039–10045; (c) Pond, S. J. K.; Rumi, M.; Levin, M. D.; Parker, T. C.; Beljonne, D.; Day, M. W.; Brédas, J.-L.; Marder, S. R.; Perry, J. W. *J. Phys. Chem. A* **2002**, *106*, 11470–11480; (d) Lin, T. C.; He, G. S.; Prasad, P. N.; Tan, L. S. *J. Mater. Chem.* **2004**, *14*, 982–991; (e) Porres, L.; Mongin, O.; Katan, C.; Charlot, M.; Pons, T.; Mertz, J.; Blanchard-Desce, M. *Org. Lett.* **2004**, *6*, 47–50; (f) Drobizhev, M.; Stepanenko, Y.; Dzenis, Y.; Karotki, A.; Rebane, A.; Taylor, P. N.; Anderson, H. L. *J. Am. Chem. Soc.* **2004**, *126*, 15352–15353; (g) Katan, C.; Terenziani, F.; Mongin, O.; Werts, M. H. V.; Porrès, L.; Pons, T.; Mertz, J.; Tretiak, S.; Blanchard-Desce, M. *J. Phys. Chem. A* **2005**, *109*, 3024–3037; (h) Le Droumaguet, C.; Mongin, O.; Werts, M. H. V.; Blanchard-Desce, M. *Chem. Commun.* **2005**, 2802–2804; (i) Kato, S.; Matsumoto, T.; Shigeiwa, M.; Gorohmaru, H.; Maeda, S.; Ishi-i, T.; Mataka, S. *Chem.—Eur. J.* **2006**, *12*, 2303–2317; (j) Bhaskar, A.; Guda, R.; Haley, M. M.; Goodson, T., III. *J. Am. Chem. Soc.* **2006**, *128*, 13972–13973; (k) Chung, S.-J.; Zheng, S.; Odani, T.; Beverina, L.; Fu, J.; Padilha, L. A.; Biesso, A.; Hales, J. M.; Zhan, X.; Schmidt, K.; Ye, A.; Zojer, E.; Barlow, S.; Hagan, D. J.; Van Stryland, E. W.; Yi, Y.; Shuai, Z.; Pagani, G. A.; Brédas, J. L.; Perry, J. W.; Marder, S. R. *J. Am. Chem. Soc.* **2006**, *128*, 14444–14445; (l) Williams-Harry, M.; Bhaskar, A.; Ramakrishna, G.; Goodson, T., III; Imamura, M.; Mawatari, A.; Nakao, K.; Enozawa, H.; Nishinaga, T.; Iyoda, M. *J. Am. Chem. Soc.* **2008**, *130*, 3252–3253; (m) Dy, J.; Ogawa, K.; Kamada, K.; Ohta, K.; Kobuke, Y. *Chem. Commun.* **2008**, 3411–3413; (n) Lin, C. C.; Velusamy, M.; Chou, H. H.; Lin, J. T.; Chou, P. T. *Tetrahedron* **2010**, *66*, 8629–8634; (o) Cheng, J. Z.; Lin, C. C.; Chou, P. T.; Chaskar, A.; Wong, K. T. *Tetrahedron* **2011**, *67*, 734–739; (p) Hrobáriková, V.; Hrobárik, P.; Gajdoš, P.; Fitilis, I.; Fakis, M.; Persephonis, P.; Zahradník, P. *J. Org. Chem.* **2010**, *75*, 3053–3068; (q) Hrobárik, P.; Hrobáriková, V.; Sigmundová, I.; Zahradník, P.; Fakis, M.; Polyzos, I.; Persephonis, P. *J. Org. Chem.* **2011**, *76*, 8726–8736.
13. (a) He, G. S.; Bhawalkar, J. D.; Zhao, C. F.; Prasad, P. N. *Appl. Phys. Lett.* **1995**, *67*, 2433–2435; (b) Ehrlich, J. E.; Wu, X. L.; Lee, I. Y. S.; Hu, Z. Y.; Röckel, H.; Marder, S. R.; Perry, J. W. *Opt. Lett.* **1997**, *22*, 1843–1845; (c) He, G. S.; Lin, T. C.; Prasad, P. N.; Cho, C. C.; Yu, L. J. *Appl. Phys. Lett.* **2003**, *82*, 4717–4719.
14. (a) Maruo, S.; Nakamura, O.; Kawata, S. *Opt. Lett.* **1997**, *22*, 132–134; (b) Cumpston, B. H.; Ananthavel, S. P.; Barlow, S.; Dyer, D. L.; Ehrlich, J. E.; Erskine, L. L.; Heikal, A. A.; Kuebler, S. M.; Lee, I. Y. S.; McCord-Maughon, D. M.; Qin, J.; Röckel, H.; Rumi, M.; Wu, X.-L.; Marder, S. R.; Perry, J. W. *Nature* **1999**, *398*, 51–54.
15. (a) Parthenopoulos;, D. A.; Rentzepis, P. M. *Science* **1989**, *245*, 843–845; (b) Kawata, S.; Kawata, Y. *Chem. Rev.* **2000**, *100*, 1777–1788.
16. (a) Denk, W.; Strickler, J. H.; Webb, W. W. *Science* **1990**, *248*, 73–76; (b) Gao, Y. H.; Wu, J. Y.; Li, Y.; Sun, P. P.; Zhou, H. P.; Yang, J. X.; Zhang, S. Y.; Jin, B. K.; Tian, Y. P. *J. Am. Chem. Soc.* **2009**, *131*, 5208–5213; (c) Parthasarathy, V.; Fery-Forgues, S.; Campioli, E.; Recher, G.; Terenziani, F.; Blanchard-Desce, M. *Small* **2011**, *7*, 3219–3229.
17. (a) Frederiksen, P. K.; Jørgensen, M.; Ogilby, P. M. *J. Am. Chem. Soc.* **2001**, *123*, 1215–1221; (b) Gao, D.; Agayan, R. R.; Xu, H.; Philbert, M. A.; Kopelman, R. *Nano Lett.* **2006**, *6*, 2383–2386.
18. Kamada, K.; Ohta, K.; Iwase, Y.; Kondo, K. *Chem. Phys. Lett.* **2003**, *372*, 386–393.
19. Ohta, K.; Kamada, K. *J. Chem. Phys.* **2006**, *124*, 124303-1–124303-11.
20. (a) Kamada, K.; Tanamura, Y.; Ueno, K.; Ohta, K.; Misawa, H. *J. Phys. Chem. C* **2007**, *111*, 11193–11198; (b) Suzuki, Y.; Tenma, Y.; Nishioka, Y.; Kamada, K.; Ohta, K.; Kawamata, J. *J. Phys. Chem. C* **2011**, *115*, 20653–20661.

21. (a) Collini, E.; Ferrante, C.; Bozio, R. *J. Phys. Chem. B* **2005**, *109*, 2–5; (b) Ray, P. C.; Sainudeen, Z. *J. Phys. Chem. A* **2006**, *110*, 12342–12347; (c) Collini, E.; Ferrante, C.; Bozio, R. *J. Phys. Chem. C* **2007**, *111*, 18636–18645; (d) Biswas, S.; Ahn, H.-Y.; Bondar, M. V.; Belfield, K. D. *Langmuir* **2012**, *28*, 1515–1522.
22. Belfield, K. D.; Bondar, M. V.; Hernandez, F. E.; Przhonska, O. V.; Yao, S. *Chem. Phys.* **2006**, *320*, 118–124.
23. Furuki, M.; Tian, M.; Sato, Y.; Pu, L. S. *Appl. Phys. Lett.* **2001**, *79*, 708–710.
24. (a) Zheng, Q.; Ohulchanskyy, T. Y.; Sahoo, Y.; Prasad, P. N. *J. Phys. Chem. C* **2007**, *111*, 16846–16851; (b) Kim, S.; Ohulchanskyy, T. Y.; Pudavar, H. E.; Pandey, R. K.; Prasad, P. N. *J. Am. Chem. Soc.* **2007**, *129*, 2669–2675; (c) Kim, S.; Pudavar, H. E.; Bonoiu, A.; Prasad, P. N. *Adv. Mater.* **2007**, *19*, 3791–3795; (d) Kim, S.; Huang, H.; Pudavar, H. E.; Cui, Y.; Prasad, P. N. *Chem. Mater.* **2007**, *19*, 5650–5656.
25. Kim, S.; Zheng, Q.; He, G. S.; Bharadi, D. J.; Pudavar, H. E.; Baev, A.; Prasad, P. N. *Adv. Funct. Mater.* **2006**, *16*, 2317–2323.
26. Lin, Z.; Shao, P.; Huang, Z.; Lin, B.; Chen, T.; Qin, J. *Chem. Commun.* **2008**, 2260–2262.
27. (a) Ogawa, K.; Ohashi, A.; Kobuke, Y.; Kamada, K.; Ohta, K. *J. Am. Chem. Soc.* **2003**, *125*, 13356–13357; (b) Ogawa, K.; Ohashi, A.; Kobuke, Y.; Kamada, K.; Ohta, K. *J. Phys. Chem. B* **2005**, *109*, 22003–22012; (c) Drobizhev, M.; Stepanenko, Y.; Rebane, A.; Wilson, C. J.; Screen, T. E. O.; Anderson, H. L. *J. Am. Chem. Soc.* **2006**, *128*, 12432–12433; (d) Dy, J. T.; Ogawa, K.; Satake, A.; Ishizumi, A.; Kobuke, Y. *Chem.—Eur. J.* **2007**, *13*, 3491–3500; (e) Kamada, K.; Hara, C.; Ogawa, K.; Ohta, K.; Kobuke, Y. *Chem. Commun.* **2012**, 7988–7990.
28. (a) Woo, H. Y.; Liu, B.; Kohler, B.; Korystov, D.; Mikhailovsky, A.; Bazan, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 14721–14729; (b) Ortony, J. H.; Chatterjee, T.; Garner, L. E.; Chworos, A.; Mikhailovsky, A.; Kramer, E. J.; Bazan, G. C. *J. Am. Chem. Soc.* **2011**, *133*, 8380–8387.
29. Hu, R.; Maldonado, J. L.; Rodriguez, M.; Deng, C.; Jim, C. K. W.; Lam, J. W. Y.; Yuen, M. M. F.; Ramos-Ortiz, G.; Tang, B. Z. *J. Mater. Chem.* **2012**, *22*, 232–240.
30. Noh, S. B.; Kim, R. H.; Kim, W. J.; Kim, S.; Lee, K.-S.; Cho, N. S.; Shim, H.-K.; Pudavar, H. E.; Prasad, P. N. *J. Mater. Chem.* **2010**, *20*, 7422–7429.
31. (a) Ishi-i, T.; Yaguma, K.; Kuwahara, R.; Taguri, Y.; Mataka, S. *Org. Lett.* **2006**, *8*, 585–588; (b) Ishi-i, T.; Hirashima, R.; Tsutsumi, N.; Amemori, S.; Matsuki, S.; Teshima, Y.; Kuwahara, R.; Mataka, S. *J. Org. Chem.* **2010**, *75*, 6858–6868.
32. Bhatt, M. V. *Tetrahedron* **1964**, *20*, 803–821.
33. (a) Mataka, S.; Eguchi, H.; Takahashi, K.; Hatta, T.; Tashiro, M. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3127–3131; (b) Mataka, S.; Shimojyo, Y.; Hashimoto, I.; Tashiro, M. *Liebigs Ann.* **1995**, 1823–1825.
34. Morisue, M.; Ogawa, K.; Kamada, K.; Ohta, K.; Kobuke, Y. *Chem. Commun.* **2010**, 2121–2123 See Supplementary data for the observed Z-scan traces and details of the analysis.
35. (a) Macak, P.; Luo, Y.; Ågren, H. *Chem. Phys. Lett.* **2000**, *300*, 447–456; (b) Macak, P.; Luo, Y.; Norman, P.; Ågren, H. *J. Chem. Phys.* **2000**, *113*, 7055–7061.
36. Ishi-i, T.; Hirayama, T.; Murakami, K.; Tashiro, H.; Thiemann, T.; Kubo, K.; Mori, A.; Yamasaki, S.; Akao, T.; Tsuboyama, A.; Mukaide, T.; Ueno, K.; Mataka, S. *Langmuir* **2005**, *21*, 1261–1268.
37. Jeong, H. C.; Piao, M. J.; Lee, S. H.; Jeong, M.-Y.; Kang, K. M.; Park, G.; Jeon, S.-J.; Cho, B. R. *Adv. Funct. Mater.* **2004**, *14*, 64–70.
38. Sheik-Bahae, M.; Said, A. A.; Wei, T.-H.; Hagan, D. G.; van Stryland, E. W. *IEEE J. Quantum Electron.* **1990**, *26*, 760–769.
39. Kamada, K.; Matsunaga, K.; Yoshino, A.; Ohta, K. *J. Opt. Soc. Am. B* **2003**, *20*, 529–537.
40. Kamada, K.; Ohta, K.; Kubo, T.; Shimizu, A.; Morita, Y.; Nakasuji, K.; Kishi, R.; Ohta, S.; Furukawa, S.; Takahashi, H.; Nakano, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 3544–3546 See Supplementary data.