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A Comparison Study of Physicochemical Properties and Stabilities of H-Shaped Molecule and the Corresponding Polymer

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Electronic Supplementary Information

Abstract Rare attention has been paid to the comparison between a monomer and its corresponding polymer in terms of the optoelectronic characteristics. In this article, a model H-shaped molecule and its corresponding polymer, both of which exhibited similar properties including blue emission and solution processing, were designed and synthesized. Optoelectronic properties and various kinds of stability features, including the thermostabilities, spectral stabilities and amplified spontaneous emission characteristic of the monomer and polymer were investigated. In general, the corresponding polymer **PH** exhibited similar optoelectronic properties but deteriorated stabilities compared with its H-shaped monomer **H-1** probably owing to the similar chemical structure but the wider molecular weight distribution and metal catalyst residue. Importantly, monomer **H-1** displayed a comparable ASE threshold value with its polymer **PH**, suggesting that H-shaped fluorene-based small molecules may be more promising optical gain media in solid state amplifiers and lasers.

Keywords Fluorene; H-shape; Stability; Optoelectronic materials

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INTRODUCTION

Organic semiconducting materials have attracted considerable attention in the scientific and industrial fields due to their great promise in various low-cost and large-area photoelectronic applications.^[1–3] In this context, diverse photoelectric devices, such as organic light-emitting diode (OLED),^[4–6] organic laser,^[7–10] organic photovoltaic (OPV),^[11–13] and organic field-effect transistor (OFET),^[14,15] have been developed in the past several decades. As a typical wide band-gap semiconductor, fluorene-based oligomers or polymers are one of the most popular blue or sky-blue emitting materials.^[16,17] Meanwhile, polyfluorenes exhibit various morphologies, including amorphous phase,^[18,19] β -phase,^[20–23] liquid crystalline,^[24] semicrystalline α - and α' -phases,^[25,26] which offer possibility for optimizing the performance of the organic devices. Besides, large steric hindrances such as bulky substituents^[27–29] and spiro-^[30,31] or star-shaped configuration^[32–34] have also been incorporated into fluorene-based optoelectronic materials to prohibit

their interchain aggregation and thus suppress the green band emission, which probably was caused by the interchain-aggregation-induced energy transfer to the fluorenone defect.^[35] Although polyfluorenes have given rise to intense academic research in this area due to morphology stability, ease of processing and versatility of functionalization, small molecules based on fluorene have their intrinsic advantages, including high repeatability, easy purification and well-defined structure. However, the comparative study about fluorene-based small molecules and their corresponding polymers is still unexplored in the literature on account of their distinction in basic photophysical properties.

In our previous work, H-shaped molecular architectures have demonstrated impressively high thermal stability,^[36,37] and nonplanar diarylfluorenes are found to serve as one series of state-of-the-art organic luminescent materials with high glass transition temperatures and environmental stability.^[22,23] Recently, asymmetrically H-shaped fluorene-based oligomers have been developed to fabricate highly air-stable and low-threshold non-doped deep blue lasing,^[36] which provide not only a platform for us to acquire high performance organic semiconductors but also a model monomer with the characteristic of blue emission and solution processing distinguished from traditional monomer. Herein, a novel H-

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shaped molecule and the corresponding wide bandgap polymer were designed and synthesized. The chemical structures, physicochemical properties and stabilities of the H-shaped molecule and its polymer were characterized by nuclear magnetic resonance (NMR) spectroscopy, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS), gel permeation chromatography (GPC), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), UV-Visible absorption spectroscopy and fluorescence spectroscopy (UV/PL). As promising materials for lasing applications, the optically pumped amplified spontaneous emission (ASE) properties for both of them were also discussed.

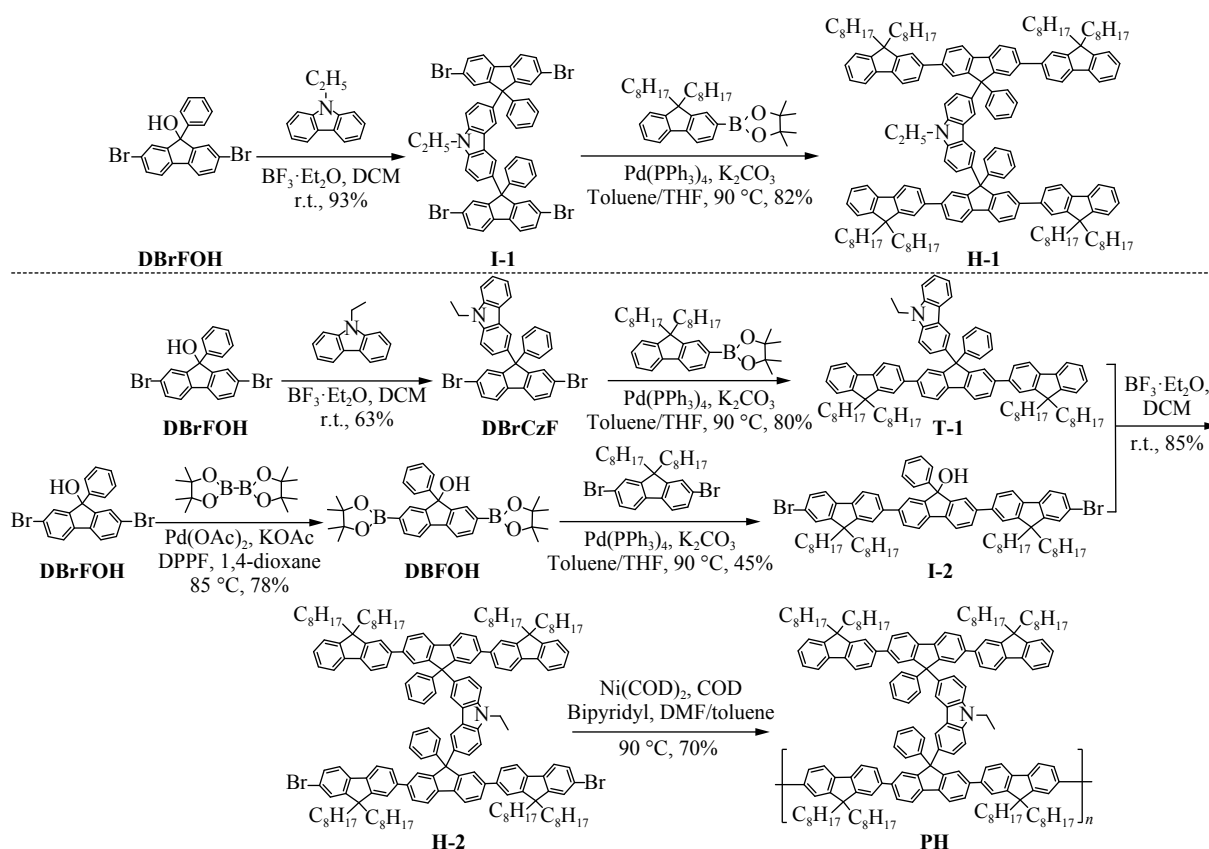
RESULTS AND DISCUSSION

Synthesis and Characterization

The synthetic routes for oligofluorene **H-1** and its polymer **PH** are illustrated in Scheme 1. Details of the synthetic route towards **H-1** and its polymer **PH** and the experimental section are provided in the electronic supplementary information (ESI). For the synthesis of oligofluorene **H-1**, only two synthetic steps are needed. Firstly, the precursor of **H-1**, compound **I-1** is obtained through $\text{BF}_3 \cdot \text{Et}_2\text{O}$ -mediated Friedel-Crafts reaction (BFR) of **DBrFOH** and *N*-ethylcarbazole with an excellent yield of 93%. Then oligofluorene **H-1** can be successfully achieved via palladium-catalyzed Suzuki cross-coupling reaction of **I-1** and 2-(pinacolato)diboron-9,9-dioctylfluorene with an overall yield of up to

76% from **DBrFOH**. For the synthesis of polymer **PH**, the polymerization method used in this work is Yamamoto coupling polymerization so that the bromine-substituted monomer should be acquired first. Compound **T-1** is synthesized in a similar way as that of **I-1** with the difference of the equivalent of 1:1 rather than 2:1 between compound **DBrFOH** and *N*-ethylcarbazole and the equivalent of 2:1 instead of 4:1 between the corresponding precursor and 2-(pinacolato)diboron-9,9-dioctylfluorene. Subsequently, the monomer **H-2** is obtained by the BFR between compound **T-1** and **I-2** that can be gained through a simple Suzuki cross-coupling reaction of **DBFOH** and 2,7-dibromo-9,9-dioctylfluorene. In the final step, the Yamamoto coupling polymerization is smoothly carried out to afford polymer **PH** with a high yield of up to 70%. Overall, H-shaped molecule and its polymer could be obtained concisely and smoothly via BFR, Suzuki cross-coupling reaction and the Yamamoto coupling polymerization. Importantly, both **H-1** and **PH** exhibit good solubility in common solvents such as chloroform, THF and toluene due to the long octyl chains at the 9-position of fluorenes and twisted conformation, guaranteeing the solution-processing in the potential photoelectronic applications.

The purities and chemical structures of **H-1**, **H-2** and **PH** are characterized via ^1H - and ^{13}C -NMR, MALDI-TOF-MS. Fig. 1(a) illustrates the ^1H -NMR spectra of **H-1** and its precursor **I-1** and 2-(pinacolato)diboron-9,9-dioctylfluorene. As shown in Fig. 1(a), the successful formation of **H-1** is validated by the disappearance of the singlet peak at 1.42 ppm of



Scheme 1 The synthetic routes to H-shaped molecule **H-1** and its polymer **PH**

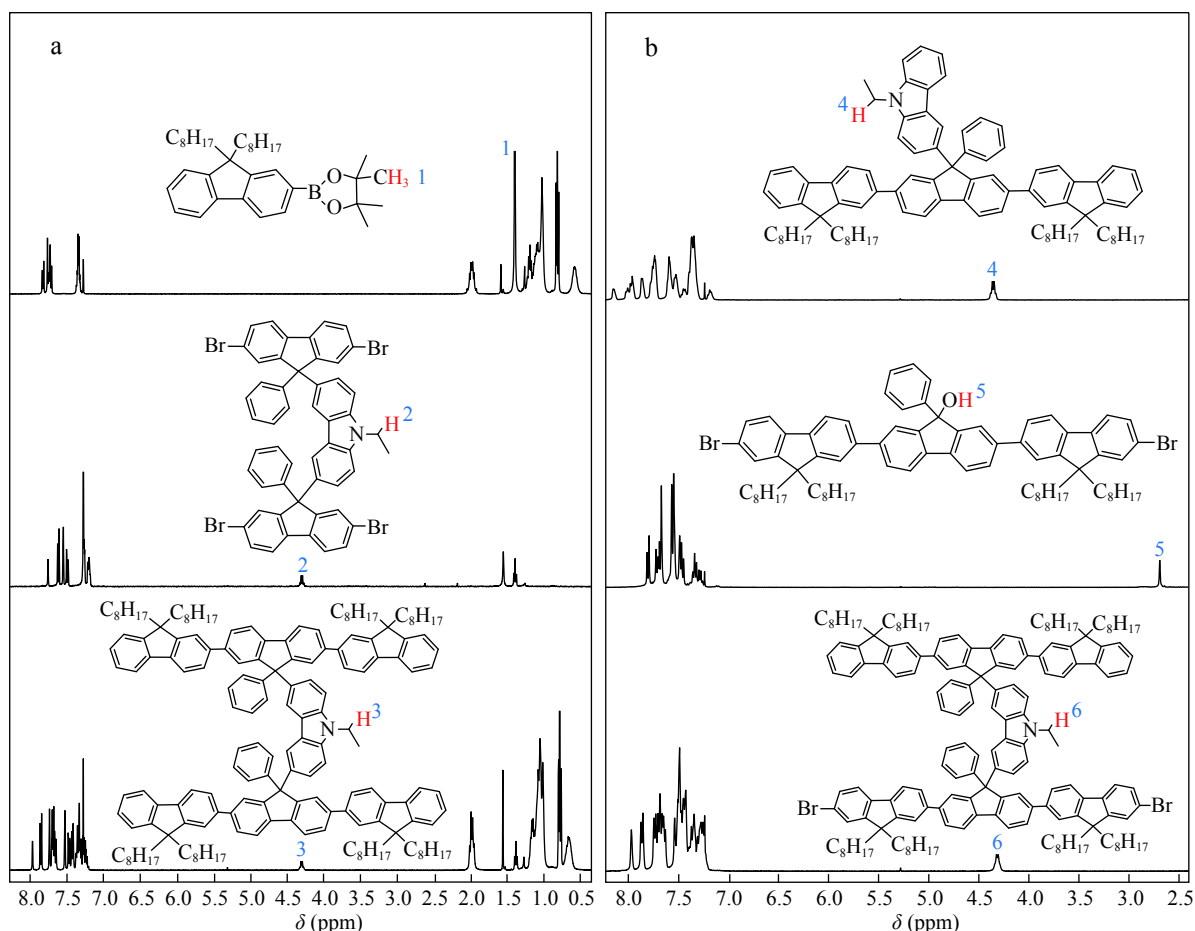


Fig. 1 (a) ^1H -NMR spectra of **H-1** and its precursors; (b) ^1H -NMR spectra of **H-2** and its precursors

^1H -NMR spectrum for the starting material 2-(pinacolato)diboron-9,9-dioctylfluorene and the appearance of a set of the alkyl peaks ranging from 0.52 ppm to 2.12 ppm, as well as quartet peak at $\delta = 4.32$ ppm in the ^1H -NMR spectrum for the product. Fig. 1(b) shows the ^1H -NMR spectra of **H-2** and its precursor **T-1** and **I-2**. It can be seen from the ^1H -NMR spectra of precursor **T-1** and **I-2** that the signals at $\delta = 4.37$ ppm and $\delta = 2.70$ ppm are ascribed to the proton at the α -carbon of alkoxy in carbazole and the proton of hydroxyl group, respectively. As can be seen in ^1H -NMR spectrum of **H-2**, the proton signal of hydroxyl group at $\delta = 2.70$ ppm disappears and the proton signal of methylene in the *N*-ethylcarbazole unit at $\delta = 4.33$ ppm appears. The result illustrates the formation of compound **H-2**. In addition, MALDI-TOF mass spectrometry of **H-2** (Fig. S15, in ESI) shows that the experimental value is 2386.5, which is well consistent with hydrocarbon of the molecular formula $\text{C}_{168}\text{H}_{195}\text{Br}_2\text{N}$. The above results fully demonstrate the formation of **H-2**. As shown in Fig. S8 (in ESI), the ^1H -NMR spectrum of **PH** is almost the same as that of its monomer **H-2**. According to the integral area of peaks, the number of the protons is confirmed. The gel permeation chromatography reveals the number-average molecular weight (M_n) of **PH** to be 4.2×10^4 Da (PDI = 1.37), indicating that the number of repeat units (n) is *ca.* 17. It can be seen from Fig. 2 that **H-1** displays a glass transition temperatures (T_g) of 86 °C and a

decomposition temperature (T_d) of up to 415 °C (5% weight loss). Upon polymerization, the polymer exhibits a similar T_d of up to 411 °C but a much higher T_g of 158 °C, suggesting both of these fluorene-based semiconductors possess excellent thermal stabilities.

Electrochemical Properties

The electrochemical behaviors of oligofluorene **H-1** and its polymer **PH** are studied by cyclic voltammetry (CV) using ferrocene as the internal standard and their corresponding data are listed in Table 1. Fig. S18 (in ESI) shows the redox CV curves of **H-1** and **PH**. The oxidation onset potential of **H-1** is recorded at 0.75 V versus Ag/Ag^+ . As a result, the HOMO energy level is estimated to be -5.52 eV according to the empirical formula $E_{\text{HOMO}} = -(E_{\text{ox}} - E_{\text{Fc}}) - 4.8$ eV, where the value of E_{Fc} for ferrocene is 0.03 V versus Ag/Ag^+ , and 4.8 eV is the energy level of ferrocene below vacuum. Obviously, the HOMO value of oligofluorene **H-1** is mainly attributed to the trifluorene moieties, which is consistent with the previous literature.^[38] There is no obvious oxidation peak of *N*-ethylcarbazole around 0.87 V probably because the carbazole group is surrounded by two trifluorenes in the H-shaped molecule.^[39] The reduction onset potential is measured to be -2.53 V for compound **H-1**, from which the LUMO energy level of **H-1** is calculated to be -2.24 eV. It is reasonable that polymer **PH** exhibits a similar redox behaviors

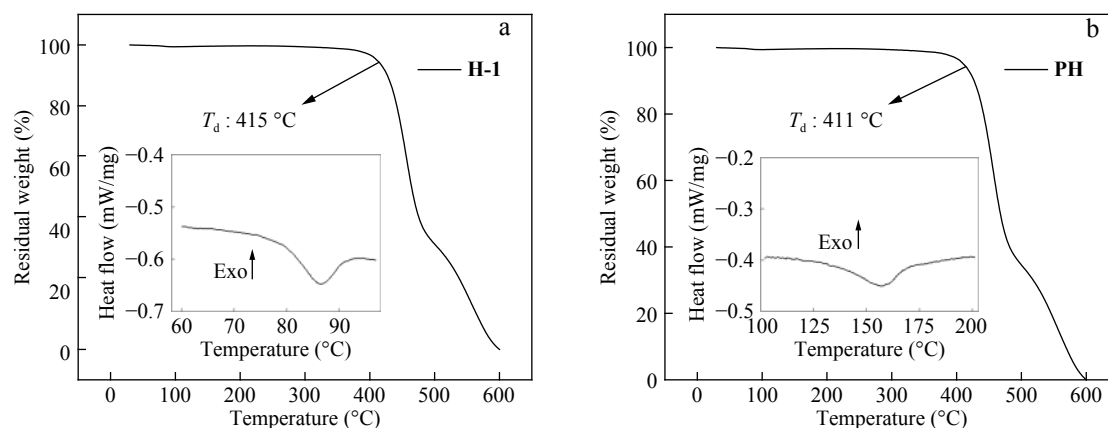


Fig. 2 (a) TGA curve of **H-1**, inset: DSC curve of **H-1**; (b) TGA curve of **H-1**, inset: DSC curve of **PH**

Table 1 Summary of basic properties of **H-1** and **PH**

	T_g (°C)	T_d (°C)	Solution				Film				LUMO (eV)	HOMO (eV)
			λ_{abs} (nm)	λ_{PL} (nm)	τ (ns)	PLQY (%)	λ_{abs} (nm)	λ_{PL} (nm)	τ (ns)	PLQY (%)		
H-1	86	415	353	398, 419, 443	0.76	100	353	404, 424, 446	0.62	45	-2.24	-5.52
PH	158	411	370	420, 446, 475	0.53	100	370	430, 450, 483	0.50	49	-2.32	-5.51

and almost identical HOMO and LUMO energy level values.

Optical and Morphological Properties

The absorption and emission spectra of oligofluorene **H-1** and its polymer **PH** in dilute chloroform solutions are shown in Fig. 3, and the characteristic data are collected in Table 1. **H-1** exhibits only one unstructured main absorption band in the ultraviolet region (250–400 nm) with the maximum absorption peak at 353 nm derived from the π - π^* transition of the trifluorene conjugated backbone. However, the emission spectra are well-structured with three apparent emission bands at 398, 419 and 443 nm for the dilute solution of **H-1**, corresponding to 0-0, 0-1, and 0-2 vibronic progressions (Fig. 3a). For the emission spectra of **H-1** spin-coated film, a distinct red-shift is observed in the spectra with the maximum emission peak at 424 nm (0-1 transition) probably due to the change of dielectric constant^[40] and/or the existence of aggregation to some extent.^[41] Not surprisingly, the photoluminescence quantum yields (PLQY) of **H-1** and **PH** are both over 40% owing to the fluorene-based structures with steric hindrance groups that suppress the interchain aggregation. Upon polymerization, as shown in Fig. 3(b), polymer **PH** displays a broader absorption band (250–425 nm) and a $\sim$ 17 nm red-shift in the absorption spectra of its solution and the film due to the extended π -conjugation and the energy transition from trifluorene to polyfluorene chain. Similarly, the corresponding emission peaks also bathochromically shift. Especially, the emission peaks of the **PH** film are bathochromic-shifted to 430, 450 and 483 nm, respectively, suggesting the amorphous state.^[42]

The changes of PL spectra in the film state after thermal annealing treatment are the most used method to evaluate the spectral stability of the light-emitting molecules and polymers. Therefore, the spectral stabilities of **H-1** and its polymer **PH** are studied in terms of PL spectra after thermal annealing treatment. As shown in Fig. 3(c), the PL spectra of **H-1** exhibit relatively well stability with *ca.* 20% enhance-

ment in intensities of the green band emission after annealing for 4 h at 180 °C in air. On the contrary, the green band emission in the PL spectrum of **PH** is dramatically increased, where the intensity is even higher than that of 0-0 transition emission (Fig. 3d), suggesting **H-1** exhibits a better spectral stability. Besides, UV light possessing high energy usually can be used as the trigger to initiate some photochemical reactions, and hence induce the photo-degradation. Actually, it is revealed that UV light can induce the green band emission of fluorene-based small molecules and polymers.^[41] To further study the photochemical stability of two materials, **H-1** and its polymer **PH** are directly and heavily irradiated by a UV lamp at 365 nm for 2 h. As shown in Fig. 3(e), there is almost no photo-degradation (rated as the intensity of the low-energy band with respect to the main fluorescence peak) after 2 h UV light irradiation for compound **H-1**. In contrast, an obvious emission band at long wavelength ranging from 500–600 nm is observed for **PH** after the same treatment (Fig. 3f), indicating **H-1** shows a much better photochemical stability than polymer **PH**. There are two possible reasons for this phenomenon: one is that polymer is a mixture of molecules with different molecular weights; the other is that some metal catalyst packaged in polymer during the polymerization cannot be completely removed in the purification processes. In this context, energy dispersive spectrometer (EDS) experiments were conducted. As shown in Fig. S17 (in ESI), the results show that there is almost no bromo in the solid polymer **PH** after purification compared with its monomer but 0.94 wt% residual nickel is observed.

ASE Properties

In order to investigate the possibility of **H-1** and **PH** applied in organic lasers, ASE properties of **H-1** and **PH** were investigated preliminarily. As shown in Fig. 4, both **H-1** and **PH** show ASE behaviour; the ASE peaks of **H-1** film and **PH** film are located at 422 and 445 nm, respectively. Besides, the ASE threshold of **H-1** is $19.23 \mu\text{J}\cdot\text{cm}^{-2}$, which is

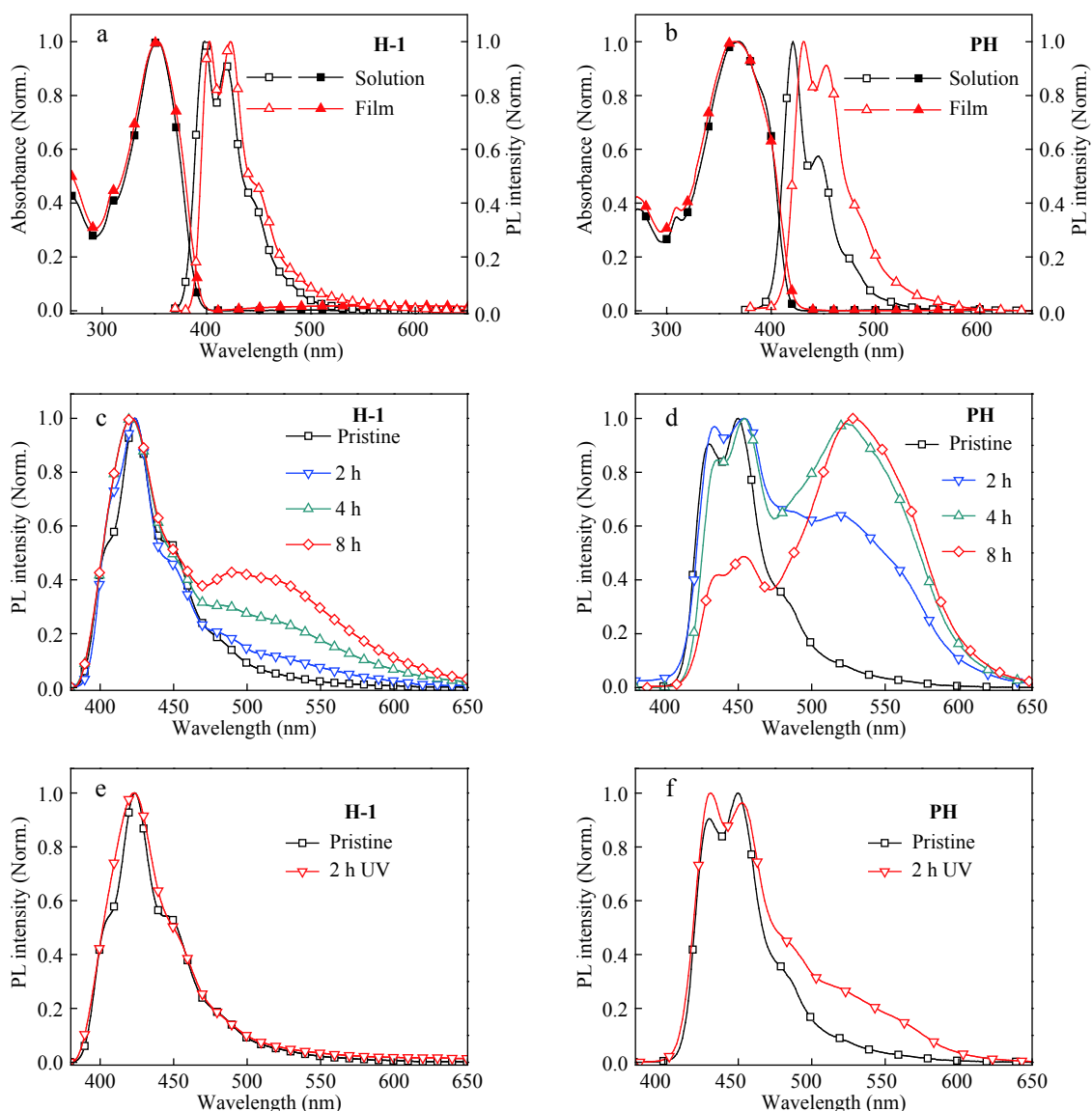


Fig. 3 UV-Vis and PL spectra of (a) **H-1** and (b) **PH** in dilute solution and film; PL spectra of (c) **H-1** and (d) **PH** film after thermal annealing at 180 °C in air; PL spectra of (e) **H-1** and (f) **PH** film under UV irradiation at 365 nm in air

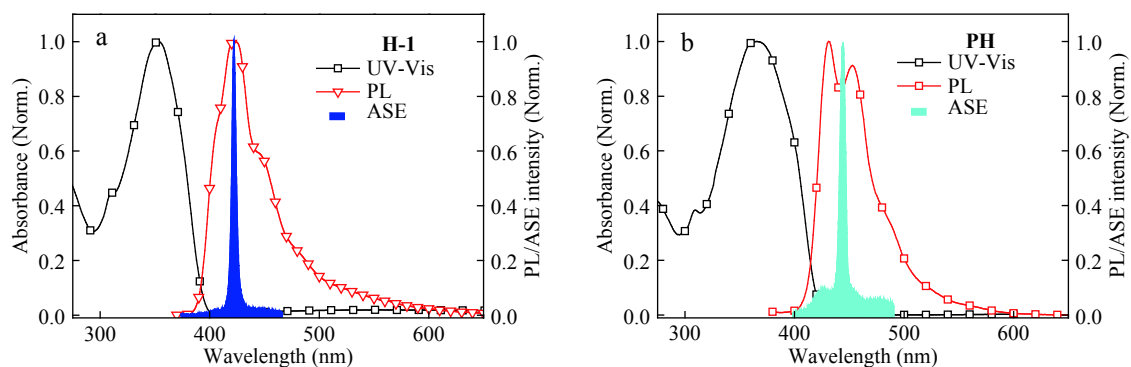


Fig. 4 ASE spectra (excited at 355 nm) of (a) **H-1** and (b) **PH**

a little higher than that of **PH** ($15.82 \mu\text{J}\cdot\text{cm}^{-2}$) on the same experimental apparatus (Table 2). The above results indicate that **H-1** is a more promising optical gain medium in terms of solid state amplifier and lasers.

CONCLUSIONS

In conclusion, a novel H-shaped molecule **H-1** and its polymer **PH** have been synthesized. Both **H-1** and **PH**

Table 2 ASE characteristic of **H-1** and **PH** films

	ASE wavelength (nm)	Transition type	ASE threshold ($\mu\text{J}\cdot\text{cm}^{-2}$)
H-1	422	0-1	19.23
PH	445	0-1	15.82

exhibit good solubility in common solvents and excellent thermal stability. As demonstrated by annealing and UV light treatment, H-shaped molecule **H-1** exhibits better spectral stability and photochemical stability than the corresponding polymer **PH**. Besides, **H-1** shows a comparable ASE threshold with **PH**. Above results indicate that **H-1** is a more promising optoelectronic material than **PH**.

Electronic Supplementary Information

The electronic supplementary information (ESI), including the experimental procedures and spectral data, is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-018-2152-5>.

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REFERENCES

- Xie, L. H.; Yin, C. R.; Lai, W. Y.; Fan, Q. L.; Huang, W. Polyfluorene-based semiconductors combined with various periodic table elements for organic electronics. *Prog. Polym. Sci.* **2012**, *37*, 1192–1264.
- Cao, Y.; Zhang, J.; Bai, Y.; Li, R.; Zakeeruddin, S. M.; Grätzel, M.; Wang, P. Dye-sensitized solar cells with solvent-free ionic liquid electrolytes. *J. Phys. Chem. C* **2008**, *112*, 13775–13781.
- Feldblyum, J. I.; McCreery, C. H.; Andrews, S. C.; Kurosawa, T.; Santos, E. J.; Duong, V.; Fang, L.; Ayzner, A. L.; Bao, Z. Few-layer, large-area, 2D covalent organic framework semiconductor thin films. *Chem. Commun.* **2015**, *51*, 13894–13897.
- White, M. S.; Kaltenbrunner, M.; Glowacki, E. D.; Gutnichenko, K.; Kettlgruber, G.; Graz, I.; Aazou, S.; Ulbricht, C.; Egbe, D. A. M.; Miron, M. C.; Major, Z.; Scharber, M. C.; Sekitani, T.; Someya, T.; Bauer, S.; Sariciftci, N. S. Ultrathin, highly flexible and stretchable PLEDs. *Nat. Photon.* **2013**, *7*, 811–816.
- Sun, M. L.; Zhong, C. M.; Li, F.; Pei, Q. B. Purified polar polyfluorene for light-emitting diodes and light-emitting electrochemical cells. *Chinese J. Polym. Sci.* **2012**, *30*, 503–510.
- Grimsdale, A. C.; Chan, K. L.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. Synthesis of light-emitting conjugated polymers for applications in electroluminescent devices. *Chem. Rev.* **2009**, *109*, 897–1091.
- Prasad, L. G. Azo dye doped polymer films for nonlinear optical applications. *Chinese J. Polym. Sci.* **2014**, *32*, 650–657.
- Ford, E. B.; Lystad, V.; Rasio, F. A. Planet-planet scattering in the epsilon Andromedae system. *Nature* **2005**, *434*, 873–876.
- Wei, Q.; Li, Y.; Liu, J. G.; Fang, Q. Y.; Li, J. W.; Yan, X. H.; Xie, L. H.; Qian, Y.; Xia, R. D.; Huang, W. A High performance deep blue organic laser gain material. *Adv. Opt. Mater.* **2017**, *5*, 1601003.
- Samuel, I. D. W.; Turnbull, G. A. Organic semiconductor lasers. *Chem. Rev.* **2007**, *107*, 1272–1295.
- Islam, A.; Liu, Z. Y.; Peng, R. X.; Jiang, W. G.; Lei, T.; Li, W.; Zhang, L.; Yang, R. J.; Guan, Q.; Ge, Z. Y. Furan-containing conjugated polymers for organic solar cells. *Chinese J. Polym. Sci.* **2017**, *35*, 171–183.
- Brabec, C. J.; Gowrisanker, S.; Halls, J. J.; Laird, D.; Jia, S.; Williams, S. P. Polymer-fullerene bulk-heterojunction solar cells. *Adv. Mater.* **2010**, *22*, 3839–3856.
- Gunes, S.; Neugebauer, H.; Sariciftci, N. S. Conjugated polymer-based organic solar cells. *Chem. Rev.* **2007**, *107*, 1324–1338.
- Sirringhaus, H. Device physics of solution-processed organic field-effect transistors. *Adv. Mater.* **2005**, *17*, 2411–2425.
- Hamadani, B. H.; Natelson, D. Temperature-dependent contact resistances in high-quality polymer field-effect transistors. *Appl. Phys. Lett.* **2004**, *84*, 443–445.
- Yap, B. K.; Xia, R. D.; Campoy-Quiles, M.; Stavrinou, P. N.; Bradley, D. D. Simultaneous optimization of charge-carrier mobility and optical gain in semiconducting polymer films. *Nat. Mater.* **2008**, *7*, 376–380.
- Yu, M. N.; Ou, C. J.; Liu, B.; Lin, D. Q.; Liu, Y. Y.; Xue, W.; Lin, Z. Q.; Lin, J. Y.; Qian, Y.; Wang, S. S.; Cao, H. T.; Bian, L. Y.; Xie, L. H.; Huang, W. Progress in fluorene-based wide-bandgap steric semiconductors. *Chinese J. Polym. Sci.* **2017**, *35*, 155–170.
- Rabe, T.; Hoping, M.; Schneider, D.; Becker, E.; Johannes, H. H.; Kowalsky, W.; Weimann, T.; Wang, J.; Hinze, P.; Nehls, B. S.; Scherf, U.; Farrell, T.; Riedl, T. Threshold reduction in polymer lasers based on poly(9,9-dioctylfluorene) with statistical binaphthyl units. *Adv. Funct. Mater.* **2005**, *15*, 1188–1192.
- Kuehne, A. J. C.; Kaiser, M.; Mackintosh, A. R.; Wallikewitz, B. H.; Hertel, D.; Pethrick, R. A.; Meerholz, K. Sub-micrometer patterning of amorphous- and β -phase in a crosslinkable poly(9,9-dioctylfluorene): dual-wavelength lasing from a mixed-morphology device. *Adv. Funct. Mater.* **2011**, *21*, 2564–2570.
- Grell, M.; Bradley, D. D. C.; Long, X.; Chamberlain, T.; Inbasekaran, M.; Woo, E. P.; Soliman, M. Chain geometry, solution aggregation and enhanced dichroism in the liquid-crystalline conjugated polymer poly(9,9-dioctylfluorene). *Acta Polym.* **1998**, *49*, 439–444.
- Kuehne, A. J. C.; Mackintosh, A. R.; Pethrick, R. A. β -Phase formation in a crosslinkable poly(9,9-dihexylfluorene). *Polymer* **2011**, *52*, 5538–5542.
- Lin, J. Y.; Zhu, W. S.; Liu, F.; Xie, L. H.; Zhang, L.; Xia, R. D.; Xing, G. C.; Huang, W. A Rational molecular design of β -phase polydiarylfuorenes: synthesis, morphology, and organic lasers. *Macromolecules* **2014**, *47*, 1001–1007.
- Liu, B.; Lin, J. Y.; Liu, F.; Yu, M. N.; Zhang, X. W.; Xia, R. D.; Yang, T.; Fang, Y. T.; Xie, L. H.; Huang, W. A Highly Crystalline and wide-bandgap polydiarylfuorene with β -phase conformation toward stable electroluminescence and dual amplified spontaneous emission. *ACS Appl. Mater. Interfaces* **2016**, *8*, 21648–21655.
- Grell, M.; Bradley, D. D. C.; Ungar, G.; Hill, J.; Whitehead, K. S. Interplay of physical structure and photophysics for a liquid crystalline polyfluorene. *Macromolecules* **1999**, *32*, 5810–5817.
- Knaapila, M.; Torkkeli, M.; Galbrecht, F.; Scherf, U. Crystalline and noncrystalline forms of poly(9,9-dihexylfluorene). *Macromolecules* **2013**, *46*, 836–843.
- Chen, S. H.; Su, A. C.; Su, C. H.; Chen, S. A. Crystalline forms and emission behavior of poly(9,9-di-n-octyl-2,7-fluorene). *Macromolecules* **2005**, *38*, 379–385.

- 27 Tang, R. P.; Tan, Z. A.; Li, Y. F.; Xi, F. Synthesis of new conjugated polyfluorene derivatives bearing triphenylamine moiety through a vinylene bridge and their stable blue electroluminescence. *Chem. Mater.* **2006**, *18*, 1053–1061.
- 28 Setayesh, S.; Grimsdale, A. C.; Weil, T.; Enkelmann, V.; Mullen, K.; Meghdadi, F.; List, E. J. W.; Leising, G. Polyfluorenes with polyphenylene dendron side chains: Toward non-aggregating, light-emitting polymers. *J. Am. Chem. Soc.* **2001**, *123*, 946–953.
- 29 Lee, J.; Cho, H. J.; Jung, B. J.; Cho, N. S.; Shim, H. K. Stabilized blue luminescent polyfluorenes: Introducing polyhedral oligomeric silsesquioxane. *Macromolecules* **2004**, *37*, 8523–8529.
- 30 Jiang, Z.; Liu, Z.; Yang, C.; Zhong, C.; Qin, J.; Yu, G.; Liu, Y. Multifunctional fluorene-based oligomers with novel spiro-annulated triarylamine: Efficient, stable deep-blue electroluminescence, good hole injection, and transporting materials with very high T_g . *Adv. Funct. Mater.* **2009**, *19*, 3987–3995.
- 31 Wu, Y. G.; Li, J.; Fu, Y. Q.; Bo, Z. S. Synthesis of extremely stable blue light emitting poly(spirobifluorene)s with Suzuki polycondensation. *Org. Lett.* **2004**, *6*, 3485–3487.
- 32 Kanibolotsky, A. L.; Berridge, R.; Skabara, P. J.; Perepichka, I. F.; Bradley, D. D. C.; Koeberg, M. Synthesis and properties of monodisperse oligofluorene-functionalized truxenes: Highly fluorescent star-shaped architectures. *J. Am. Chem. Soc.* **2004**, *126*, 13695–13702.
- 33 Zhou, X. H.; Yan, J. C.; Pei, J. Synthesis and relationships between the structures and properties of monodisperse star-shaped oligofluorenes. *Org. Lett.* **2003**, *5*, 3543–3546.
- 34 Liu, X. M.; Xu, J. W.; Lu, X. H.; He, C. B. Novel glassy tetra(*N*-alkyl-3-bromocarbazole-6-yl)silanes as building blocks for efficient and nonaggregating blue-light-emitting tetrahedral materials. *Org. Lett.* **2005**, *7*, 2829–2832.
- 35 Chen, X. W.; Tseng, H. E.; Liao, J. L.; Chen, S. A. Green emission from end-group-enhanced aggregation in polydioctylfluorene. *J. Phys. Chem. B* **2005**, *109*, 17496–17502.
- 36 Qian, Y.; Wei, Q.; Del Pozo, G.; Mroz, M. M.; Luer, L.; Casado, S.; Cabanillas-Gonzalez, J.; Zhang, Q.; Xie, L.; Xia, R.; Huang, W. H-shaped oligofluorenes for highly air-stable and low-threshold non-doped deep blue lasing. *Adv. Mater.* **2014**, *26*, 2937–2942.
- 37 Xie, L. H.; Hou, X. Y.; Tang, C.; Hua, Y. R.; Wang, R. J.; Chen, R. F.; Fan, Q. L.; Wang, L. H.; Wei, W.; Peng, B.; Huang, W. Novel H-shaped persistent architecture based on a dispiro building block system. *Org. Lett.* **2006**, *8*, 1363–1366.
- 38 Zhao, L.; Wang, S. M.; Shao, S. Y.; Ding, J. Q.; Wang, L. X.; Jing, X. B.; Wang, F. S. Stable and efficient deep-blue terfluorenes functionalized with carbazole dendrons for solution-processed organic light-emitting diodes. *J. Mater. Chem. C* **2015**, *3*, 8895–8903.
- 39 Li, M.; Tang, S.; Shen, F. Z.; Liu, M. R.; Xie, W. J.; Xia, H.; Liu, L. L.; Tian, L. L.; Xie, Z. Q.; Lu, P.; Hanif, M.; Lu, D.; Cheng, G.; Ma, Y. G. Highly luminescent network films from electrochemical deposition of peripheral carbazole functionalized fluorene oligomer and their applications for light-emitting diodes. *Chem. Commun.* **2006**, 3393–3395.
- 40 Ou, C. J.; Ding, X. H.; Li, Y. X.; Zhu, C.; Yu, M. N.; Xie, L. H.; Lin, J. Y.; Xu, C. X.; Huang, W. Conformational effect of polymorphic terfluorene on photophysics, crystal morphologies, and lasing behaviors. *J. Phys. Chem. C* **2017**, *121*, 14803–14810.
- 41 Giovannella, U.; Botta, C.; Galeotti, F.; Vercelli, B.; Battiato, S.; Pasini, M. Perfluorinated polymer with unexpectedly efficient deep blue electroluminescence for full-colour OLED displays and light therapy applications. *J. Mater. Chem. C* **2013**, *1*, 5322–5329.
- 42 Yu, M. N.; Soleimaninejad, H.; Lin, J. Y.; Zuo, Z. Y.; Liu, B.; Bo, Y. F.; Bai, L. B.; Han, Y. M.; Smith, T. A.; Xu, M.; Wu, X. P.; Dunstan, D. E.; Xia, R. D.; Xie, L. H.; Bradley, D. D. C.; Huang, W. Photophysical and fluorescence anisotropic behavior of polyfluorene β -conformation films. *J. Phys. Chem. Lett.* **2018**, *9*, 364–372.