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Indole-Based Aza[n]helicenes (n = 5, 6) with Violet-Blue Fluorescence and Two-Photon Absorption (TPA)

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Abstract: New indole-based helicenes, namely, 15-hexyl-15Htetraphenyl[1,2-e]indole (HTPI), 14-hexyl-14H-benzo[4',5']thieno [2',3':7,8]naphtha[1,2-e]indole (HBTNI), 7-hexyl-7H-indolo[5,4-k] phenanthridine (HIPD) and 3-hexyl-3H-phenanthro [4,3-e]indole (HPI) were successfully synthesized by a three-step or four-step reaction. They exhibited good solubility and high thermal stability of $T_d = 247$, 388, 294 and 251°C, respectively. These compounds emitted violetblue light with maximum emission peaks at 415, 397, 397 and 391 nm in hexane. Among them, HBTNI had excellent thermal stability, narrow and sharp emission peaks, and highest photoluminescence quantum yields. Thus, HBTNI was an ideal candidate for the violetblue emitters of OLEDs. Furthermore, four compounds had twophoton absorption and two-photon excited fluorescence. HTPI achieved the maximum TPA with the TPA cross-section (δ) of 171.5 GM at 770 nm. They were rare examples of helicenes with both violet-blue emission and TPA.

Introduction

Helicenes have attracted considerable attention in the last decades owing to their intriguing structural features and physical properties,^[1] and various applications in the fields of non-linear optics (NLO),^[2] circularly polarized luminescence (CPL),^[3] two-photon absorption (TPA),^[4] electronic and optoelctronic devices.^[5] Heterohelicenes can be regarded as heteroatom-substituted helicenes at no less than one carbon position in the screw skeleton of carbohelicenes. They constitute an important class of helicenes with characteristics properties and diverse biological activities.^[6] Small core or peripheral modifications of helical structures might give rise to a great difference in the physicochemical properties, which prompts us to explore new heterohelicenes through structural modifications.

Indole is easily modified and a fundamental structural unit in a myriad of natural products, pharmaceutical agents.^[7] It is not only an electron-rich molecule but also a potential hydrogen bond donor.^[8] Indole units have been utilized as good building blocks for red electroluminescent materials.^[9] Incorporation of indole unit with anthracene, dibenzothiophene, quinoline or naphthalene unit into aza[*n*]helicenes (n = 5, 6) generates the title compounds **HTPI**, **HBTNI**, **HIPD** and **HPI** (Figure 1). Herein, four novel indole-based aza[*n*]helicenes (n = 5, 6), that is, 15hexyl-15*H*-tetraphenyl[1,2-e]indole (**HTPI**), 14-hexyl-14*H*-benzo [4',5']thieno[2',3':7,8]naphtha[1,2-e]indole (**HBTNI**), 7-hexyl-7*H*indolo[5,4-k]phenanthridine (**HIPD**) and 3-hexyl-3*H*-phenanthro [4,3-e]indole (**HPI**), were prepared from commercially available 1*H*-indole-5-carbaldehyde (**ICD**). Up to date, it is not reported that helicenes have both violet-blue fluorescence and TPA.

As for violet-blue luminescence materials, violet-blue-colored (<450 nm) light-emitting diodes (LEDs) are few^[10] and costly to fabricated, but suitable for applications in optical detectors,[11] fluorescence-based chemical and biological sensors,[12] and wide-color gamut, full-color displays.^[13] Nowadays, violet InGaNbased LEDs are made by way of expensive high-temperature and high-vacuum thin-film growth techniques.^[14] Therefore, it is of vital importance to seek inexpensive and easily processed organic materials as the emitters in violet-blue LEDs. Likewise, helicenes with TPA and Two-photon excited fluorescence (TPEF) are also rare. Grafting of one or two tetracyanobutadienes in positions 2 and 15 on carbo[6]helicenes achieved the experimental δ in the range 5 - 40 GM for mono-substituted 1b,^[4b] similar to those of 2-cyano-carbo[6]helicene,^[4a] and 1-6 GM for bis-substituted helicene **1c**.^[4b] Instead of the substitution by electron-accepting groups in the helical peripheral, the title compounds were constructed via combinating indole unit with anthracene unit, and so on in donor-acceptor helical cores. They had TPA, TPEF, and HTPI achieved the maximum TPA with δ = 171.5 GM at 770 nm, which amounted to approximately 5-fold compared with 1b and 2-cyano-carbo[6]helicene. The occurrence of an undecabenzo[7]carbohelicene^[4c] demonstrated the huge potential of helicenes for TPA materials once again.



Figure 1. Chemical structures of HTPI, HBTNI, HIPD and HPI.

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Scheme 1. Synthesis of HTPI, HBTNI, HIPD and HPI. a) PPh₃, PhMe, 90°C, 12 h. b) 1-Bromohexane, KI, K₂CO₃, Acetone, 100°C, 48 h. c) [Ph₃PCH₃]⁺I⁻, KOtBu, THF, -10°C, 10 min. d) Pd(OAc)₂, K₂CO₃, 2-Bromoanthracene, Tri(o-tolyl)phosphine, DMF, 100°C, 48 h. e) I₂, PO, Benzene, uv, 30 min. f) Pd(OAc)₂, K₂CO₃, 2-Bromodibenzothiophene, Tri(o-tolyl)phosphine, DMF, 100°C, 48 h. g) Pd(OAc)₂, K₂CO₃, 3-Bromoquinolin, Tri(o-tolyl)phosphine, DMF, 80°C, 48 h. h) KOtBu, THF, -10°C, 15min. i) I₂, PO, Benzene, uv, 90 min.

Results and Discussion

Synthesis and characterization

Over the past two decades, various approaches to synthesizing heterohelicenes have been further developed, such as photocyclization,^[15] substitution reaction,^[16] metal-catalyzed cyclization,^[17] the Diels-Alder reaction,^[18] the Ramberg-Bäcklund rearrangement,^[19] homolytic aromatic substitution reaction.^[20] Herein, HTPI, HBTNI, HIPD and HPI, were facilely prepared through a three-step or four-step reaction including the key step photocyclization. **HIC** was synthesized by introducing the hexyl group to ICD at first, and then HVI and HNVI were obtained through Wittig reaction within 10 and 15 minutes.^[21] Then, HVI reacted with 2-Bromoanthracene, 2-Bromodibenzothiophene or 3-Bromoguinoline through Mizoroki-Heck reaction to afford AVHI, DTVHI and HIVQ, respectively.^[22]At last, HTPI, HBTNI, HIPD and HPI were harvested through photocyclization reaction using the Hanovia high-pressure mercury lamp in 30 or 90 minutes (Scheme 1). ¹H NMR, ¹³C NMR and HRMS of synthetic compounds, and single crystal structure data for HIVQ (CCDC 1961630) were contained in the Figures S1-S24, Table S7 and Figure S29.

Thermal properties

The thermal behavior of **HTPI**, **HBTNI**, **HIPD** and **HPI** was examined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Their decomposition temperatures (T_d , corresponding to 5% weight loss) were determined at 247°C, 388°C, 294°C and 251°C, respectively (Figure 2). Especially, **HBTNI** showed a high melting point (T_m) of 136°C, close to $T_m = 130.9^{\circ}$ C of the carbazole-based monoaza[6]helicene,^[23] and a high T_d of nearly 400°C, which was favorable to form uniform films upon thermal evaporation.^[24]



Figure 2. TG and DSC curves of (a) HTPI, (b) HBTNI, (c) HIPD and (d) HPI.

These results manifested that **HBTNI** was most thermally stable and suitable for vacuum thermal evaporation for device fabrication among them.

Electrochemical properties

Cyclic voltammetry (CV) was used to identify the electrochemical behavior of HTPI, HBTNI, HIPD and HPI (Figure 3). The oxidation peak of HTPI was located at 1.54 V with the onset oxidation potential of 0.96 V while that of HBTNI was at 1.10 V with the onset oxidation potential of 0.80 V. Introducing electrondonating atom S to the HTBNI resulted in the lower oxidation potential and onset oxidation potential compared with HTPI. This exhibited that HTPI had more tolerance to oxidation and airstable than HTBNI.[3b] In contrast, the onset oxidation potential of HPI was at 0.76 V with the oxidation peak of 1.30 V and the reduction peak of -0.04 V while that of HIPD was determined at 0.75 V. Thus, the redox processes of HBTNI, HIPD were thought to be irreversible and HTPI, HPI were quasi-reversible. The HOMOs (highest occupied molecular orbital) energy levels of HTPI, HBTNI, HIPD and HPI were calculated to be -5.20 eV, -5.04 eV, -5.00 eV and -4.99 eV, respectively. Correspondingly, the LUMOs (lowest unoccupied molecular orbital) energy levels of HTPI, HBTNI, HIPD and HPI were determined from the optical band gaps and energy levels of HOMOs, whose values were -2.34 eV, -2.03 eV, -2.12 eV and -2.07 eV, respectively. In addition, energy levels of HOMOs and LUMOs for these [6]helicenes were in the order HTPI < the carbazole-based monoaza[6]helicene^[23] < HBTNI, indicating that HTPI had excellent electrochemical stablity.[25]

Ultraviolet-visible (UV-vis) absorption and single-photon excited fluorescence (SPEF).

HTPI, HBTNI, HIPD and HPI were soluble in the common solvents such as anhydrous hexane, dichloromethane, ethyl acetate, trichloromethane and methanol. Figure 4 showed the absorption and fluorescence spectra of HTPI, HBTNI, HIPD and



Figure 3. Cyclic voltammograms of (a) HTPI, (b) HBTNI, (c) HIPD and (d) HPI.

HPI in hexane and in thin-films. The photophysical parameters were presented in Table S1 and Table S2. HTPI, HBTNI, HIPD and HPI had absorption maximum peaks at 299, 298, 228 and 229 nm in hexane, which were mainly due to the HOMO – 1 \rightarrow LUMO + 2, HOMO – 1 \rightarrow LUMO + 1, HOMO – 5 \rightarrow LUMO and HOMO – 1 \rightarrow LUMO + 3 transitions, respectively (Figure 5 and Tables S3-S6). The HOMO energy level of HTPI by theoretical calculations was almost identical to that from CV, while HOMOs energy levels of HBTNI, HIPD and HPI were a little lower than those from CV (Figures 3 and S28). The considerably blueshifted absorption maxima of HIPD and HPI compared with HTPI and HBTNI was attributed to the decreased π-conjugation length. In addition, they all exhibited several weak absorptions in the range of 370 - 390 nm, which were characteristic absorption of helicenes.^[26] As for HTPI and HIPD, the weak absorption bands in the range of 400 - 420 nm were assigned to the intramolecular charge transfer (ICT) transition from indole group to anthracene group or guinoline group.^[27] Redshifts for HTPI. HBTNI, HIPD and HPI in films compared to those in hexane were found.

As shown in Figure 4, HTPI, HBTNI, HIPD and HPI displayed well-defined vibronic structures in PL spectra of hexane solutions, indicating that they had a rigid backbone structure.^[28] These compounds exhibited maximum emission peaks at 415 nm, 397 nm, 397 nm and 391 nm, respectively, which were rare violet light. The majority of helicenes emitted blue light up to date.^[29] These compounds revealed two high fluorescence peaks at the range of 390 - 440 nm, corresponding to $0 \rightarrow 0$ and $0 \rightarrow 1$ radiative transitions, respectively. The emission bathochromic shifts and broadening of HTPI, HIPD and HPI in films as relative to those of hexane solutions were pronounced. It might be attributed to two causes: (i) relatively strong π - π interactions in the excited solid state and (ii) self-absorption phenomenon.^[30] From solution to film, the ignorable emission bathochromic shift of HBTNI demonstrated the suppressed intermolecular aggregation. In addition, the strong peak weakened and sub-strong emission peak became the main fluorescence peak in thin-film for HBTNI, because the PL spectrum overlapped with absorption spectrum, resulting in the



Figure 4. Normalized absorption and PL spectra of (a) HTPI, (b) HBTNI, (c) HIPD, and (d) HPI.

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Figure 5. TD-DFT calculated absorption spectra of (a) HTPI, (b) HBTNI, (c) HIPD and (d) HPI compared with the experimental absorption spectra of HTPI, HBTNI, HIPD and HPI in methanol.

wavelengths.[31] self-absorption phenomenon at short Photoluminescence quantum yields (PLQY) of HTPI, HBTNI, HIPD and HPI in solvents were measured ranging from 8% -21%, 12% - 32%, 3% - 15%, and 6% - 13%, respectively (Tables S1 and S2). The PLQY of HIPD and HPI were lower than those of HTPI and HBTNI, due to reduced π -conjugation of HIPD and HPI. In addition, HBTNI had the highest oscillator strength of nearly 0.1 for electronic transitions from HOMOs to LUMOs (Tables S3-S6). This demonstrated that HBTNI possessed more characteristic of allowed transition, which might be favorable for efficient fluorescence. Especially, the maximum emission peaks of HBTNI in solvents and thin-film were blue-shifed by ca. 24 -26 nm and 22 nm compared with the carbazole-based monoaza[6]helicene.^[23] Meanwhile, the PLQY of HBTNI were higher than those of the carbazole-based monoaza[6]helicene (17% - 21%). Therefore, HBTNI exhibited better fluorescence performance than the carbazole-based monoaza[6]helicene. Furthermore, T_d of **HBTNI** was 141°C higher than that of **HTPI** while T_d of HIPD was ca. 43°C higher than that of HPI. This indicated more heteroatoms in the screw skeleton could give rise to increase of T_d (Figure 2). These results indicated that heteroatoms such as sulfur and nitrogen of HBTNI might avail to increase thermal stability and fluorescence quantum yield.^[32]

TPA and TPEF

Coumarin 307 of 1×10^{-4} M in MeOH was selected as reference for δ calculations.^[33] Both the SPEF parameters and the TPEF properties of compounds **HTPI**, **HBTNI**, **HIPD**, **HPI**, Fluorescein and Coumarin 307 were displayed in Table 1. Power-squared dependence of two-photon-excited fluorescence for **HTPI** at the excitation wavelength of 800 nm was investigated. As show in Figure 6a, when the laser power was lower than 350 mW, power-squared dependence of two-photon excited fluorescence was linear. Thus, laser power was set as 235 mW in the measurement to assure that all the fluorescence came from twophoton excitation. The test results revealed that four compounds had two-photon absorption and TPEF at excitation wavelengths of 730 - 870 nm. Among them, **HTPI** achieved the maximum TPA and TPEF (Figure S26). The TPEF spectrum of **HTPI** at the excitation wavelength of 770 nm was shown in Figure 6b. **HTPI** had emission band in the region of 405 - 600 nm, and the maximum emission peak was at 450 nm. The TPEF spectrum and SPEF spectrum of **HTPI** had almost similar patterns, revealing the same excited state for the radiative decay processes.^[34] Values of **HTPI** two-photon absorption crosssections at different excitation wavelengths were shown in Figure 6c. **HTPI** achieved maximum two-photon absorption at excitation wavelengths of 730 - 870 nm, and the maximum δ was 171.5 GM at 770 nm. In comparison, **HBTNI**, **HIPD** and **HPI** had maximum δ of 4.2 GM at 750 nm, 2.5 GM at 750 nm, and 3.4 GM at 730 nm, respectively (Figure S27).

Although the absorption spectra of **HTPI**, **HBTNI**, **HIPD** and **HPI**, which located at 298 - 420, 298 - 397, 228 - 410 and 229 - 389 nm, overlapped with the two-photon absorption band, **HTPI** had the strongest absorption and others had weak absorption in the region of 370 - 430 nm (Figure S25). Therefore, **HTPI** had more opportunities to undergo two-photon absorption.^[35] **HTPI**, **HBTNI**, **HIPD** and **HPI** presented a screw-shaped nonplanar structure, which resulted in conjugation blocking.^[23] However, **HTPI** had a larger π -conjugated system compared with **HBTNI**,



Figure 6. (a) Power-squared dependence of two-photon-excited fluorescence for HTPI at the excitation wavelength of 800 nm. (b) The TPEF spectrum of HTPI at the excitation wavelength of 770 nm and the SPEF spectrum of HTPI at the excitation wavelength of 340 nm in dichloromethane. (c) δ values of HTPI at different excitation wavelengths.

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Table 1. Comparison of the photophysical properties of compounds with commercial dyes.					
Compounds	ε ^[a] [M ⁻¹ cm ⁻¹]	$\Phi_{i}^{[b]}$	δ ^[c] [GM]	$\boldsymbol{\delta}\times\boldsymbol{\varPhi}^{[d]}\left[GM\right]$	Solvents
НТРІ	149323	0.18	171.5	30.9	Dichloromethane
HBTNI	87067	0.32	4.2	1.3	Dichloromethane
HIPD	104950	0.15	2.5	0.4	Acetonitrile
HPI	927261	0.13	3.4	0.4	Dichloromethane
Fluorescein	89350	0.95	38	37	PBS ^[e]
Coumarin 307	17600	0.56	19 ^[f]	11 ^(f)	МеОН
1b ^[g]	42000 ^[g]	/	33 _[a]	/	Dichloromethane
1c ^[g]	65000 ^[g]	/	5.5 ^[g]	1	Dichloromethane

[a] ε (M⁻¹ cm⁻¹): molar absorptivity at maximum absorption wavelengths (HTPI: 302 nm, HBTNI: 301 nm, HIPD: 228 nm, HPI: 233 nm, Fluorescein: 490 nm, Coumarin 307: 396 nm, 1b: 280 nm, 1c: 280 nm). [b] ϕ_i : compounds quantum yield at the maximum absorption wavelengths determined using quinine sulfate ($\phi = 0.55$) as reference. [c] δ (GM): (HTPI: $\lambda_{ex} = 770$ nm, HBTNI: $\lambda_{ex} = 750$ nm, HIPD: $\lambda_{ex} = 750$ nm, HIPI: $\lambda_{ex} = 730$ nm, Fluorescein: $\lambda_{ex} = 780$ nm, Coumarin 307: $\lambda_{ex} = 776$ nm, 1b and 1c: $\lambda_{ex} = 690$ nm). [d] $\delta \times \phi_i$ (GM): TPEF action cross-sections (the excitation wavelengths are consistent with those of δ). Concentration of HTPI, HBTNI, HIPD, HPI and Coumarin 307 for TPEF: 1×10^{-4} M. [e] PH = 13. [f] Ref.^[33] [g] 1b and 1c were reported in Ref.^[4b]

HIPD and **HPI** due to its linear component anthracene. Theoretical studies have shown that the large π -conjugated system can effectively increase the probability of two-photon absorption.^[36] In addition, **HTPI** also possessed a relatively strong electron-accepting group anthracene (Figure S28). Hence **HTPI** possessed the TPA cross-section of 171.5 GM at 770 nm. The two-photon absorption parameters of **HTPI** were much higher than those of Coumarin 307. This confirmed that core structural changes of heterohelicenes could enhance two-photon absorption performance.

This work aimed to synthesize new indole-based helicenes with special properties. We found that these compounds had violet-blue fluorescence and two-photon absorption properties. As is known, the geometry of a helicene results in π -conjugation blocking for wide band gaps and the nonplanar twist structure which reduces molecular aggregations.^[23, 37] Therefore, indoleembedded helicenes could exhibit more fluorescence of the indole unit and so on. Fluorescence peaks of N-Alkyl-5arylindole-3-carboxaldehydes mainly located within 325-425 nm.[38] Thus, indole-embedded helicenes can emit violet-blue light due to π -conjugation blocking. In addition, HTPI had a larger π -conjugated system due to its linear component and strong electron-accepting relativelv aroup. anthracene. Consequently, HTPI possessed the largest TPA cross-section among them.

Conclusion

In summary, **HTPI**, **HBTNI**, **HIPD** and **HPI** were synthesized successfully. Their thermal, electrochemical, UV-vis absorption, SPEF, TPA properties, and DFT calculations were investigated. **HTPI**, **HBTNI**, **HIPD** and **HPI** emitted violet-blue light with maximum emission peaks at 415 nm, 397 nm, 397 nm and 391 nm in hexane. Among them, **HBTNI** was most thermally stable and had best fluorescence performance. Furthermore, the four compounds had TPA and TPEF, and **HTPI** achieved the maximum δ = 171.5 GM at 770 nm. They were rare examples of

helicenes with both violet-blue fluorescence and TPA. The study disclosed that helicenes with characteristic properties could be acquired through core modifications of helical structures. This class of helicenes was promising for potential applications in two-photon excited fluorescence probes, optoelectronics, and other fields.

Experimental Section

Materials and Methods

Reagents were used as purchased without further purification unless otherwise stated. DMF was dried with molecular sieves. THF was refluxed with sodium in the presence of benzophenone. HTPI, HBTNI, HPI and HIPD were synthesized by photocyclization using the Hanovia high-pressure mercury lamp (500 W). ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Advance 400 spectrometer. Matrix-assisted laser-desorption/ionization time-of-flight (MALDI-TOF) mass spectrum (MS) was recorded on a Bruker Biflex III mass spectrometer that was equipped with a 337 nm nitrogen laser. High resolution mass spectra (HRMS) were recorded on a Q-TOF6510 spectrograph (Agilent). X-ray diffraction intensity data were collected on a Bruker APEX3 (Bruker, 2017) area-detector diffractometer equipped with graphite-monochromated Cu- $K\alpha$ radiation (λ = 1.54178 Å) at the temperature of 120 K. The intensity data were processed by using the Bruker SMART routine and the structure was solved by using Bruker APEX3 (Bruker, 2017) and refined by a full-matrix least-squares technique based on F² with the SHELXL-2014/7 (Sheldrick, 2014) program.

Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC) curves were obtained on a SDT Q600 V8.3 Differential Scanning Calorimeter under nitrogen atmosphere with heating and cooling rates of 10°C min⁻¹ from room temperature to 600°C.

Cyclic voltammetry (CV) measurements of **HTPI**, **HBTNI**, **HIPD** and **HPI** were run on a CHI660D electrochemical workstation. A three-electrode cell with a glassy carbon working electrode, a platinum auxiliary electrode and a saturated Ag/AgCI reference electrode was used.^[23] The potential of the Ag/AgCI reference electrode in CH₂Cl₂ (0.1 M tetrabutylammonium perchlorate) was calibrated by using the ferrocene/ferrocenium (Fc/Fc⁺)

redox system.^[39] In this arrangement, the half-wave potential of Fc/Fc⁺ ($E_{1/2,FOC}$) was measured to be 0.56 V (vs. Ag/AgCl). $E_{HOMO} = -e(E_{onset(ox)} - E_{1/2,FOC}) - 4.8 \text{ eV}.^{[40]}$ The optical band gaps were estimated from the onset wavelength of the Ultraviolet-visible (UV-vis) absorptions.^[41]

Ultraviolet-visible (UV-vis) absorption spectroscopy was performed on a TU-1800 spectrophotometer (Hitachi). PL spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. The neat films were prepared by spin-coating on SiO₂ glass slides. Fluorescence quantum yields were calculated by using quinine sulfate in 0.1 M H₂SO₄ solution as reference.^[42]

Two-photon excited fluorescence (TPEF) was measured using a SpectroPro300i and the pump laser beam came from a mode-locked Ti:sapphire laser system at the pulse duration of 220 fs and a repetition rate of 76 MHz (Coherent Mira900-D). The excitation source of the TPEF spectrometer had wavelengths of *ca.* 730 - 870 nm. TPEF of compounds **HTPI**, **HBTNI**, **HIPD** and **HPI** at different excitation wavelengths under the room temperature was systematically investigated in CH_2CI_2 or acetonitrile. TPA cross-sections have been measured using the two-photon induced fluorescence method. Coumarin 307 in MeOH was selected as reference.^[33] The cross-sections can be calculated using Equation (1):

$$\delta_{\rm s} = \delta_{\rm r} \frac{\Phi_{\rm r}}{\Phi_{\rm s}} \frac{c_{\rm r}}{c_{\rm s}} \frac{n_{\rm r}}{n_{\rm s}} \frac{F_{\rm s}}{F_{\rm r}} \tag{1}$$

Where the subscripts s and r refer to the sample and the reference materials, respectively. δ is the TPA cross-section value, *c* is the concentration of the solution, *n* is the refractive index of the solution, *F* is the two-photon excited fluorescence integral intensity and ϕ is the fluorescence quantum yield.

Theoretical calculations were carried out using the Gaussian 09 program.^[43] The molecular geometry was optimized by density functional theory (DFT) methods at the B3LYP function and the 6-31 G(d) basis sets. Vertical electronic transitions were obtained by time-dependent density functional theory (TD-DFT) methods at the B3LYP/6-31 G(d) level. The UV-vis absorption spectra were calculated by the Origin program, revision 9.1, at the Gaussian model.

Synthesis

Bromo(naphthalen-2-ylmethyl)triphenylphosphorane (BNTP): BNTP was synthesized referring to the literature by our research group.^[23]

1-hexyl-1H-indole-5-carbaldehyde (HIC): Potassium iodide (200 mg, 1.20 mmol), 1*H*-indole-5-carbaldehyde (**ICD**) (1462 mg, 10.00 mmol) and K₂CO₃ (2073 mg, 15.00 mmol) were added into acetone (30 mL) under argon atmosphere. Then, 1-Bromohexane (C₆H₁₃Br, 2 mL, 15.00 mmol) dissolved in acetone (15 mL) was slowly added dropwise into the reaction mixture. After addition, the reaction mixture was then stirred at 100°C for 48 h under argon atmosphere. A few drops of water were added to quench the reaction. The mixture was extracted by CH₂Cl₂ (3 × 100 mL). The organic layer was washed with water for three times (3 × 100 mL) and dried over anhydrous Na₂SO₄. The solvent was removed *in vacuo*, the residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 40:1 v/v) to give a yellow liquid **HIC** (894 mg). Yield: 39%. HRMS: calcd for C₁₅H₁₉NO [M+H]⁺: 230.1539; found: 230.1513.

1-hexyl-5-vinyl-1*H***-indole (HVI):** Methyltriphenylphosphonium iodide ([Ph₃PCH₃]⁺I⁻, 1314 mg, 3.25 mmol) was dissolved in dry THF (10 mL) under argon atmosphere and the solution was cooled to -10°C. Potassium *t*-butoxide (KOtBu, 480 mg, 4.28 mmol) was added and stirred for 1 min. A solution of **HIC** (745 mg, 3.25 mmol) in dry THF (10 mL) was

added dropwise into the reaction mixture. After addition, the mixture was stirred for 10 min. A few drops of water were added to guench the reaction. The mixture was extracted by CH_2Cl_2 (3 × 100 mL). The organic layer was washed with water for three times (3 \times 100 mL) and dried over anhydrous Na₂SO₄. The solvent was removed in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether) to give a cololess liquid HVI (310 mg). Yield: 42 %. ¹H NMR (400 MHz, CDCl₃): δ = 7.55 (d, J = 1.2 Hz, 1H; Ar-H), 7.27 (dd, J = 5.0 Hz, 1H; Ar-H), 7.19 (t, J = 8.8 Hz, 1H; Ar-H), 6.99 (d, J = 3.2 Hz, 1H; Ar-H), 6.76 (dd, J = 14.4 Hz, 1H; Ar-H), 6.39-6.37 (m, 1H; Ar-H), 5.62 (dd, J = 9.2 Hz, 1H; Ar-H), 5.05 (dd, J = 5.8 Hz, 1H; Ar-H), 4.01 (t, J = 7.2 Hz, 2H; hexyl-H), 1.74 (t, J = 7.2 Hz, 2H; hexyl-H), 1.21 (t, J = 6.4 Hz, 6H; hexyl-H), 081-0.77 (m, 3H; hexyl-H) ppm. ¹³C NMR (400 MHz, CDCl₃): δ = 136.91, 134.80, 128.13, 127.64, 127.29, 118.47, 118.37, 109.60, 108.41, 100.18, 45.47, 30.39, 29.20, 25.61, 21.50, 12.98 ppm. HRMS: calcd for C16H21N [M+H]+: 228.1746; found: 228.1702.

(E)-5-(2-(anthracen-2-yl)vinyl)-1-hexyl-1H-indole (AVHI): K2CO3 (691 mg, 5.00 mmol), 2-Bromoanthracene (1286 mg, 5.00 mmol), Tri(otolyl)phosphine (1522 mg, 5.00 mmol), Palladium acetate (112 mg, 0.50 mmol) and HVI (1136 mg, 5.00 mmol) were added into anhydrous DMF (30 mL) under argon atmosphere. After bubbling argon for 30 min, the reaction mixture was then stirred at 100°C for 48 h under argon atmosphere. A few drops of water were added to quench the reaction. The mixture was extracted by CH_2Cl_2 (3 × 100 mL). The organic layer was washed with water for three times (3 \times 100 mL) and dried over anhydrous Na₂SO₄. The solvent was removed in vacuo, the residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 40:1 v/v) to give a yellow solid AVHI (585 mg). Yield: 29%. ¹H NMR (400 MHz, CDCl₃): *δ* = 8.35 (d, *J* = 2.4 Hz, 2H; Ar-H), 7.97-7.92 (m, 4H; Ar-H), 7.79 (d, J = 8.4 Hz, 2H; Ar-H), 7.51-7.22 (m, 6H; Ar-H), 7.08 (d, J = 2.0 Hz, 1H; Ar-H), 6.51 (d, J = 2.4 Hz, 1H; Ar-H), 4.08 (t, J = 7.2 Hz, 2H; hexyl-H), 1.83 (t, J = 6.8 Hz, 2H; hexyl-H), 1.30 (s, 6 H; hexyl-H), 0.87 (t, J = 6.8 Hz, 3H; hexyl-H) ppm. ¹³C NMR (400 MHz, CDCl₃): $\delta = 135.98$, 135.10, 132.18, 132.15, 131.64, 131.15, 130.68, 129.00, 128.98, 128.50, 128.48, 128.24, 128.12, 126.13, 126.04, 125.44, 125.20, 123.22, 120.11, 119.94, 109.77, 101.42, 46.57, 31.45, 30.29, 26.69, 22.56, 14.02 ppm. HRMS: calcd for C₃₀H₂₉N [M+H]⁺: 404.2372; found: 404.2329.

15-hexyl-15H-tetraphenyl[1,2-e]indole (HTPI): Argon was bubbled through a solution of AVHI (182 mg, 0.45 mmol) in benzene (500 mL) with stirring for 30 min. After I2 (117 mg, 0.46 mmol) and propylene oxide (18 mL, 258.00 mmol) were added into the solution, the reaction mixture was irradiated by a 500 W high pressure mercury lamp through a quartz filter. The reaction was stopped 30 min later. The residue was dissolved in CH₂Cl₂ (20 mL) when the solvent had been removed in vacuo. The solution was then washed with aqueous $Na_2S_2O_3$ (60 mL, 15%) and water sequentially. The organic layer was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 25:1 v/v) to give a yellow solid HTPI (18 mg). Yield: 10%. ¹H NMR (400 MHz, CDCl₃): δ = 8.37 (s, 2H; Ar-H), 7.98 (d, J = 9.2 Hz, 4H; Ar-H), 7.82-7.79 (m, 1H; Ar-H), 7.59 (s, 1H; Ar- H), 7.56-7.53 (m, 1H; Ar-H), 7.48-7.40 (m, 2H; Ar- H), 7.35 (s, 1H; Ar-H), 7.32- 7.24 (m, 1H; Ar-H), 7.18 (s, 1H; Ar-H), 4.10 (t, J = 7.2 Hz, 2H; hexyl-H), 1.82 (t, J = 6.4 Hz, 2H; hexyl-H), 1.34-1.25 (m, 6H; hexyl-H), 0.88 (t, J = 7.2 Hz, 3H; hexyl-H) ppm. ¹³C NMR (400 MHz, $CDCl_3$): $\delta = 136.02, 134.83, 132.34, 132.14, 132.10, 131.69, 131.18,$ 130.85, 130.09, 129.99, 128.57, 128.24, 128.12, 126.91, 126.47, 126.13, 126.08, 125.48, 125.28, 123.10, 121.24, 119.93, 110.04, 55.51, 46.95, 31.39, 30.33, 26.60, 22.51, 14.00 ppm. MS (MALDI-TOF): calcd for C₃₀H₂₇N [M+H]⁺: 403.22; found: 403.02. HRMS: calcd for C₃₀H₂₇N [M+H]⁺: 403.2177; found: 403.2256.

(*E*)-5-(2-(dibenzo[b,d]thiophen-2-yl)vinyl)-1-hexyl-1*H*-indole (DTVHI): 2-Bromodibenzothiophene (1316 mg, 5.00 mmol), K_2CO_3 (691 mg, 5.00 mmol), Tri(o-tolyl)phosphine (1522 mg, 5.00 mmol), Palladium acetate (112 mg, 0.50 mmol) and HVI (1136 mg, 5.00 mmol) were added into anhydrous DMF (30 mL) under argon atmosphere. After bubbling argon for 30 min, the reaction mixture was then stirred at 100°C for 48 h under



argon atmosphere. A few drops of water were added to quench the reaction. The mixture was extracted by CH_2Cl_2 (3 × 100 mL). The organic layer was washed with water for three times (3 \times 100 mL) and dried over anhydrous Na₂SO₄. The solvent was removed in vacuo, the residue was purified by flash chromatography on silica gel (petroleum ether) to give a white solid **DTVHI** (593 mg). Yield: 29%. ¹H NMR (400 MHz, CDCI₃): δ = 8.25 (d, J = 1.2 Hz, 1H; Ar-H), 8.23-8.19 (m, 1H; Ar-H), 7.87-7.82 (m, 1H; Ar-H), 7.79 (t, J = 3.6 Hz, 2H; Ar-H), 7.67 (dd, J = 4.2 Hz, 1H; Ar-H), 7.51-7.43 (m, 3H, Ar-H), 7.35 (t, J = 8.0 Hz, 2H, Ar-H), 7.25 (t, J = 4.8 Hz, 1H, Ar-H), 7.10 (s, 1H, Ar-H), 6.51 (d, J = 2.0 Hz, 1H; Ar-H), 4.11 (t, J = 7.2 Hz, 2H; hexyl-H), 1.84 (m, 2H; hexyl-H), 1.5-1.27 (m, 6H; hexyl-H), 0.88 (t, J = 6.8 Hz, 3H; hexyl-H) ppm. ¹³C NMR (400 MHz, CDCl₃): δ = 139.94, 137.90, 136.04, 135.91, 135.56, 134.87, 130.11, 128.97, 128.92, 128.46, 126.73, 125.70, 124.96, 124.39, 122.91, 122.81, 121.64, 120.01, 119.78, 119.21, 109.74, 101.37, 46.58, 31.44, 30.29, 26.68, 22.55, 14.01 ppm. HRMS: calcd for C₂₈H₂₇NS [M+H]⁺: 410.1936; found: 410.1899.

14-hexyl-14H-benzo[4',5']thieno[2',3':7,8]naphtha[1,2-e]indole

(HBTNI): Argon was bubbled through a solution of DTVHI (184 mg, 0.45 mmol) in benzene (500 mL) with stirring for 30 min. After I₂ (117 mg, 0.46 mmol) and propylene oxide (18 mL, 258.00 mmol) were added into the solution, the reaction mixture was irradiated by a 500 W high pressure mercury lamp through a quartz filter. The reaction was stopped 30 min later. The residue was dissolved in CH2Cl2 (20 mL) when the solvent had been removed in vacuo. The solution was then washed with aqueous $Na_2S_2O_3$ (60 mL, 15%) and water sequentially. The organic layer was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 25:1 v/v) to give a white solid HBTNI (26 mg). Yield: 14%. ¹H NMR (400 MHz, CDCl₃): *δ* = 9.69 (s, 1H; Ar-H), 8.69 (s, 1H; Ar-H), 8.33-8.30 (m, 1H; Ar-H), 7.91-7.88 (m, 3H; Ar-H), 7.72 (d, J = 19.2 Hz, 1H; Ar-H), 7.68 (d, J = 2.4 Hz, 2H; Ar- H), 7.52-7.49 (m, 2H; Ar-H), 7.41 (d, J = 3.2 Hz, 1H; Ar-H), 4.30 (t, J = 7.2 Hz, 2H; hexyl-H), 1.93 (t, J = 7.2 Hz, 2H; hexyl-H), 1.34-1.31 (m, 6H; hexyl-H), 0.88 (t, J = 6.8 Hz, 3H; hexyl-H) ppm. ¹³C NMR (400 MHz, CDCl₃): δ = 140.25, 137.87, 135.42, 134.95, 134.00, 130.66, 130.37, 127.68, 127.63, 127.57, 127.22, 124.59, 124.48, 124.23, 123.19, 123.16, 122.88, 121.90, 120.54, 119.31, 110.93, 103.28, 46.86, 31.45, 30.51, 26.70, 22.55, 14.00 ppm. HRMS: calcd for C28H25NS [M+H]+: 408.1780; found: 408.1743.

(E)-3-(2-(1-hexyl-1H-indol-5-yl)vinyl)quinoline (HIVQ): HVI (454 mg, 2.00 mmol), 3-Bromoquinoline (416 mg, 2.00 mmol), K2CO3 (276 mg, 2.00 mmol), Tri(o-tolyl)phosphine (609 mg, 2.00 mmol) and Palladium acetate (45 mg, 0.20 mmol) were added into anhydrous DMF (30 mL) under argon atmosphere. After bubbling argon for 30 min, the reaction mixture was then stirred at 80°C for 48 h under argon atmosphere. A few drops of water were added to quench the reaction. The mixture was extracted by CH_2CI_2 (3 × 100 mL). The organic layer was washed with water for three times (3 \times 100 mL) and dried over anhydrous Na₂SO₄. The solvent was removed in vacuo, the residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 25:1 v/v) to give a yellow solid HIVQ (298 mg). Yield: 42%. ¹H NMR (400 MHz, CDCl₃): δ = 9.18 (d, J = 2.4 Hz, 1H; Ar-H), 8.18 (t, J = 8.4 Hz, 2H; Ar-H), 7.86 (t, J = 3.6 Hz, 2H; Ar-H), 7.72-7.69 (m, 1H; Ar-H), 7.61-7.48 (m, 3H; Ar-H), 7.39 (d, J = 8.8 Hz, 1H; Ar-H), 7.22 (d, J = 16.4 Hz, 1H; Ar-H), 7.14 (d, J = 2.8 Hz, 1H; Ar-H), 6.55 (d, J = 3.2 Hz, 1H; Ar-H), 4.15 (t, J = 7.2 Hz, 2H; Hexyl-H), 1.88 (t, J = 7.2 Hz, 2H; Hexyl-H), 1.34 (t, J = 6.8 Hz, 6H; Hexyl-H), 0.91 (d, J = 14 Hz, 3H; Hexyl-H) ppm. ¹³C NMR (400 MHz, CDCl₃): δ $= 149.37, \ 146.77, \ 136.16, \ 132.64, \ 131.65, \ 131.19, \ 128.94, \ 128.93,$ 128.90, 128.66, 128.34, 128.24, 127.72, 126.97, 121.99, 120.28, 120.01, 109.84, 101.51, 46.57, 31.42, 30.27, 26.65, 22.53, 14.00 ppm. HRMS: calcd for C25H26N2 [M+H]+: 355.2168; found: 355.2176.

7-hexyl-7H-indolo[5,4-k]phenanthridine (HIPD): Argon was bubbled through a solution of **HIVQ** (159 mg, 0.45 mmol) in benzene (500 mL) with stirring for 30 min. After I_2 (117 mg, 0.46 mmol) and propylene oxide (18 mL, 258 mmol) were added into the solution, the reaction mixture was irradiated by a 500 W high pressure mercury lamp through a quartz filter. The reaction was stopped 90 min later. The residue was dissolved

in CH₂Cl₂ (20 mL) when the solvent had been removed *in vacu*o. The solution was then washed with aqueous Na₂S₂O₃ (60 mL, 15%) and water sequentially. The organic layer was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 50:1 v/v) to give a yellow liquid **HIPD** (90 mg). Yield: 57%. ¹H NMR (400 MHz, CDCl₃): δ = 9.36 (s, 1H; Ar-H), 9.15 (d, *J* = 9.2 Hz, 1H; Ar-H), 8.31 (d, *J* = 7.6 Hz, 1H; Ar-H), 8.06 (d, *J* = 8.4 Hz, 1H; Ar-H), 7.81-7.73 (m, 4H; Ar-H), 7.54 (t, *J* = 7.2 Hz, 1H; Ar-H), 7.16-7.10 (m, 2H; Ar-H), 4.26 (t, *J* = 7.2 Hz, 2H; Hexyl-H), 1.93 (t, *J* = 7.2 Hz, 2H; Hexyl-H), 1.35-1.31 (m, 6H; Hexyl-H), 0.89 (t, *J* = 6.8 Hz, 3H; Hexyl-H) ppm. ¹³C NMR (400 MHz, CDCl₃): δ = 152.32, 145.31, 134.65, 131.29, 131.00, 129.54, 128.80, 128.32, 127.81, 125.71, 125.47, 124.58, 124.52, 124.34, 123.45, 122.70, 121.97, 113.10, 105.41, 46.79, 31.43, 30.56, 26.70, 22.55, 14.01 ppm. HRMS: calcd for C₂₅H₂₄N₂ [M+H]⁺: 353.2011; found: 353.2016.

BNTP (E)-1-hexyl-5-(2-(naphthalen-2-yl)vinyl)-1H-indole (HNVI): (1138 mg, 2.36 mmol) was dissolved in dry THF (10 mL) under argon atmosphere and the solution was cooled to -10°C. Potassium t-butoxide (KOtBu, 557 mg, 4.96 mmol) was added and stirred for 1 min. A solution of HIC (541 mg, 2.36 mmol) in dry THF (10 mL) was added dropwise into the reaction mixture. After addition, the mixture was stirred for 15 min. A few drops of water were added to quench the reaction. The mixture was extracted by CH_2Cl_2 (3 \times 100 mL). The organic layer was washed with water for three times (3 \times 100 mL) and dried over anhydrous Na₂SO₄. The solvent was removed in vacuo, the residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 50:1 v/v) to give a white solid HNVI (325 mg). Yield: 39%. ¹H NMR (400 MHz, CDCl₃): δ = 7.89-7.82 (m, 6H; Ar-H), 7.56-7.52 (m, 1H; Ar-H), 7.51-7.44 (m, 2H; Ar-H), 7.39 (t, J = 4.8 Hz, 2H; Ar-H), 7.29 (d, J = 6 Hz, 1H; Ar-H), 7.13 (d, J = 2.8 Hz, 1H; Ar-H), 6.55 (d, J = 2.8 Hz, 1H; Ar-H), 4.15 (t, J = 7.2 Hz, 2H; Hexyl-H), 1.88 (t, J = 7.2 Hz, 2H; Hexyl-H), 1.32 (d, J = 19.6 Hz, 6H; Hexyl-H), 0.92 (t, J = 6.8 Hz, 3H; Hexyl-H) ppm. ¹³C NMR (400 MHz, CDCl₃): δ = 135.93, 135.67, 133.88, 132.76, 130.59, 128.96, 128.93, 128.48, 128.19, 127.89, 127.70, 126.22, 125.88, 125.84, 125.50, 123.64, 120.04, 119.88, 109.75, 101.38, 46.58, 31.46, 30.30, 26.69, 22.57, 14.04 ppm. HRMS: calcd for C₂₆H₂₇N [M+H]⁺: 354.2215; found: 354.2219.

3-hexyl-3H-phenanthro[4,3-e]indole (HPI): Argon was bubbled through a solution of HNVI (159 mg, 0.45 mmol) in benzene (500 mL) with stirring for 30 min. After I₂ (117 mg, 0.46 mmol) and propylene oxide (18 mL, 258.00 mmol) were added into the solution, the reaction mixture was irradiated by a 500 W high pressure mercury lamp through a quartz filter. The reaction was stopped 90 min later. The residue was dissolved in CH_2Cl_2 (20 mL) when the solvent had been removed in vacuo. The solution was then washed with aqueous Na2S2O3 (60 mL, 15%) and water sequentially. The organic layer was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 50:1 v/v) to give a brown liquid HPI (90 mg). Yield: 57%. ¹H NMR (400 MHz, CDCl₃): δ = 9.12 (d, J = 8.4 Hz, 1H; Ar-H), 7.93 (t, J = 9.6 Hz, 2H; Ar-H), 7.86 (d, J = 8.4 Hz, 1H; Ar-H), 7.80 (d, J = 8.4 Hz, 1H; Ar-H), 7.75 (d, J = 8.8 Hz, 1H; Ar-H), 7.67-7.61 (m, 2H; Ar-H), 7.54 (t, J = 7.2 Hz, 1H; Ar-H), 7.43 (t, J = 8 Hz, 1H; Ar-H), 7.01 (d, J = 2.8 Hz, 1H; Hexyl-H), 6.98 (d, J = 3.2 Hz, 1H; Ar-H), 4.15 (t, J = 7.2 Hz, 2H; Hexyl-H), 1.85 (t, J = 7.2 Hz, 2H; Hexyl-H), 1.29 (s, 6H; Hexyl-H), 0.86 (t, J = 6.8 Hz, 3H; Hexyl-H) ppm. ¹³C NMR (400 MHz, CDCl₃): *δ* = 134.43, 132.79, 131.76, 130.33, 129.10, 129.07, 128.36, 127.62, 127.24, 127.03, 126.70, 125.94, 125.05, 124.73, 124.55, 123.74, 123.62, 122.82, 111.10, 105.54, 46.76, 31.53, 30.60, 26.79, 22.64, 14.12 ppm. HRMS: calcd for C₂₆H₂₅N [M+H]⁺: 352.2059; found: 352.2507.

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FULL PAPERS

Novel indole-based helicenes **HTPI**, **HBTNI**, **HIPD** and **HPI** were facilely prepared through a three-step or fourstep reaction. They emitted violet-blue light with maximum peaks ranging from 391 nm to 415 nm in hexane. Furthermore, they all possessed TPA and TPEF, and **HTPI** achieved the maximum TPA with the TPA crosssection of 171.5 GM at 770 nm.



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Indole-Based Aza[*n*]helicenes (*n* = 5, 6) with Violet-Blue Fluorescence and Two-Photon Absorption (TPA)

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