Supporting Information

Chain-Length-Dependent Exciton Dynamics in Linear Oligothiophenes Probed Using Ensemble and Single-Molecule Spectroscopy

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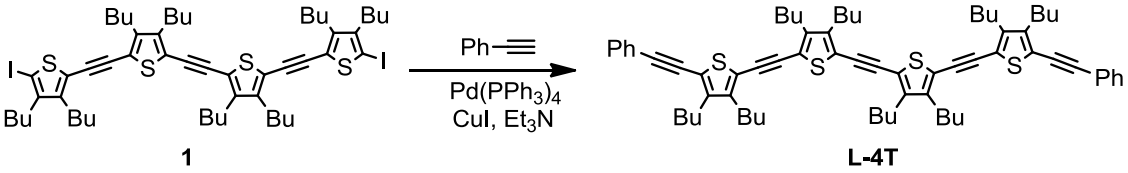
Experimental Methods

Samples and Steady-State Ensemble Spectra. **L-6T**[1] and **L-10T**[2] were prepared according to the reported methods. For our study, **L-4T** were newly synthesized by using diiodide **1**[1] as a key starting material. All of the linear oligothiophenes, **L-4T**, **L-6T**, and **L-10T**, are stable crystalline or amorphous powder and can be stored in air at room temperature for more than 1 year. Steady-state absorption spectra were measured by UV-VIS-NIR spectrometer (Varian, Cary 5000), and steady-state fluorescence spectra were obtained by using a fluorescence spectrophotometer (Hitachi, F-2500). Steady-state excitation anisotropy spectra were obtained by changing the polarization of fluorescence detection either parallel or perpendicular to the polarization of the excitation light. The fluorescence excitation anisotropy values were calculated as follows:

$$r = \frac{\mathrm{I_{VV}} - \mathrm{GI_{VH}}}{\mathrm{I_{VV}} + 2\mathrm{GI_{VH}}}$$

where I_{VV} (or I_{VH}) is the fluorescence excitation spectrum when the excitation light is vertically polarized and only the vertically (or horizontally) polarized portion of the fluorescence is detected, that is, the first and second subscripts represent excitation and detection polarization, respectively. The factor G is defined by I_{HV}/I_{HH} , which is equal to the ratio of the sensitivities of the detection system for vertically and horizontally polarized fluorescence. All spectra were measured at room temperature and ambient condition. All the steady-state spectroscopic measurements were carried out at ambient temperature.

Synthesis of Linear Oligothiophene L-4T.



To a mixture of **1**[1] (255mg, 0.231 mmol), CuI (9.1 mg, 0.048 mmol), and $Pd(PPh_3)_4$ (55.2 mg, 0.048 mmol) were added phenylaceylene (51 mg, 0.50 mmol) and triethylamine (10 ml), and the mixture was stirred for 12 h at room temperature. The reaction was quenched by adding an aq. NH_4Cl solution, and the mixture was extracted with ether. The organic layer was washed with brine and dried with MgSO4. After filtration, the filtrate was evaporated *in vacuo* to give a residue that was purified by column chromatography on deactivated silica gel (activity V) using hexane as eluent to afford **L-4T** (211 mg, 87%). **L-4T**, orange crystals, mp 106–107.5 ºC, ^{1}H NMR (CDCl3, 500 MHz) δ 7.50 (4H, m), 7.35 (6H, m), 2.70 (16H, m), 1.60 (16H, m), 1.43 (16H, m), 0.97 (24H, m); ^{13}C NMR (CDCl3, 125 MHz) δ 146.9, 146.71, 146.70, 146.68, 131.4, 128.53, 128.47, 123.2, 119.9, 119.8, 119.6, 119.2, 96.3, 89.7, 89.6, 89.3, 82.9, 32.6, 32.5, 28/6, 28.4, 22.9, 22.8, 14.14, 14.11; LDI-TOF-MS *m/z* 1650 (M^+). Anal. Calcd for $C_{70}H_{82}S_4$: C, 79.94%; H, 7.86%. Found: C, 79.90%; H, 7.92%.

Picosecond Time-resolved Fluorescence Measurements. A time-correlated single-photon-counting (TCSPC) system was used for measurements of spontaneous fluorescence decay. As an excitation light source, we used a mode-locked Ti:sapphire laser (Spectra Physics, MaiTai BB) which provides ultrashort pulse (center wavelength of 800 nm with 80 fs at full width half maximum, fwhm) with high repetition rate (80 MHz). This high repetition rate slows down to 800 kHz by using homemade pulse-picker. The pulse-picked output pulse was frequency-doubled by a 1 mm thickness of a BBO crystal (type-I, θ = 29.2°, EKSMA). The fluorescence was collected by a microchannel plate photomultiplier (MCP-PMT, Hamamatsu, R3809U-51)

with a thermoelectric cooler (Hamamatsu, C4878) connected to a TCSPC board (Becker & Hickl SPC-130). The overall instrumental response function was about 25 ps (fwhm). A vertically polarized pump pulse by a Glan-laser polarizer was irradiated to samples, and a sheet polarizer, set at an angle complementary to the magic angle (54.7°), was placed in the fluorescence collection path to obtain polarization-independent fluorescence decays.

Femtosecond Time-Resolved Fluorescence Anisotropy. A femtosecond fluorescence up-conversion apparatus was used for the time-resolved spontaneous fluorescence. The beam sources were a mode-locked Ti:sapphire laser also used in TCSPC system. The second harmonic pulses around 450 nm generated by a 200-μm thick BBO crystal (type-I, θ = 29.2°, EKSMA) and residual fundamental pulses were compressed by prism pairs and used as pump and gate pulses, respectively. The pump beam was focused onto a 500-μm thick quartz cuvette containing sample solution using a 5-cm focal length plano-convex lens with a magic angle (54.7°) in order to prevent polarization-dependent signals. The cuvette was mounted on a motor-driven stage and moved constantly back and forth to minimize photo-degradation. Collection of the fluorescence and focusing into a 500 μm-thick BBO crystal (type-I, θ = 44.3°, EKSMA) for frequency conversion was achieved by a reflecting microscope objective lens (Coherent). The gate pulses was focused on to the same BBO and overlapped with fluorescence pulses by plano-convex lens with a focal length of 20 cm. Up-converted photons (sum-frequency generation between fluorescence and gate photons) were propogated into a monochromator (focal length of 30 cm, Dongwoo Optron) and detected by PMT (R3234-01, Hamamatsu). The gated photon counter (SR400, Stanford Research Systems) were used for the analogue-to-digital converting (ADC) for data acquisition and storage into a PC. The FWHM of the cross-correlation function between the scattered pump pulse and the gate pulse is measured to be 140 fs. The average excitation power

was kept at a level below 1 mW in order to minimize thermal lens effect. In this excitation intensity regime the fluorescence dynamics was be independent of the excitation intensity for all samples. Time-resolved fluorescence anisotropy decays were obtained by changing the detection polarization on the fluorescence path to parallel or perpendicular to the polarization of the excitation pulses. The calculation of anisotropy decay then was followed by:

$$r(t) = \frac{I_{VV}(t) - GI_{VH}(t)}{I_{VV}(t) + 2GI_{VH}(t)}$$

where $I_{VV}(t)$ [or $I_{VH}(t)$] represent up-converted signals with polarization of excitation and fluorescence vertically and horizontally polarized, respectively. The correction factor G was obtained by tail matching fluorescence (I_{VV} and I_{VH}) for a coumarin 1 at long times.

Femtosecond Broadband Fluorescence Upconversion Measurements.[3-5] A femtosecond broadband fluorescence up-conversion apparatus was used for obtaining the transient fluorescence spectra. A Ti:sapphire laser system (Spectra-Physics, Spitfire) provides 30 fs, 400 μJ pulses at 800 nm with 10 kHz repetition rate. The output beam is divided by beam splitter with the equivalent ratio. A pulse of 200 μJ is used to pump an optical parametric amplifier (TOPAS, Light Conversion) which delivers 50 fs, ~40 μJ gate pulses in range of 1150-1400 nm with the vertical polarization. For achieving the best experimental condition, the wavelength of gates pulse was selected from 1160 to 1450 nm depending on the wavelengths of pump pulse and fluorescence. The gate beam passes through a periscope, which adjusts the height and rotates the vertically polarized pulse to be horizontally polarized. Then, the gate pulse passes a sequence of SF50 prism (55.5°) compressor with optimal separation of 12 cm between the apexes of each prism. Finally, the gate beam is relayed onto the nonlinear crystal (type-II BBO, $\theta = 32°$, $\phi = 0°$,

d = 1 mm, EKSMA) by a lens (f = 100 mm, Tc = 2 mm). The pulse energy of the gate beam is attenuated by the ND filter to keep a level below 50 mW. The rest of the fundamental light is used as a source for the tunable homemade optical parametric amplifiers (OPA) system. This homemade OPA system is based on noncollinearly phase-matching geometry which is easily color-tuned by controlling optical decay between white light continuum seed pulses (450-1400 nm) produced by using a sapphire window (d = 2 mm) and visible pump pulses (400 nm) generated by frequency doubling nonlinear crystal (type-I BBO, EKSMA). The generated visible OPA pulses had a pulse width of ~20 fs and an average power of 35 mW at 10 kHz repetition rate in the range of 480-700 nm with vertical polarization. In order to adjust the pulse polarization to prism compressors, the pulse passes through the periscope and then passes through a fused-silica prism compressor (69°), which has the optimal separation of 95 cm. In order to prevent polarization-dependent signals, the pulse polarization is controlled with a half wave plate to be a magic angle (54.7°) and finally the beam is focused onto a 500 μm thick quartz cuvette containing sample with a lens (f = 300 mm, Tc = 2 mm). The pulse energy is attenuated by the ND filter to keep a level below 60 nJ. Moreover, the cuvette is mounted on a motor-driven stage and continuously moved back and forth to avoid photo-degradation and the thermal lens effect. Collection of the fluorescence is achieved by a reflecting microscope objective lens (Newport). Finally, the collected fluorescence is relayed onto the nonlinear crystal by the off-axis parabolic mirror (Newport, f = 50 mm). The horizontally polarized upconverted signal is emitted from the type II nonlinear crystal at an angle different from the original fluorescence. Unwanted light of horizontal polarization, stemming from the original fluorescence and the pump pulse (or Rayleigh scattered light), is mostly ejected by a wire-grid polarizer (Moxtec PPL04C). Moreover, the upconverted signals pass a wire-grid polarizer (Moxtec

PPL04C) in order to eliminate unwanted light of vertical polarization, originating from the remaining original fluorescence. The upconverted signals are imaged dispersion-free onto the entrance slit of a spectrograph (Dongwoo Optron, Monora 320i) and then the upconverted spectrum is finally registered with a CCD camera (Andor Technology, DV420 BU). The FWHM of the cross-correlation functions between the scattered pump pulse (i.e., 400 nm) and the gate pulse (i.e., 1340 nm) is measured to be 120 fs.

Single-molecule Confocal Microscopy. Samples for single-molecule measurements were prepared by spincoating a toluene solution of the linear oligothiophenes (~10^{-10} M) containing polystyrene (PS) (10 mg/mL; Sigma-Aldrich, Mw = 31,600) on rigorously cleaned glass cover slips at 2,000 rpm for 60 s, yielding thin polymer films (~100 nm thick, as measured by atomic force microscopy). In the films, the average molecular density was kept as low as five single molecules in an area of 4 × 4 μm^2.

Detection of single molecule fluorescence was performed with a confocal laser scanning microscope (Eclipse Ti-U, Nikon) at room temperature under ambient conditions. The sample was excited by a circularly polarized light from a picosecond pulsed diode laser (LDH-D-C-420, Picoquant, 420 nm, 10 MHz repetition rate) prepared by a Berek compensator (5540, New Focus). In the set-up, a scanning lens was mounted on a XY translation stage (M-605.1DD, Physik Instrumente) to image the different sample area, and an identical lens was used to recollimate the laser beam. After being deflected by a reflective mirror (21015, Chroma Technology), the laser beam was focused onto the focal plane of the oil immersion objective (UplanSApo, 1.4 NA, 100×, Olympus). The fluorescence was collected using the same objective, trace back along the same pathway as the excitation beam, and passed through a dichroic mirror (T425lpxr, Chroma Technology). A notch filter (HNPF-420.0AR-1.0, Kaiser Optical Systems

Inc.) in combination with long pass filters (Chroma Technology HQ425lp, and Semrock FF-01-430/LP-25) was used to remove the Rayleigh scattered light. The transmitted fluorescence was focused onto an active area of an avalanche photodiode (APD) (SPCM-AQRH-15-TR, Excelitas Technologies).

After an individual molecule was positioned in the laser focus, the fluorescence signal detected by the APD was registered by a time-correlated single photon counting (TCSPC) PC card (SPC 830, Becker & Hickl) operated in first-in-first-out regime, in which the arrival time after the beginning of the acquisition and the time lag with respect to the excitation pulse were stored for each detected photon. The fwhm of the overall instrumental response function was about 250-300 ps. These data were processed using BIFL data analyzer software (Scientific Software Technologies Center) to obtain the FITs with a user-defined binning time, and the time-resolved fluorescence decays using photons belonging to a user-defined region in the trajectories.

Table S1. Photophysical Parameters of the Linear Oligothiophenes in Toluene.

Samples	Absorption (nm)	Fluorescence (nm)	Q.Y.	$I_{0\text{-}0}/I_{0\text{-}1}$	τ_r (ns)	k_r[a] ($\times 10^8$ s^{-1})	k_{nr}[b] ($\times 10^8$ s^{-1})
L-4T	426	495, 529	0.22	1.54	0.35	6.3	22
L-6T	435	514, 550	0.29	1.75	0.36	8.1	20
L-10T	448	522, 558	0.29	2.00	0.38	7.6	19

[a, b] Radiative and nonradiative decay rates calculated using fluorescence quantum yields and lifetimes.

Table S2. Fitting Parameters for the Fluorescence Decay Profiles at Various Probe Wavelengths from Time-Resolved Fluorescence Spectra of the Linear Oligothiophenes.

Samples	τ_1 (ps)	τ_2 (ps)	τ_{fl} (ps)	A_1 (%)	A_2 (%)	A_{dp}[a] (%)	τ_{dp}[b] (ps)
L-4T	8.2	24	350	7.8	4.9	12.7	14.3
L-6T	8.7	35	360	10.5	5.4	15.9	17.6
L-10T	9.1	45	380	8.7	4.9	13.6	22.1

[a] Amplitude sum of dynamic planarization (A_1+A_2). [b] Amplitude-weighted average time constant of dynamic planarization.

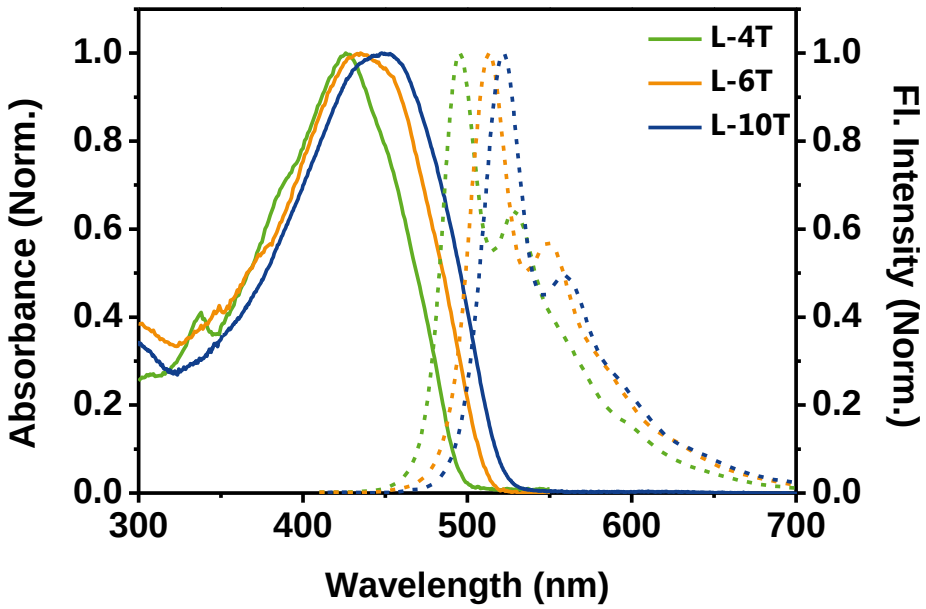


Figure S1. Steady-state absorption spectra (solid lines) and fluorescence emission spectra (short dashed lines) spectra for the linear oligothiophenes (**L-4T**, **L-6T**, and **L-10T**) in toluene solution.

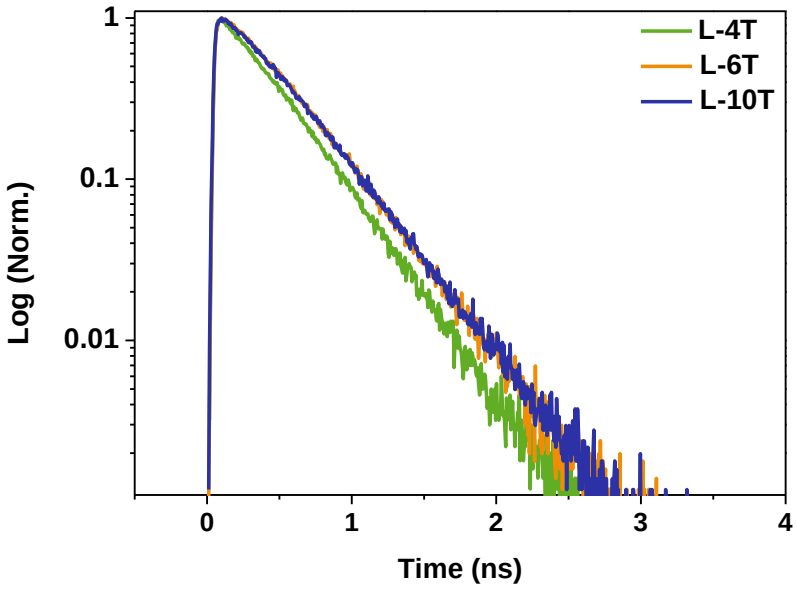


Figure S2. Fluorescence decay profiles for the linear oligothiophenes obtained using TCSPC measurements.

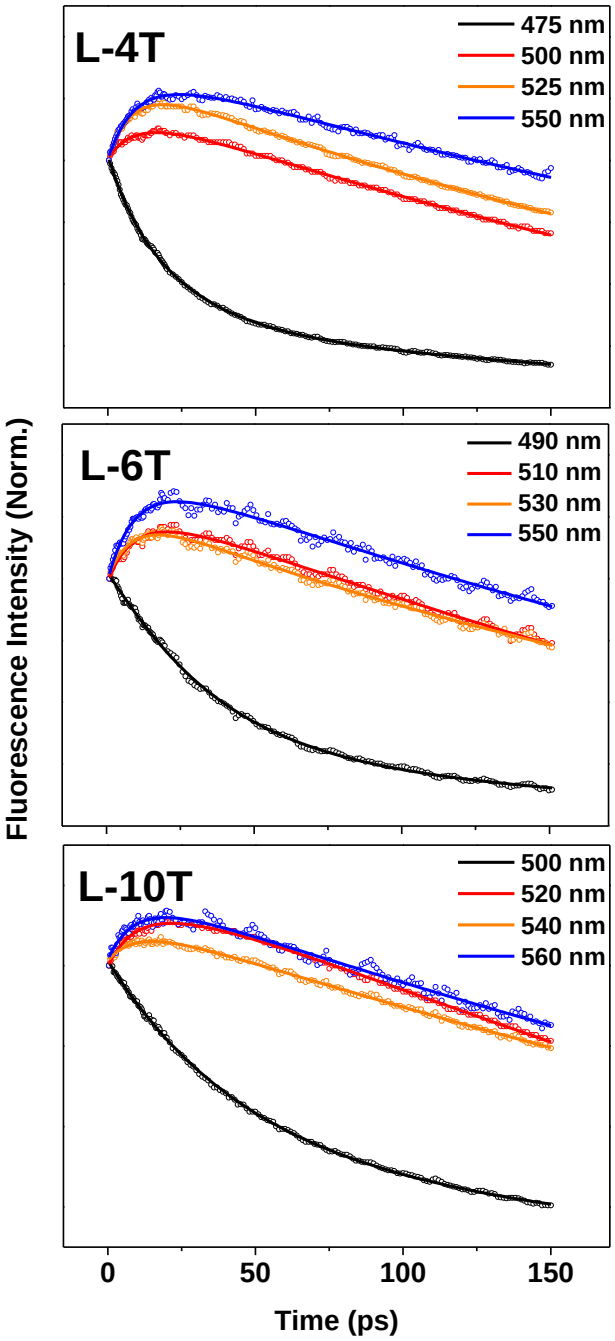


Figure S3. Fluorescence decay profiles for the linear oligothiophenes at various wavelengths obtained using femtosecond broadband fluorescence upconversion measurements. Fitting parameters are summarized in Table S2.

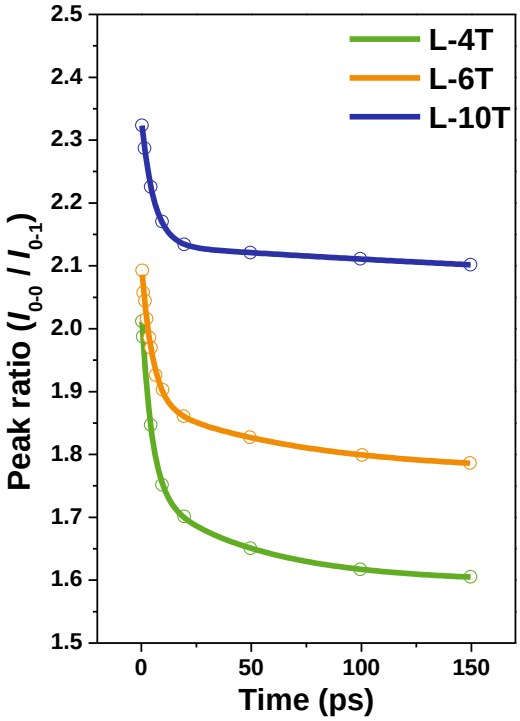


Figure S4. Temporal evolution of $I_{0\text{-}0}/I_{0\text{-}1}$ calculated from the spectrally integrated emission intensities of the 0-0 and 0-1 vibronic peaks.

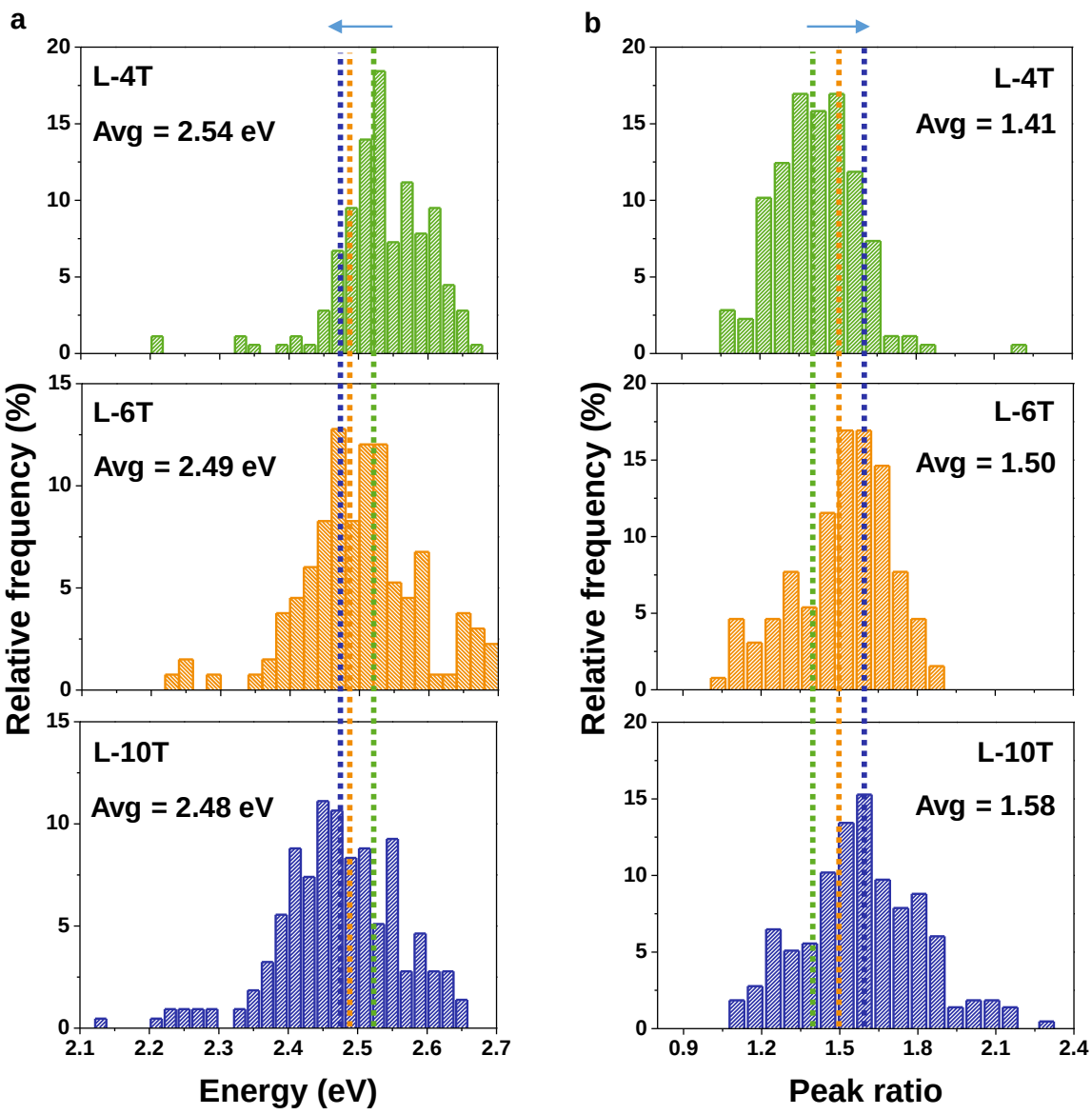


Figure S5. Statistical distributions of (a) the fluorescence energies and (b) the Spectral peak ratios ($I_{0\text{-}0}/I_{0\text{-}1}$) for single **L-4T** (top), **L-6T** (middle), and **L-10T** (bottom) molecules obtained using the single-molecule fluorescence spectroscopy.

References

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