

Supporting Information

**Superior light-resistant Dithieno[3,2-*b*:2',3'-*d*]arsole-
based polymers exhibiting ultrastable amplified
spontaneous emission**

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Materials

Tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct, S-Phos, rhodamine-6G, cellulose acetate and poly(3-hexylthiophene-2,5-diyl) regioregular (average $M_w = 50,000-100,000$) were purchased from Sigma-Aldrich Co., Ltd. Chloroform (CHCl_3), hexane, methanol (MeOH), toluene, ethyl acetate, magnesium sulfate (MgSO_4), 28% ammonia solution, 35% hydrochloric acid solution and diacetone alcohol were purchased from Nacalai Tesque, Inc. Tetrahydrofuran (THF), neutral alumina, distilled water, copper(I) Iodide and potassium carbonate (K_2CO_3) were purchased from Wako Pure Chemical Industry, Ltd. Tetrabutylammonium bromide (TBAB), 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene, and, 5,5'-Dibromo-2,2'-bithiophene were purchased from Tokyo Chemical Industry Co., Ltd. SiliaMetS (R) Thiol (40-63 μmol 60 Å, functionalized Silica) was purchased from SiliCycle Inc. All solvents using in Pd-catalyzed coupling reaction were purified by distillation or freeze degasification. 4-Phenyl-2,6-dibromo-dithieno[3,2-*b*:2',3'-*d*]arsole (**DTA-Br**), **DTA-FL**, **DTA-EB**, **DTA-BT**, **DTA-EB'**, **EB-BT** were prepared according to the previous literatures.

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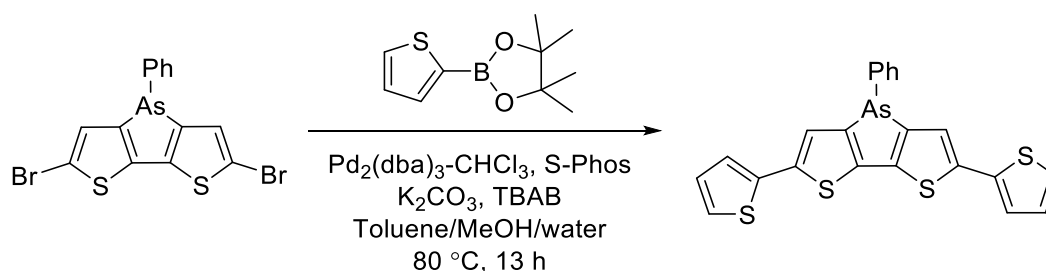
Measurements

^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker AVANCE III 400 NMR spectrometer, and samples were measured in CDCl_3 or Acetone- d_6 using Me_4Si as an internal standard. The following abbreviations are used; s: singlet, d: doublet, t: triplet, m: multiplet. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102A spectrometer. The following abbreviation is used: s: singlet. The UV-vis spectra were recorded on a Jasco spectrophotometer (V-670 KKN). Emission spectra were obtained on an FP-8500 instrument (JASCO), and absolute PL quantum yields (Φ) were determined using a JASCO ILFC-847S instrument; the quantum yield of quinine sulfate reference was 0.52, which is in agreement with the literature value. The absolute method directly obtains the quantum yield by detecting all sample fluorescence through the use of an integrating sphere. Gel permeation chromatography (GPC) was performed using a Shimadzu LC-6AD (Shimadzu, Kyoto, Japan) with a Shodex KF-805 column (Showa Denko, Tokyo, Japan). Tetrahydrofuran (THF) was used as an eluent at a flow rate of 1.0 mL/min. Polystyrene (PS) standards were used to calibrate the GPC system. Amplified spontaneous emission (ASE) from the spin-coated film were monitored using a Tokyo Instruments multichannel spectrometer equipped with 1200 lines/500 nm gratings and an Andor iDus charge-coupled device when the sample film was pumped by a pulse laser delivering 30 ps pulse duration at 355 and 532 nm with 10 Hz repetition rate (Ekspla PL-2403, Lithuania). A pump beam with a diameter of 6.5 mm was focused onto the waveguide type film device using a cylindrical lens ($f = 300$ mm) to make a stripe shape (with length of 6.5 mm and width of 33 μm) excitation beam. The spectrum resolution of multichannel spectrometer is 0.2 nm. The excitation energy reflected by a half-mirror was monitored using Ophir photodiode-type

pyrometer PD10 equipped with a Nova II Display. The energy of ASE emitted from the edge of the waveguide film was monitored using an optical fiber-coupled photodiode pyrometer (Ophir PD-10-P and NOVA II Display, USA) equipped with an optical filter to cut out the incident excitation beam.

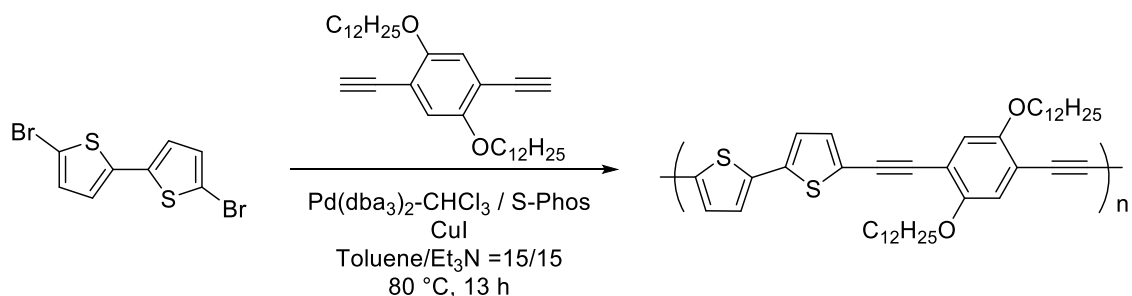
Synthetic procedure

Synthesis of model compound; **DTA-BT'**



DTA-Br (0.1128 g, 0.24 mmol), 2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene (0.112 g, 0.53 mmol), Pd₂(dba)₃-CHCl₃ (4.7 mg, 4.5 μmol), S-Phos (8.4 mg, 20.5 μmol), K₂CO₃ (0.6999 g, 5.8 mmol), TBAB (0.3695 g, 1.1 mmol) were dissolved in a mixture of toluene and MeOH and H₂O solution (25 mL/3.0 mL/1.0 mL) under inert atmosphere. After stirring at 80 °C for 13 h, the mixture was diluted with CHCl₃ before cooling, and washed with 1 M NH₃aq and 1 M HCl aq. Then, SilliaMetS(R) Thiol (10 eq) were added to the CHCl₃ solution. After stirring at ambient temperature for 6 h, the insoluble part was removed with filtration. The obtained solution was dried over MgSO₄. After filtration, the solvents were removed in vacuo. The residue was subjected to column chromatography on neutral alumina (eluent: hexane/ EtOAc= 100/0 to 9/1) and recrystallized with CH₂Cl₂/MeOH to obtain orange crystal of DTA-BT' (0.0767 g, 0.160 mmol, 67%). ¹H-NMR (400 MHz, Acetone-*d*₆): δ 7.55 (s, 2H), 7.46-7.45 (m, 4H), 7.34 (dd, *J* = 3.64 Hz, *J* = 1.12 Hz, 2H), 7.32-7.30 (m, 3H), 7.10 (dd, *J* = 5.16 Hz, *J* = 3.64 Hz, 2H) ppm. ¹³C-NMR (100 MHz, CDCl₃): δ 149.3, 141.7, 138.7, 137.4, 137.3, 132.6, 129.1, 129.0, 127.9, 124.5, 124.4, 123.6 ppm. HR-FAB-MS (*m/z*): calculated for C₂₂H₁₃AsS₄ [M]⁺; 479.9116, observed; 479.9120. The melting point was 196.9–197.5 °C

Synthesis of arsenic-free polymer; **EB-BT**³



5,5'-Dibromo-2,2'-bithiophene (0.0812 g, 0.25 mmol), 1,4-bis(dodecyloxy)-2,5-diethynylbenzene (0.1235 g, 0.25 mmol), $\text{Pd}_2(\text{dba})_3\text{-CHCl}_3$ (5.2 mg, 5.0 μmol), S-Phos (8.2 mg, 20.0 μmol), CuI (4.6 mg, 0.024 mmol) were dissolved in a mixture of toluene and Et_3N solution (15 mL/15 mL) under inert atmosphere. After stirring at 80 $^\circ\text{C}$ for 13 h, the mixture was diluted with CHCl_3 before cooling, and washed with 1 M NH_3aq and 1 M HClaq . Then, SilliaMetS(R) Thiol (10 eq) were added to the CHCl_3 solution. After stirring at ambient temperature for 6 h, the insoluble part was removed with filtration. The obtained solution was dried over MgSO_4 . After filtration, the solvents were removed in vacuo. Reprecipitation in methanol gave orange solids of **EB-BT** (0.1276 g, 78%). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.17 (m, 2H), 7.09 (m, 2H), 6.98 (m, 2H), 4.02 (m, 4H), 1.83 (m, 4H), 1.25 (m, 36H), 0.87 (m, 6H) ppm. $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 153.60, 138.34, 132.79, 127.89, 124.20, 124.04, 123.60, 116.44, 91.51, 69.70, 31.96, 29.77, 29.71, 29.49, 29.42, 29.35, 26.13, 25.97, 22.64, 14.15 ppm. $M_n = 8,500$, $M_w/M_n = 2.2$

NMR spectra

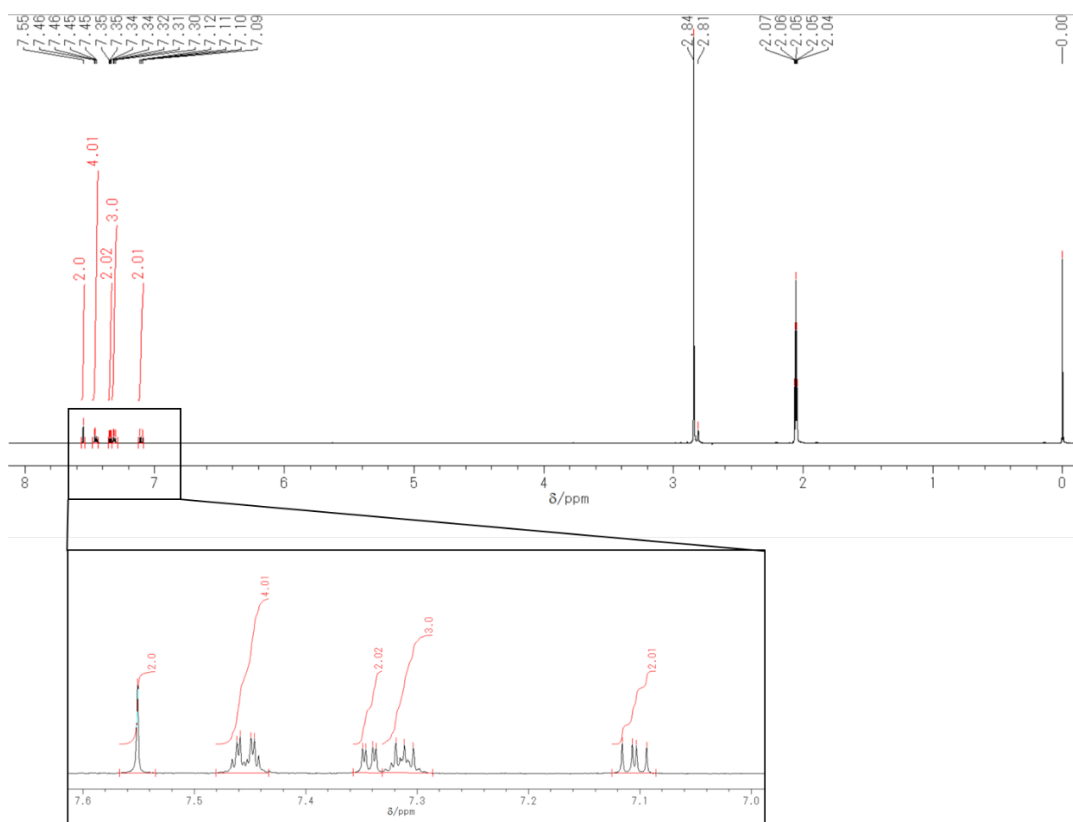


Figure S1. $^1\text{H-NMR}$ spectrum (400 MHz, Acetone- d_6) of DTA-BT'.

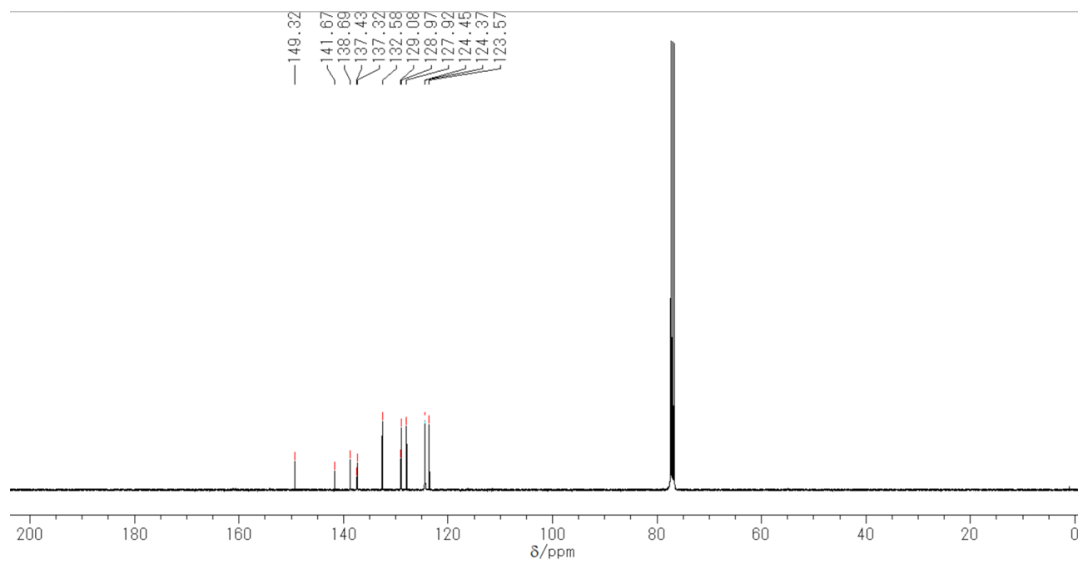


Figure S2. $^{13}\text{C-NMR}$ spectrum (100 MHz, CDCl_3) of DTA-BT'.

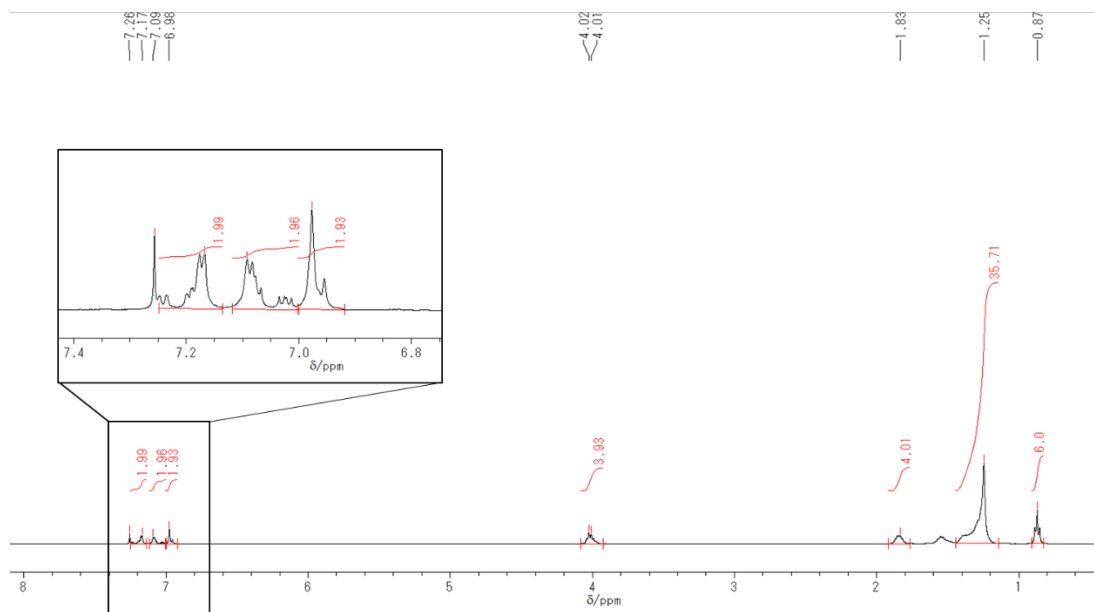


Figure S3. ^1H -NMR spectrum (400 MHz, CDCl_3) of **EB-BT**.

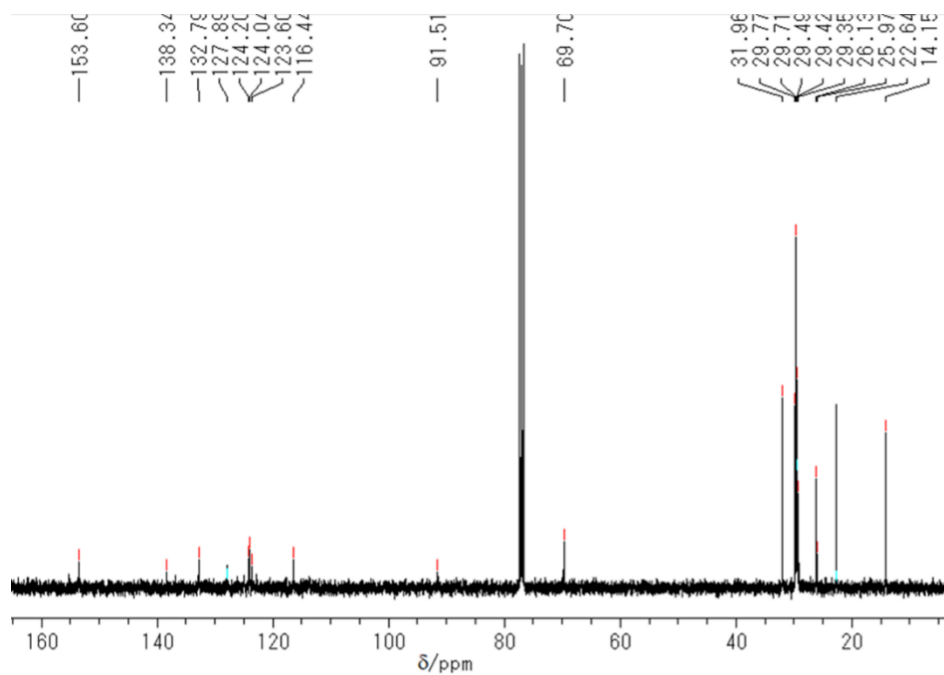


Figure S4. ^{13}C -NMR spectrum (100 MHz, CDCl_3) of **EB-BT**.

Optical properties

Table S1. Optical properties of the model compounds and arsenic-free polymers and rhodamine 6G (R6G) in spin-coated film.⁴

	DTA-BT'	DTA-EB'	P3HT	EB-BT	R6G ⁴
λ_{abs} (nm)	434	436	470	482	533
λ_{em} (nm)	520	554	690	563	558
ϕ	<0.01	n.d.	<0.01	n.d.	0.56

Table S2. Optical properties of DTA-based polymers.

	THF solution ^a		Spin-coated film ^b		Drop-casted film dispersed in PMMA ^{c*}	
	λ_{em} (nm) ²	ϕ ²	λ_{em} (nm)	ϕ	λ_{em} (nm)	ϕ
DTA-FL	524	0.52	554	n.d.	610	0.006
DTA-EB	536	0.40	569	0.021	650	0.011
DTA-BT	583	0.23	601	0.014	666	0.009

^a 1.0×10^{-5} M THF solution (excited at $\lambda_{\text{abs, max}}$)². ^bSpin-coating from THF solution (excited at 350 nm). ^cDispersion film of DTA-based polymers in PMMA from THF solution (excited at 350 nm).

*Preparation of dispersion film; each DTA-based polymer (1.5 mg) and PMMA (15.6 mg) was dissolved in THF (1.4 g). This solution was drop-cast onto a quartz substrate at room temperature and dried in oven 80 °C for 1 h.

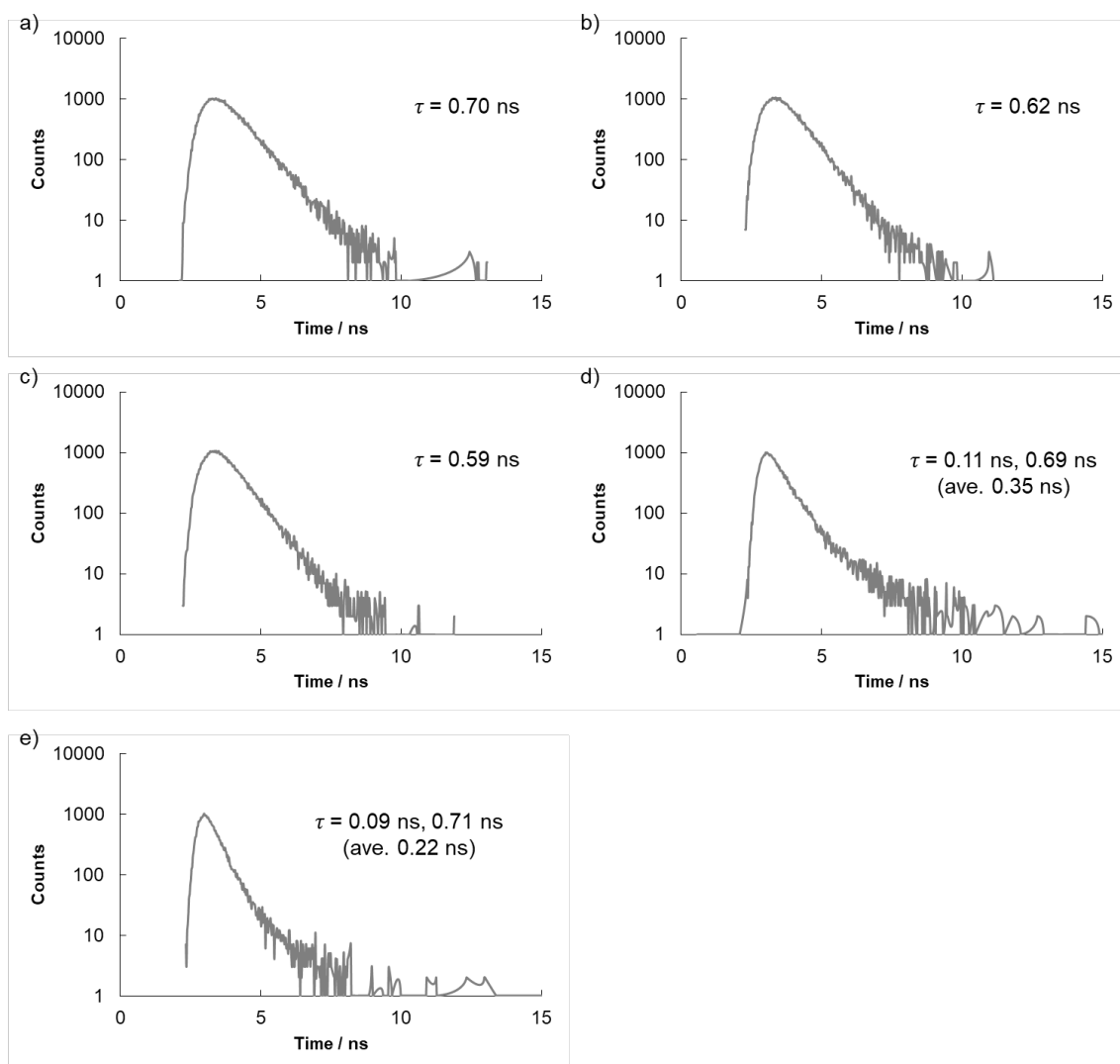


Figure S5. The emission decay kinetics of (a) DTA-FL, (b) DTA-EB, (c) DTA-BT in THF solutions (1.0×10^{-5} M), and (d) DTA-EB, (e) DTA-BT in spin-coated films.

Fabrication of waveguide type film devices for ASE measurements

DTA polymers and their model compounds and arsenic-free polymers were dissolved in tetrahydrofuran (THF). Each THF solution was spin-coated on a quartz substrate (30 mm × 30 mm, with 1 mm thickness) at 500 rpm for 30 s at room temperature. The obtained spin-coated sample was dried in oven at 80 °C for 1 h. The film of rhodamine 6G (R6G) dispersed in cellulose acetate (CA), which is commonly used for laser dyes, was prepared according to previous report.^{4,5}

ASE measurements

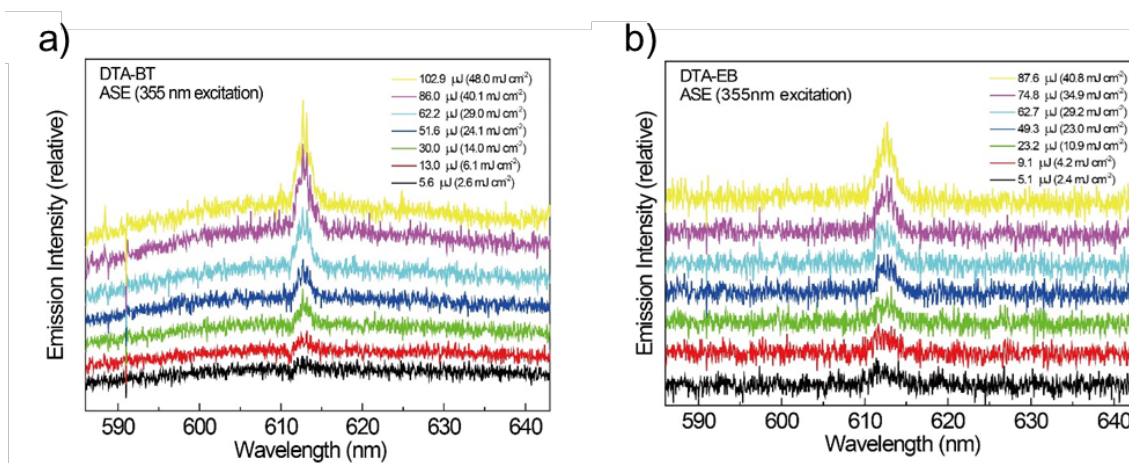


Figure S6. Series of ASE spectra obtained by varying the pump intensity for (a) DTA-BT and (b) DTA-EB by excitation at 355 nm.

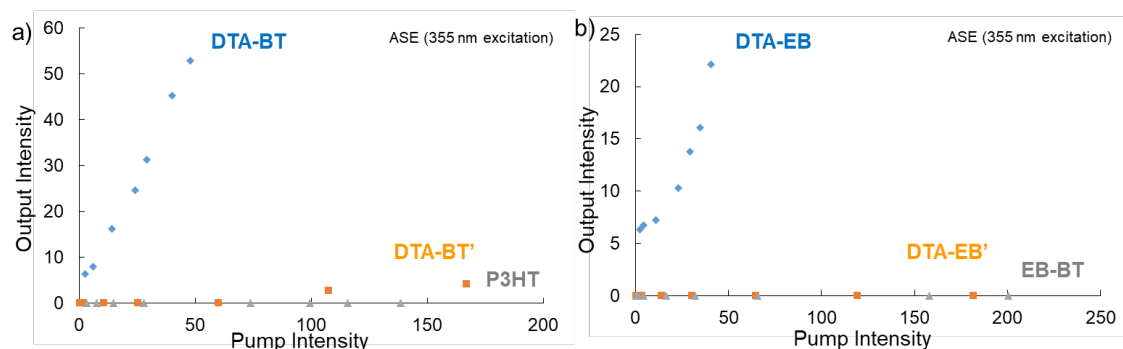


Figure S7. Amplified spontaneous emission (ASE) performance of DTA-based polymer (DTA-EB, DTA-BT), model compounds (DTA-EB', DTA-BT') and arsenic free polymers (EB-BT, P3HT) in spin cast film. Output intensity versus pump intensity by excitation at 355 nm.

Optical gain

The plots of ASE as a function of pump-length are fitted by the theoretical expression given in equation (1) that is based on the one-dimensional approximation with a saturation effect.⁶ The details are described in several previous reports.^{5,6} The measured optical gain and parameters are summarized in Table S3.

$$I_{\text{ASE}} = \frac{I_{\text{sat}}}{1 + C_{\text{sat}}e^{-g(\lambda)x}} - \frac{I_{\text{sat}}}{1 + C_{\text{sat}}} \quad (1)$$

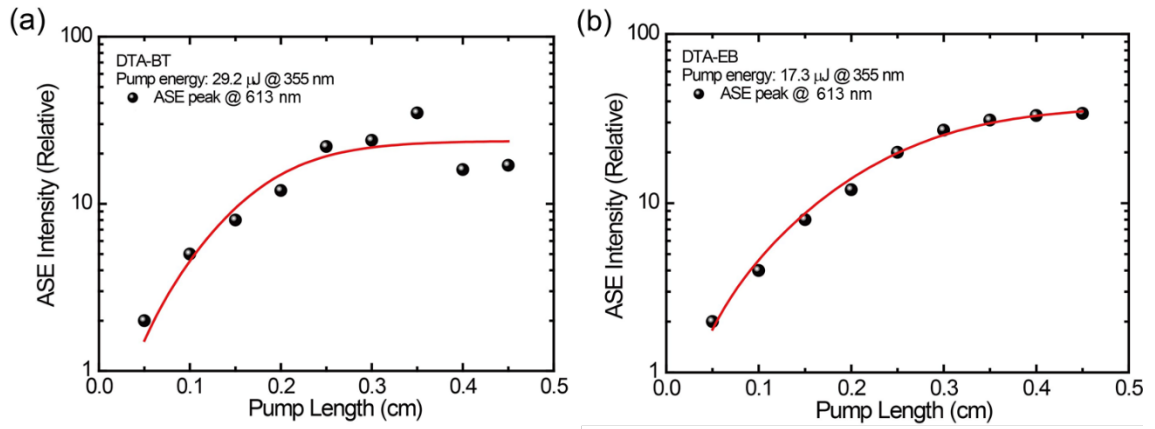


Figure S8. Plots of the ASE intensity as a function of optical length. ASE at 613 nm by excitation at 355 nm for (a) DTA-BT and (b) DTA-EB.

I_{ASE} is the ASE intensity propagating along the x axis, $g(\lambda)$ is the net optical gain per length at the wavelength λ , and I_{sat} is the signal saturation intensity, defined by $I_{\text{sat}} = \frac{h\nu}{\sigma\tau}$ for a four-level amplifier, where σ is the emission cross section, τ is the radiative life time, and C_{sat} is the saturation constant.

The saturation length L_s can be calculated by the inflection point of the red curve in Figure S8 obtained by fitting the data to Eq. (1). From the second derivatives of Eq. (1), L_s can be determined as

$$L_s = \frac{\ln(C)}{g(\lambda)} \quad (2)$$

The calculated optical gains for ASE with saturation and the calculated saturation lengths are summarized in Table S3. The saturation length of 0.16-0.23 cm is adequate because above this value, the ASE intensity saturated as shown in Figure S5.

Table S3. Fluorescence intensity, excitation wavelength, pump energy, ASE peak, optical gain, I_{sat} and C_{sat} values for DTA-BT and DTA-EB.

Sample	Excitation wavelength (nm)	Pump energy (mJ cm^{-2})	ASE peak (nm)	Optical gain (cm^{-1})	I_{sat}	C_{sat}	L_S (cm)
DTA-BT	355	13.6	613	18.1	24.9	20.7	0.17
DTA-EB	355	8.07	613	11.7	40.4	14.9	0.23

ASE intensity versus the number of pump pulses of Rhodamine 6G

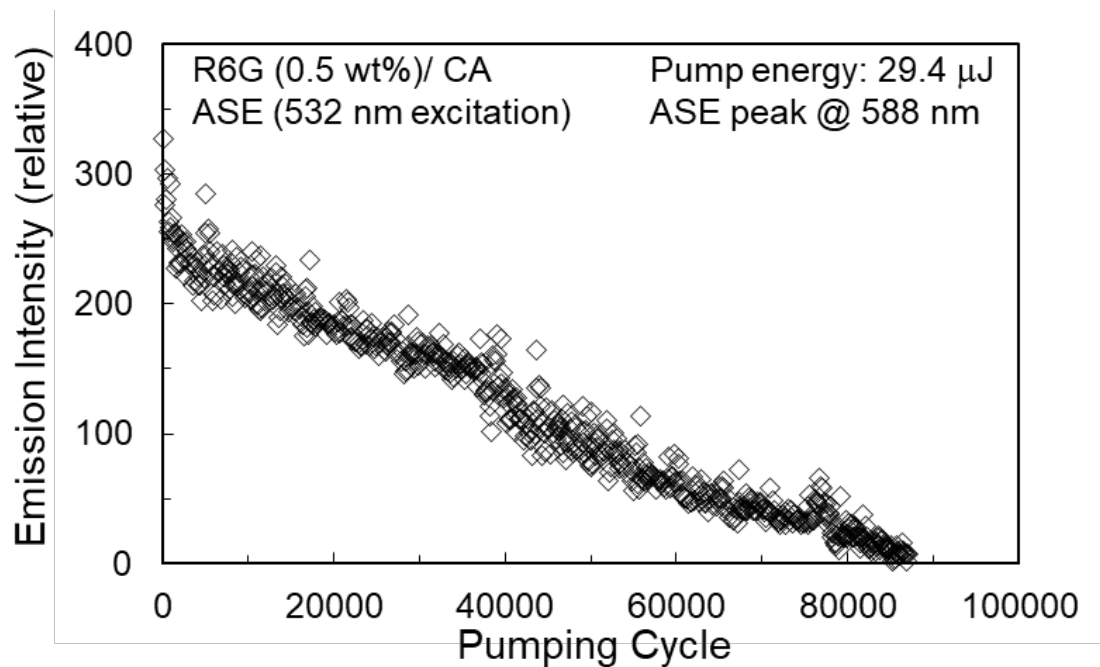


Figure S9. ASE peak at 588 nm obtained by excitation at 532 nm for rhodamine 6G (R6G). The pumping energy is 0.15 μJ (0.070 mJ cm^{-2}).

X-ray diffraction for DTA-based polymers

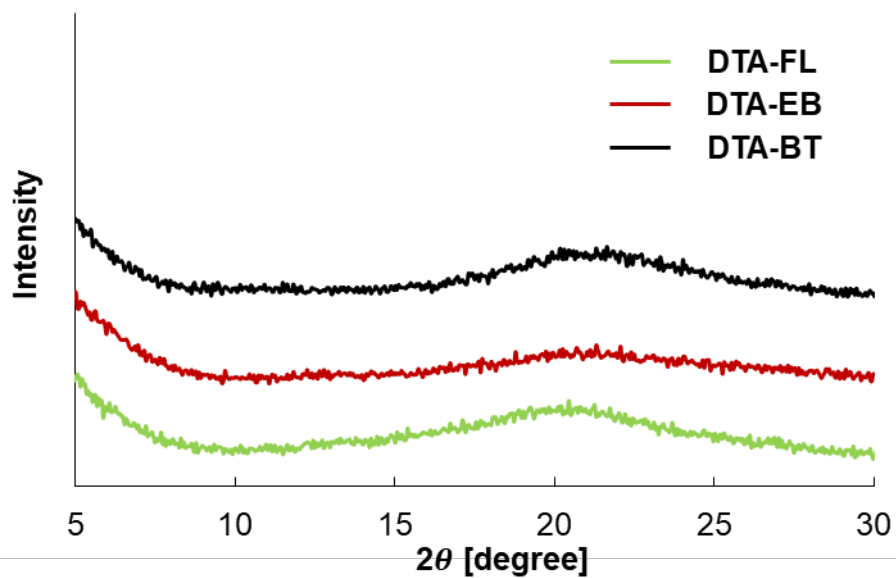


Figure S10. XRD curves of DTA-based polymer films spin-coated from THF solutions (10 mg/mL)

Reference

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