Observation of Size-Dependent Optical Properties Based on Surface and Quantum Effects in Nanocrystals of 5,5′-Bis(4-Biphenylyl)-2,2′-Bithiophene

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Herein, 5,5′-bis(4-biphenylyl)-2,2′-bithiophene (BP2T or PPTTPP) nanocrystals are prepared via a modified miniemulsion technique. X-ray diffraction and selected area electron diffraction analyses reveal that the BP2T molecules stand almost upright against the crystal basal plane. With decreasing nanocrystal size, the peak energies of photoluminescence (PL) spectra are blue-shifted in the photon energy range from the bulk crystal to the monomer state. Energy-wavevector dispersion plots reproduced using the data of size-dependent PL spectra indicate that the size dependence of optical properties cannot be explained by the conventional quantum confinement effect used in inorganic nanocrystals. The micro-PL and time-resolved PL measurements of the BP2T nanocrystals reveal that the size-dependent optical properties can be attributed to a combined effect based on the surface effects as well as lattice softening, and quantum effects involving specific surface area-dependent site shift effect and exciton confinement. Moreover, amplified spontaneous emission is observed from the nanocrystals ≈600–1000 nm in size, which is smaller than the size previously reported for organic systems.

1. Introduction

The size-dependent spectroscopic behavior of organic molecular nanoparticles/nanocrystals provides considerable versatility and flexibility in the design and fabrication of optoelectronic devices.[1–21] The size-dependent optical properties of organic crystals have not yet been investigated in sufficient detail compared to those of inorganic crystals.[22–24] Therefore, the need for enhancing our understanding of the optical properties, such as surface and quantum effects, including quantum confinement effects manifesting in the organic nanocrystals,[22–24] leads to the stimulation of novel nanoscience studies. Biological applications may include the use of biocompatible organic nanocrystals for fluorescent biological labeling and bioimaging with biomolecule-anchoring proteins and ligands to target cells.[18,19,25] For inorganic semiconductor quantum dots, the confinement effect on electron-hole pairs (Wannier excitons) in three dimensions results in size-tunable optical properties. Although a confinement effect on molecular excitons is not expected because of the small radius of the Frenkel exciton, some studies have demonstrated the delocalization of excited states in organic systems.[26–28] An extended delocalization of the exciton wave function up to 100 molecular units in the J-aggregates has been reported, and this deviation from the Frenkel exciton model has been attributed to the strong in-line dipole–dipole coupling and exciton–optical phonon coupling.[27] The size effect that reflects the delocalization of excited states in organic nanocrystals is a developing research area because no theoretical model has been developed yet.

The optical properties of organic materials have been investigated mainly for bulk crystals and thin films, and an understanding of those of organic nanoparticles/nanocrystals has not sufficiently developed.[29,16] In nanoparticles comprising organic dyes and π-conjugated polymers, size-dependent optical properties have been observed.[1–1.5–7,13,16,17] In nanoparticles of 1-phenyl-3-((dimethylamino)styryl)-5-((dimethylamino)phenyl)-2-pyrazoline (PDDP) or 1,3-diphenyl-3-pyrenyl-2-pyrazoline (DPP),[1,2] an extended charge-transfer (CT) state was formed, originating from the closely stacked PDDP molecules, and blue-shifts of the CT peaks were observed with decreasing nanoparticle size due to exciton confinement. The CT emission properties are attributed to the surface effects, and the tunable emission is due to the alteration of both the excitation wavelength and nanoparticle size. It has been reported that lattice softening,
which weakens intermolecular interactions and modifies the bandgap, is responsible for the size-dependent absorption and fluorescence properties of nanoparticles of poly(3-[2-(N-dodecylcarbamoyloxy)ethyl]-thiophene-2,5-diy] (P3DDUT) with mean diameters of 40–400 nm, prepared by a reprecipitation method. Asahi et al. reported that the lattice instability caused by the large surface-to-volume ratio is responsible for lowering the lattice vibration or rigidity by decreasing the crystal size, which leads to the up-shift of the excimer energy level in perylene nanocrystals. They discussed that the size effect is attributed to the change in the elastic properties of the nanocrystal, and this effect is due to the structural confinement of perylene nanocrystals with sizes of a few tens and a few hundreds of nanometers. In perylene nanocrystals, although the blue-shifts of self-trapped exciton (STE, or excimer) emission are probably due to an unusual quantum size effect, the mechanism of this phenomenon for a crystal size more than ten times larger than the size of inorganic nanocrystals is not well understood. In a study investigating the dependence of the optical properties of 9,10-bis(phenylethynyl)anthracene (BPEA) on the crystal size, the absorption spectra showed a redshift with increasing crystal size. A change in the relative proportions of the two emissive sites originating from the molecules in the peripheral and inner portions of the crystals was responsible for the size-dependent fluorescence.

Especially for organic nanocrystals, although the origin of spectral shifts has been attributed to surface effects such as lattice softening, the details of the influence of surface effects on the size-dependent optical properties are not yet understood. In this article, we report the observation of absorption and photoluminescence (PL) blue-shifts in nanocrystals with decreasing crystal size using 5,5′-bis(4-biphenylyl)-2,2′-bithiophene (BP2T or PPTTPP), which is a species of thiophene/phenylene co-oligomer (TPCO). The impact of the surface effects and quantum effects (internal effects) on the BP2T nanocrystals were investigated. Moreover, the rarely reported light amplification properties in organic nanocrystals has been demonstrated using BP2T nanocrystals.

2. Results and Discussion

2.1. Characterization of BP2T Nanocrystals

BP2T nanocrystals were prepared using a modified miniemulsion technique. By adjusting the amount of sodium dodecyl sulfate (SDS) (C$_{12}$H$_{25}$NaO$_4$S), which is a surfactant and BP2T powder, nanocrystals with sizes ranging from 100 to 1,000 nm were prepared. The molecular structure of BP2T is shown in Figure 1a. The transition dipole moment of BP2T, indicated by the blue line, makes an angle of 6.7° with the molecular long axis indicated by the black dashed line. Figure 1b–e shows transmission electron microscopy (TEM) images of BP2T nanocrystals of different sizes. Although it was deduced from the TEM images that the BP2T nanocrystals had a round shape, the nanocrystals are seen to have a platelet-like morphology (disk shape). Figure 1f–h shows TEM images of BP2T nanocrystals obtained by electron energy loss spectroscopy (EELS) and the EELS maps of oxygen (O) and sodium (Na), respectively. The region surrounded by white dashed-circles indicates the position of...
the BP2T nanocrystal, as shown in Figure 1f. The white dots on the nanocrystal in the EELS maps of O and Na indicate that the surface of the BP2T nanocrystal was densely covered by SDS. Figure 2a displays the X-ray diffraction (XRD) pattern of BP2T nanocrystals drop-cast on a quartz substrate. XRD $\theta/2\theta$ measurements revealed that the diffraction peaks were observed at 6.83°, 10.1°, 11.3°, and 13.6° corresponding to the (004), (006), (012), and (008) planes, respectively. Figure 2b,c shows the reproduced crystal structure and molecular packing using the reported data for BP2T (monoclinic $P_2_1/n$, $a = 0.57081$ nm, $b = 0.76036$ nm, $c = 5.2869$ nm, $\beta = 97.147^\circ$). Figure 2d shows the selected area electron diffraction (SAED) pattern of the BP2T nanocrystals shown in Figure 1c. The SAED pattern corresponds to the (010) diffraction pattern of the crystalline phase of BP2T. The XRD and SAED patterns indicate that most of the BP2T molecules stand almost upright against the crystal basal plane.

### 2.2. Size-Dependent Optical Properties of BP2T Nanocrystals

To elucidate the size-dependent optical properties of BP2T nanocrystals, we primarily measured the absorption spectra of the nanocrystal suspensions. As a reference, we also measured the absorption spectra of the solution-grown BP2T bulk crystal and dilute solution (monomer state, 0.01 mg mL$^{-1}$ in chlorobenzene). The BP2T bulk crystal was affixed to a quartz substrate for measurement. The BP2T nanocrystal suspensions and monomer solution were placed in a rectangular quartz cell (2 mm path-length) for measurement. Figure 3a shows the absorption spectra of the BP2T bulk crystal measured at 10 K and room temperature (RT, 300 K), nanocrystal suspensions, and monomer solution indicated in black, green, and gray respectively. The black circles, triangles, and diamonds in Figure 3a indicate the absorption peaks of the 0 → 0, 0 → 1, and 0 → 2 vibronic bands, respectively. The size of the BP2T nanocrystals dispersed in ultrapure water was evaluated by dynamic light scattering (DLS) (LB − 550, HORIBA) as indicated in Figure 3b,c. DLS measurements of the two nanocrystal suspensions revealed that the average size of the BP2T nanocrystals was 620 (Figure 3b) and 320 nm (Figure 3c), respectively. To clearly identify the absorption band of the BP2T bulk crystal, the absorption spectrum was measured at 10 K. From a micro-Raman spectroscopy, the vibrational spacing of 1457 cm$^{-1}$ was obtained for the BP2T single crystal, as shown in Figure S1 (Supporting Information). In the bulk crystal at 10 K, 0 → 0, 0 → 1, and 0 → 2 absorption bands corresponding to the transitions from ground state to singlet excited states appeared at 2.53, 2.72, and 2.91 eV, respectively. In the bulk crystal at RT, 0 → 1 and 0 → 2 absorption bands were observed at 2.64 and 2.79 eV, respectively. Owing to the antiparallel exciton coupling between the adjacent molecules aligned in the $ab$-plane of the crystal, although the lowest 0 → 0 transition is forbidden, a weak 0 → 0 transition is observed in the BP2T crystals similar to other TPCO crystals. In the nanocrystal suspension
containing crystals with an average size of 620 nm, 0 – 1 and 0 – 2 absorption bands were observed at 2.73 and 2.91 eV, respectively. The peak energy of each absorption band is blue-shifted, but the absorption edge energy positions appear to be almost unchanged due to Mie scattering. For the nanocrystal suspension containing crystals with an average size of 320 nm, 0 – 0, 0 – 1, and 0 – 2 absorption bands were observed at 2.68 and 2.86 eV, respectively. In the monomer solution, 0 – 0, 0 – 1, and 0 – 2 absorption bands appeared at 2.93 and 3.10 eV, respectively. The blueshift of the absorption peak energy and the appearance of the 0 – 0 band cannot be explained by a change in molecular aggregation and light scattering effects, such as excitation of Mie resonances.\[41,42\]

In this section, we present the results of investigating the correspondence relation between the micro-photoluminescence (micro-PL) spectra and nanocrystal sizes determined using the atomic force microscopy (AFM) images. Because the positions of BP2T nanocrystals on a substrate are random when the nanocrystal suspension is drop-casted onto a mica substrate, it is necessary to locate their positions to correlate the PL spectra and nanocrystal sizes. To locate the positions of the BP2T nanocrystals, a commercial index grid for TEM was attached to the back of the mica substrate. Micro-PL measurements and AFM observations were performed by attaching the mica substrate with the index grid to a quartz substrate, as shown in the schematic illustration in Figure S2, Supporting Information.

The micro-PL spectra and AFM images of the BP2T nanocrystals are shown in Figure 4. Black circles, triangles, diamonds, and squares in Figure 4a indicate the PL peaks of the 0 – 0, 0 – 1, and 0 – 2 emission bands, respectively. In the bulk crystal, the PL spectrum is characterized by a vibrational progression at 2.33 (0 – 1 emission), 2.18 (0 – 2 emission), and 2.03 eV (0 – 3 emission), which are assigned to transitions from singlet ground state to singlet excited state, as explained earlier. In sample #1-NC, 0 – 1, 0 – 2, and 0 – 3 emission peaks were observed at 2.36, 2.20, and 2.04 eV, respectively. As such, the peak energy is slightly blue-shifted and the vibrational spacing increases by 0.01 eV as compared to that of the bulk crystal. This can be attributed to surface effects, such as molecular torsion in the vicinity of the nanocrystal surface and lattice distortions. As determined by AFM, the diameter and height of sample #1-NC were found to be \( \approx 800 \) and 80 nm, respectively. In sample #2-NC, the entire emission band was clearly blue-shifted by 0.17 eV (0 – 0: 2.66, 0 – 1: 2.50, 0 – 2: 2.34, 0 – 3: 2.18 eV) in comparison to that in the bulk crystal. The diameter and height of sample #2-NC were \( \approx 600 \) and 27 nm, respectively. As the nanocrystals with the size smaller than 600 nm have a larger specific surface area, it is considered that the partially allowed 0 – 0 transition results from a lack of

![Figure 3](https://www.advancedsciencenews.com)

**Figure 3.** a) Optical absorption spectra of BP2T bulk crystal measured at 10 K and room temperature (RT, 300 K) (black), nanocrystal suspensions (green), and monomer solution (gray). Black circles, triangles, and diamonds in (a) indicate the absorption peaks of 0 – 0, 0 – 1, and 0 – 2 absorption bands, respectively. Size distributions of BP2T nanocrystals evaluated by dynamic light scattering (DLS): b) Average size of 620 nm and c) average size of 320 nm.
Figure 4. a) The micro-PL spectra of BP2T bulk crystal, nanocrystals, and monomer solution. Black circles, triangles, diamonds, and squares in (a) indicate the PL peaks of 0–0, 0–1, 0–2, and 0–3 emission bands, respectively. b) Fluorescence images of single BP2T nanocrystals corresponding to each spectrum in (a). Atomic force microscopy (AFM) images of BP2T nanocrystals for samples c) #1-NC, d) #2-NC, e) #3-NC, and f) #4-NC. We observed the micro-PL spectra for the nanocrystals surrounded by white circles in (c–f). g) Cross-sectional profile of the sample #4-NC in (f).
adjacent molecules at the nanocrystal surfaces. In samples #3-NC and #4-NC, 0 - 0, 0 - 1, 0 - 2, and 0 - 3 emission bands appeared at 2.95, 2.81, 2.65, and 2.49 eV, respectively. The diameter and height for sample #3-NC were 300 and 20 nm, and for sample #4-NC were 150 and 7.4 nm, respectively. The diameters and heights of the BP2T nanocrystals are listed in Table S1, Supporting Information. The cross section of sample #4-NC is shown in Figure 4f. The BP2T nanocrystals have a shape (disk shape) similar to typical TPCO single crystals with a thin platelet-like morphology. This is because of the favorable growth of the ab-plane of the crystal due to π – π stacking of molecules, which results in the molecules standing almost upright against the crystal basal plane (and substrate).[34,35] This was also confirmed by the XRD and SAED measurements as described above. In the monomer solution, 0 - 0, 0 - 1, 0 - 2, and 0 - 3 emissions were observed at 2.92, 2.75, 2.58, and 2.41 eV, respectively. Although 0 - 0 emission was observed at 2.95 eV for samples #3-NC and #4-NC, the reason for the narrower vibrational spacing between the 0 - 0 and 0 - 1 emission bands was due to the absorption of the portion of 0 - 0 emission by a low-pass filter (λ < 420 nm) that was set in front of the spectrometer. Moreover, as with typical TPCO single crystals with a thin platelet-like morphology, the BP2T nanocrystals have a similar shape, as can be seen in Table S1, Supporting Information. The spectral shifts may be attributed to Mie scattering, effect of surface excitons, luminescence due to defects, surface effects, or quantum confinement effects.[13-17,10,11,17,41-46] Because PL spectra was observed under excitation at 405 nm and the Mie scattering spectra can be tuned over a broad photon energy range by varying the particle size,[41,42] it can be inferred that the origin of the blue-shifted PL in the present study is not Mie scattering. Additionally, the change in the vibrational spacing of the BP2T nanocrystals cannot be explained by Mie scattering. Because the PL spectrum is expected to be characterized by a superposition of contributions from the surface and bulk excitons, a broad PL spectrum can be observed. However, PL spectra was observed to have a vibrational spacing of 0.15 or 0.16 eV which are similar to the bulk crystal. As for defect-related emission, because the defect emission can be observed at a lower photon energy region than the bulk emission, it is unlikely that a blue-shifted size-dependent defect emission is observed. In earlier studies on organic nanoparticles, it has been considered that the increase in surface area causes lattice softening, and the Coulombic interaction energies between molecules become smaller, leading to wider bandgaps. In perylene nanocrystals with sizes of a few hundreds of nanometers, a blueshift of the excimer fluorescence peak of ≈70 meV due to lattice softening has been reported.[10] Hence, the possible reasons for the spectral blueshift with decreasing nanocrystal size are the conventional surface effects, quantum effects involving the site shift effect,[47,48] (Figure S3, Supporting Information) depending on the specific surface area (characteristic of organic nanocrystals) and the exciton confinement, lattice softening, or combined effect. The amount of blueshift due to the site shift effect is difficult to estimate accurately because of the large number of constituent molecules of BP2T nanocrystals. However, this amount is expected to be part of the maximum site shift energy of 440 meV estimated from the 0 - 0 absorption energies of the bulk crystal and monomer solution.

![Figure 5](image-url) **Figure 5.** a) The peak energy dependence of 0–1 emission band on the BP2T nanocrystal size (crystal width) plotted using the values listed in Table 1. b) Relationship between the peak energy shift amount from bulk crystal and the change in specific surface area. The values were determined from the data of Figure 4. Error bars were added to account for the broad spectral width.

In this section, we will discuss the size-dependent optical properties of BP2T nanocrystals in terms of the quantum confinement effect used in inorganic semiconductor nanocrystals. The energy of exciton $E$ in the weak confinement regime is expressed as follows[45,46] 

$$E = E_{ex} + \frac{\hbar^2}{2M_{ex}} \left( \frac{\pi}{L} \right)^2$$  

(1)
where $E_{\text{ex}}$, $\hbar$, $M_{\text{ex}}$, and $L$ are the exciton energy of the bulk crystal, Dirac’s constant, the translational mass of exciton, and the size of exciton confinement, respectively. This equation results in the quantization of the wavevector, $k = n\pi/L$ ($n = 1, 2, \ldots$).

Using the values listed in Table S1, Supporting Information, and the values of energy shift from the bulk crystal, dispersion plots of energy $E$ versus wavevector $k$ were obtained, as shown in Figure S3, Supporting Information. Green circles and orange diamonds indicate dispersion plots when the width and thickness directions of the BP2T nanocrystals are quantized. The black dashed line shows the bulk exciton energy ($E_{\text{ex}}$) of $2.49$ eV determined from the absorption spectrum at 10 K.

The $M_{\text{ex}}$ values when the width and thickness directions of the BP2T nanocrystals are quantized were in the range of $6.14 \times 10^{-6} - 3.63 \times 10^{-5} m_0$ ($m_0$: electron mass in vacuum) and $3.03 \times 10^{-3} - 1.49 \times 10^{-2} m_0$, respectively. Comparing these values with the translational masses in CdS and CuCl nanocrystals,[49,50] the values were $10^{-6} - 10^{-2}$ times smaller. Considering the almost upright molecular orientation of the BP2T nanocrystals with respect to the $ab$-plane of the crystal, light confinement along the width direction of the crystal is expected. However, neither of the dispersion plots based on the quantum confinement effects along the width and thickness directions of the nanocrystal agreed with the exciton energy that has no dispersion in the wavenumber range shown in Figure S4, Supporting Information. Even when the dispersion plots are fitted with polynomials, the contribution of the quantum confinement effect is expected to be less than a few percent. Considering that the limiting value of the energy shift is the peak energy of the monomer, the $E - k$ plots in the BP2T nanocrystals are not consistent with the $E - k$ dispersion obtained based on the quantum confinement effect in the inorganic semiconductor nanocrystals. Therefore, the blue-shifted optical properties of the BP2T nanocrystals cannot be interpreted by the conventional quantum confinement effect.

Further, we examined the surface effects that have mostly been regarded as the origin of the size-dependent optical properties in organic nanocrystals. The influence of surface effects on the PL properties by measuring the PL spectra under different atmospheres were investigated. Measurements were made for the PL spectra at 300 K in vacuum ($4 \times 10^{-4}$ Pa) and in atmosphere for the BP2T nanocrystals with average sizes of 620 and 320 nm, as shown in Figure 6a,b, respectively. For the PL spectra of the BP2T nanocrystals with an average size of 620 nm, no difference was observed between the two PL spectra measured under vacuum and atmosphere indicated in black and blue, respectively. Meanwhile, in the PL spectra of the BP2T nanocrystals with an average size of 320 nm, the PL spectrum measured in the atmosphere had a higher peak energy of about 37 meV than that measured in vacuum, as shown in Figure 6b. Because the PL spectra were measured using the nanocrystal assembly, the influence of the atmosphere on the PL spectra of single nanocrystals is not clear, but the observed shift of about 37 meV demonstrates that the surface effect has a small impact on the blueshift in the PL spectra.

The PL quantum yields (PLQYs) of the BP2T nanocrystals were also investigated to verify the surface effects, which are expected to be the most significant contributor to the combined effect. In conventional surface effects, as the specific surface area increases, defect states due to lattice defects and impurities are generated, which lead to a decrease in the PLQY. To determine the PLQY in BP2T nanocrystals, the emission decay curves of the 0–1 bands were examined. Figure 7a,b shows the emission decay curves of the 0–1 band measured at 300 K for the BP2T nanocrystals with an average size of 620 (same nanocrystals as shown in Figure 3b) and 280 nm. The average crystal size of 280 nm was examined by DLS measurements, as shown in Figure 7c. By a convolution fitting (red solid lines) with the incident laser pulse (black dashed lines), it was observed that the emission decay profiles were characterized by two time constants of 370 ps (61%) and 1.14 ns (39%) for the nanocrystals with an average size of 620 nm and 320 ps (45%) and 1.11 ns (55%) for the nanocrystals with an average size of 280 nm. The fast and slow components are attributed to the surface trapping of excitons or excitons generated in the vicinity of the nanocrystal surface and radiative processes from excitons generated in the inner core.

Figure 6. The PL spectra of the BP2T nanocrystals with the average size of a) 620 nm and b) 320 nm measured in vacuum (black) and atmosphere (blue). The dotted lines in (b) indicate the energy of the 0–0 emission band. The spectra were observed at 300 K.
part of the nanocrystals (bulk region), respectively. The slightly shorter lifetime of BP2T nanocrystals with an average size of 280 nm might be attributed to the partial contribution of surface effects and exciton confinement. The presence of the short-lived components, which accounts for nearly half of the emission decay profiles, indicates that the surface effects influence the optical properties even when the specific surface area is as small as 4 – 16% (Figure 5b). Figure 7d shows the temperature dependence of the 0 – 1 band emission lifetime due to the interior of the nanocrystals (longer lifetime components) with an average size of 620 nm (red circles) and 280 nm (blue diamonds), respectively. We have recently reported the PLQY value of BP2T bulk crystals (microcrystals) to be 40% by examining the temperature dependence of the 0 – 1 emission band lifetime.\cite{51} The equation used for analysis is as follows

\[ \tau(T) = \frac{1}{(k_r + k_{nr})\exp(-E_a/(k_B T))} \]

where \( r, k_r, k_{nr}, E_a, k_B, \) and \( T \) are the spontaneous emission lifetime, radiative transition rate constant, nonradiative transition rate constant, activation energy of nonradiative transition, Boltzmann constant, and temperature, respectively.\cite{33,51} By fitting the experimental data using Equation (2), the parameters of \( k_r, k_{nr}, \) and \( E_a \) were determined for the BP2T nanocrystals with an average size of 620 and 280 nm. These values are presented in Table 1. The BP2T nanocrystals with an average size of 280 nm are temperature-tolerant because of the high \( E_a \) value of 25 meV, which is comparable to the thermal energy at room temperature \((k_B T)\). The values of PLQY \( \Phi \) were determined using the equation \( \Phi = k_f/(k_r + k_{nr}) \). The PLQY values are presented in Table 1. The PLQY value in nanocrystals is expected to decrease due to surface effects such as emission quenching by surface defects and oxygen, but the PLQY value in the BP2T nanocrystals with an average size of 280 nm was \( \approx 1.15 \) times higher than that of the bulk crystal. The fact that the enhancement of PLQY in the smaller-sized BP2T nanocrystals may reflect exciton confinement although the quantum confinement effect is small.

In addition, time-resolved PL measurements were performed to provide further insight into the surface and quantum effects of the BP2T nanocrystals. Figure 8a,b shows the time-resolved PL spectra measured for the BP2T nanocrystals with average sizes of 620 and 280 nm, respectively. In Figure 8a, black, blue, and purple lines indicate the PL spectrum integrated over the entire time range, the PL spectrum integrated from 0 to 10 ns, and the PL spectrum integrated from 0 to 5 ns, respectively. Error bars were estimated to be 0.05 ns by the fitting of temperature-dependent emission lifetimes.

### Table 1. The parameters of \( k_r, k_{nr}, E_a, \) and \( \Phi \) determined for the BP2T nanocrystals with the average size of 620 and 280 nm. The values in Table 1 include an error of \( \approx 5\% \) obtained from the two experimental values.

| BP2T nanocrystals | Average size: 620 nm | Average size: 280 nm |
|-------------------|----------------------|----------------------|
| \( k_r \)         | \( (4.3 \pm 0.2) \times 10^8 \text{ s}^{-1} \) | \( (6.3 \pm 0.3) \times 10^8 \text{ s}^{-1} \) |
| \( k_{nr} \)      | \( (6.7 \pm 0.3) \times 10^7 \text{ s}^{-1} \) | \( (7.5 \pm 0.4) \times 10^7 \text{ s}^{-1} \) |
| \( E_a \)         | \( 12.0 \pm 0.6 \text{ meV} \) | \( 25 \pm 1 \text{ meV} \) |
| \( \Phi \)        | \( 0.39 \pm 0.02 \) | \( 0.45 \pm 0.02 \) |
0.4 ns, and the PL spectrum integrated over the time range from 0.4 to 17.7 ns, respectively. Likewise, for Figure 8b, black, blue, and purple lines indicate the PL spectrum integrated over the entire time range, the PL spectrum integrated over the time range of 0–0.4 ns, and the time range of 0.4–8.9 ns, respectively. Figure 8a shows that the emission spectrum of the long-lived component is similar to the spectrum integrated over the entire time range, whereas the emission band of the short-lived component is blue-shifted by $55 \text{ meV}$ in comparison to that of the long-lived component. The blueshift of the emission of the short-lived component was due to the surface effect. Figure 8b shows that the PL spectra of the long-lived and short-lived components are similar to the spectrum integrated over the entire time range. In Figure 8b, broader PL spectra with an indistinct vibrational structure were observed owing to the superposition of emissions from the nanocrystals of different sizes (main contribution: nanocrystals with the size of 280 nm (see Figure 7c)). The reason for the similar PL spectra originating from short-lived and long-lived components is that the blueshift due to the surface effects and the energy upshift with a decrease in nanocrystal size became comparable because a nanocrystal assembly with an average crystal size of 280 nm was measured in the present case. For smaller nanocrystals, it is difficult to distinguish between the surface effects and quantum effects, as both affect the optical properties. Although it is difficult to make an accurate comparison of the PL spectra of a single nanocrystal and the nanocrystal assembly, the PL spectra of the nanocrystal and bulk crystal, PL spectra under different atmospheres, and time-resolved PL measurements indicate that the amount of blueshift due to the surface effects was estimated to be $20–55 \text{ meV}$. The values correspond to $12–32\%$ of the blueshift of 170 meV in the BP2T nanocrystals with an average size of 600 nm.

In perylene nanocrystals with sizes of a few hundreds of nanometers, size effects were observed in the PL spectra. The nanocrystal sizes manifesting the size effects were comparable to those of the BP2T nanocrystals, but only the emission band of the excimer was blue-shifted due to the size effect. Meanwhile, it was considered that the blueshift in the entire emission band of the BP2T nanocrystals caused the widening of the optical bandgaps. Considering the results obtained hitherto, there is more than one origin for the strong size-dependent optical properties of the BP2T nanocrystals. Although it is difficult to evaluate this quantitatively, the possible origins of the optical properties are the combined effect based on the surface effects including the lattice softening and the quantum effects involving the specific surface area-dependent site shift effect and exciton confinement. The widening of the bandgap based on the lattice softening is shown in Figure 9. Figure 9a–c shows schematic adiabatic potential diagrams against the generalized coordinate $Q$ for monomers, nanocrystals, and bulk crystals, respectively. The slightly broadened PL spectra of the BP2T nanocrystals in comparison to those of the bulk crystal (Figure 4a) are considered to be due to relaxed excited states. In the nanocrystals, wider bandgaps are obtained because of the smaller Coulombic interaction energies between the molecules caused by the large surface-to-volume ratio (lattice softening). In addition, the free excitons are stabilized by lattice relaxations based on lattice distortions near the nanocrystal surfaces (relaxed exciton state). The fact that the spectral widths and emission lifetimes in the BP2T nanocrystals are not significantly different from those in the bulk crystal suggests that they are due to shallow self-trapped exciton states.

2.3. ASE in BP2T Nanocrystals

To elucidate the potential of BP2T nanocrystals as a laser medium, the excitation density dependence of the PL spectra of the BP2T nanocrystals was examined using a nanosecond pulsed Nd:YAG laser. Figure 10 shows the excitation density
dependence of the PL spectra of the BP2T nanocrystals. The PL spectra of the nanocrystal assembly (size distribution is shown in Figure 3b) drop-casted on the quartz substrate was measured. As shown in Figure 10a, 0–1, 0–2, and 0–3 emission bands were observed at 2.36, 2.22, and 2.05 eV, respectively. The peak energies of each emission band are similar to those of sample #1-NC in Figure 4a. The PL spectra predominantly consist of emissions from BP2T nanocrystals larger than 600 nm. At a weak excitation density of 117 μJ/cm², full width at half maximum (FWHM) of 95.6 meV in the 0–1 emission band was observed. With increasing excitation density, the integrated PL intensity of the 0–1 emission band increased almost linearly, and it increased superlinearly above an excitation density of 206 μJ/cm². The FWHM value decreased to 61.7 meV at 278 μJ/cm². This superlinear increase in the PL intensity and the decrease in the FWHM value above the threshold excitation density of 206 μJ/cm² was attributed to the amplified spontaneous emission (ASE). In organic crystals, although lasing and ASE at a low threshold have been reported for organic nanowires and low-dimensional crystals, there are few reports on emission amplification in organic nanocrystals with sizes of less than 1 μm. Although there is a recent report on lasing from wide-bandgap 2,20-bi(9,9-dimethylfluorene) (BMeF) nanocrystals at a low threshold of 2.77 μJ/cm², the BMeF nanocrystals have a morphology of elongated hexagon disks with a size larger than 13.2 μm. In the present study, we observed the ASE in the spectra, which consisted predominantly of emission from the nanocrystals of ≈600 – 1000 nm size. Nanocrystal-size-dependent ASE and lasing are ongoing investigations to demonstrate wavelength-tunable lasing.

3. Conclusion
BP2T nanocrystals were prepared using the modified miniemulsion technique. From the EELS maps of O and Na for the
nanocrystal, it was found that the surface of the BP2T nanocrystal was densely covered by SDS. From the XRD and SAED measurements, it was found that the BP2T molecules were almost upright against the crystal basal plane. Optical absorption and micro-PL measurements demonstrated that the optical spectra were blue-shifted with decreasing nanocrystal size. The size-dependent PL properties revealed that the peak energies of the PL spectra were blue-shifted in the photon energy range from the bulk crystal to the monomer state. The strong size-dependent optical properties of the BP2T nanocrystals were demonstrated from the results of the BP2T nanocrystal size dependence of $E_k$ (energy-wavevector) dispersion, the blue-shifted PL spectra with the decrease in the nanocrystal size, the PL spectra of the nanocrystals measured in vacuum and atmosphere, and the high PLQY values in the nanocrystals (39% and 45%). The size dependence of the PL spectra indicated that the emission color varied from yellow to blue. The origins of the size-dependent optical properties can be attributed to the combined effect (surface effects + quantum effects) based on the surface effects, including the lattice softening and the quantum effects involving the specific surface-area-dependent site effect and exciton confinement (small contribution). As for the results of verifying the usefulness of the BP2T nanocrystals as the laser active medium, ASE was observed for the first time from the nanocrystals of $\approx 600 - 1000$ nm size, which is smaller than that previously reported for organic crystals.

4. Experimental Section

Preparation of BP2T Nanocrystals and Bulk Crystals: BP2T was purchased from Wako Pure Chemicals Industries, Ltd. (purity >99%) and used after purification by sublimation. SDS was purchased from Sigma-Aldrich Co. Ltd. In the present miniemulsion technique, BP2T (0.05 - 0.3 mg) was dissolved in chlorobenzene (1 mL), and the solution was filtered before stirring for 60 min at 60 °C. To disperse the nanocrystals into water, SDS (33 - 40 m) as a surfactant was dissolved in ultrapure water (3 mL), and the solution was stirred at 500 rpm and 100 °C for 25 min. Then, the chlorobenzene solution of BP2T was mixed with the SDS aqueous solution, and the emulsion was sonicated using an ultrasonic homogenizer (THU – 80, 20 kHz, AS ONE Corporation) for 60 s. The chlorobenzene in the miniemulsion was evaporated by stirring at 800 rpm and 60 °C for 12 h. The prepared miniemulsion was centrifuged at 4000 rpm for 7 min using a centrifuge tube (Amicon Ultra – 4, Millipore, 10 kDa), and after discarding the supernatant, ultrapure water (4 mL) was added to the precipitates. The water-dispersed BP2T nanocrystals were obtained by repeating the process four times to remove excess SDS in the suspension. To suppress the aggregation of BP2T nanocrystals, ammonia water was added to the nanocrystal suspension to adjust the pH to 12. Bulk crystals of BP2T were prepared using the following method: After the powder (1.5 mg) was dissolved in o-dichlorobenzene (20 mL) (Nakalai Tesque) by heating at 170 °C, crystals were precipitated by slowly cooling to 40 °C in 28 h. After filtering the resulting solution, thin platelet crystals of different sizes and shapes were obtained. A single crystal of a few hundred micrometers in size was selected using a tungsten needle to carry out the optical measurements.

Characterization of BP2T Nanocrystals: TEM images and EELS maps of BP2T nanocrystals were obtained using a TEM (JEM-1400Plus, JEOL) operated at an acceleration voltage of 100 kV. To prepare the samples for the TEM observations, an aqueous dispersion of the BP2T nanocrystals was drop-cast onto a standard TEM copper grid with a holey carbon film. The SAED pattern of the BP2T nanocrystals was obtained using a TEM (JEM-3100FEF, JEOL) operated at 300 kV. For the XRD measurement, the BP2T nanocrystal suspension was drop-cast onto the quartz substrate. The θ/2θ XRD pattern was obtained using an XRD (SmartLab, Rigaku) using monochromatic CuKα radiation (λ = 0.154 nm). The size of the BP2T nanocrystals was examined using AFM (JSPM-5200, JEOL).

Optical Measurements: The absorption spectrum at 10 K was measured using a cryostat (Daikin, V202CSL), a tungsten lamp (JASCO, PS-H150), a spectrometer (JASCO, CT-25CS), a lock-in amplifier (Stanford Research Systems, SR830), and a Si detector (Hamamatsu Photonics, S1337-BQ). The optical absorption spectra of BP2T bulk crystal, nanocrystal suspensions, and dilute solution (monomer solution) were measured at room temperature (300 K) using a UV–visible (UV–Vis) spectrophotometer (JASCO, V–530, Japan). To investigate the vibrational spacing in BP2T single crystal, micro-Raman spectroscopy (NRS-4100-30, JASCO Co., Japan) was performed. For the micro-PL measurements, an excitation laser (continuous-wave laser diode, λex = 405 nm, ≈1 W cm$^{-2}$) was incident at an angle of 66° against the substrate surface. Spatially resolved PL spectra of individual BP2T nanocrystals were observed using a microscopic PL measurement system with a diode laser. The PL spectra of the individual BP2T nanocrystals were measured using a 20× magnification objective lens and a pinhole (diameter: 200 μm). The PL spectra were obtained from selected areas of the BP2T nanocrystal using a charge-coupled device (CCD) spectrometer (Spec-10, Princeton Instrumets, Roper Scientific). To reproduce the micro-PL spectra of the BP2T nanocrystals shown in Figure 4a, we measured them for ≈100 nanocrystals in total. For the measurement of atmosphere dependence of the PL spectra, the quartz substrate with the BP2T nanocrystals was mounted on a cryostat, and we measured the PL spectra under vacuum by evacuating inside the chamber. We used the PL spectra under atmospheric pressure by returning it to atmospheric pressure. For the time-resolved PL measurements, we used a Ti:sapphire pulsed laser (Coherent, Mira Model 900-F) with a time duration of 100 – 150 fs and a repetition rate of 76 MHz. To detect fluorescence from the BP2T nanocrystals, an imaging polychromator (Hamamatsu, CS094) was coupled to a streak camera (Hamamatsu, CS134A) (time resolution: 15 ps) for simultaneous measurement of both the time and wavelength domains. The second harmonic light was used as the excitation source (λex = 400 nm). For ASE measurements, an excitation light from the Nd:YAG laser (λex = 355 nm, repetition rate: 1.2 kHz, pulse width: <1.1 ns) was used. A stripe-shaped excitation light (p-polarization) was focused on the BP2T nanocrystals with an incident angle of ≈45° against the substrate, and light emission from the nanocrystals was detected using a CCD spectrometer (Hamamatsu, PMA-50).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.
Author Contributions
H.M. conceived and designed this study. K.B. constructed an optical setup for micro-PL spectroscopy measurements. T.J. performed all the experimental work and data analysis with the assistance of H.M. T.J. wrote the manuscript with contributions from H.M., K.B., F.S., and H.Y.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
5,5′-bis(4-biphenyl)-2,2′-bithiophene (BP2T or PPTTPP), combined effect, nanocrystals, size-dependent optical properties, thiophene/phenylene co-oligomers (TPCOs)

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