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Highly Luminescent Solution-Grown Thiophene-Phenylene Co-Oligomer Single Crystals

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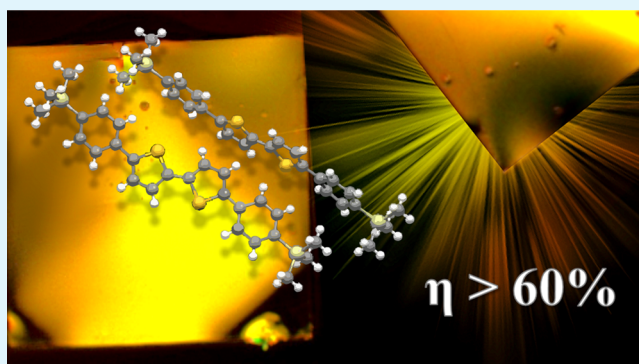
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Supporting Information

ABSTRACT: Thiophene-phenylene co-oligomers (TPCOs) are among the most promising materials for organic light emitting devices. Here we report on record high among TPCO single crystals photoluminescence quantum yield reaching 60%. The solution-grown crystals are stronger luminescent than the vapor-grown ones, in contrast to a common believe that the vapor-processed organic electronic materials show the highest performance. We also demonstrate that the solution-grown TPCO single crystals perform in organic field effect transistors as good as the vapor-grown ones. Altogether, the solution-grown TPCO crystals are demonstrated to hold great potential for organic electronics.

KEYWORDS: photoluminescence quantum yield, oligo(thiophene-phenylenes), single crystals, organic electronics, field-effect transistors



Thiophene-phenylene co-oligomers (TPCOs) are among the most promising materials for organic light-emitting devices as their single crystals combine efficient charge transport and luminescence.^{1–4} The photoluminescence (PL) external quantum yield (QY) of up to 38% was reported for vapor-grown TPCO single crystals^{5,6} with 100% internal PL QY suggested.⁷ Such remarkable electronic properties of TPCO single crystals together with their high thermal stability and high quality surfaces make them attractive candidates for electrically pumped organic lasers.^{8–10}

Typically, the highest performance is reported for organic semiconducting crystals grown from the vapor phase using physical vapor transport (PVT) technique.¹ On the other hand, thin single-crystalline TPCO films can also be grown using solution methods,^{11–13} which are preferential for practical applications. Recently, monoexponential PL kinetics in the broad dynamic range have been reported for solution-grown TPCO crystals, which signifies their low-defect electronic structure.¹³ Furthermore, TPCO single crystals grown at the gas–solution interface demonstrate a molecularly smooth

surface,¹³ which is indispensable for high performance organic field-effect transistors (OFETs). All these facts inspire further investigation of the solution-grown TPCO crystals for their optical and charge transport properties.

Here we report on record high PL QY among TPCO single crystals reaching 60%, which is higher for the solution-grown crystals than for the vapor-grown ones. We show that packing of TPCOs in an ordered crystal structure does not hinder but increases the PL QY by a factor of 3, most probably due to suppression of the radiationless relaxation channel. Furthermore, the solution-grown TPCO single crystals perform in OFETs as good as the vapor-grown ones. All in all, the solution-grown semiconducting TPCO crystals are demonstrated to hold great potential for organic electronics.

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Figure 1a depicts the structural formula of the studied molecule (TMS-PTTP-TMS) with the thiophene-phenylene

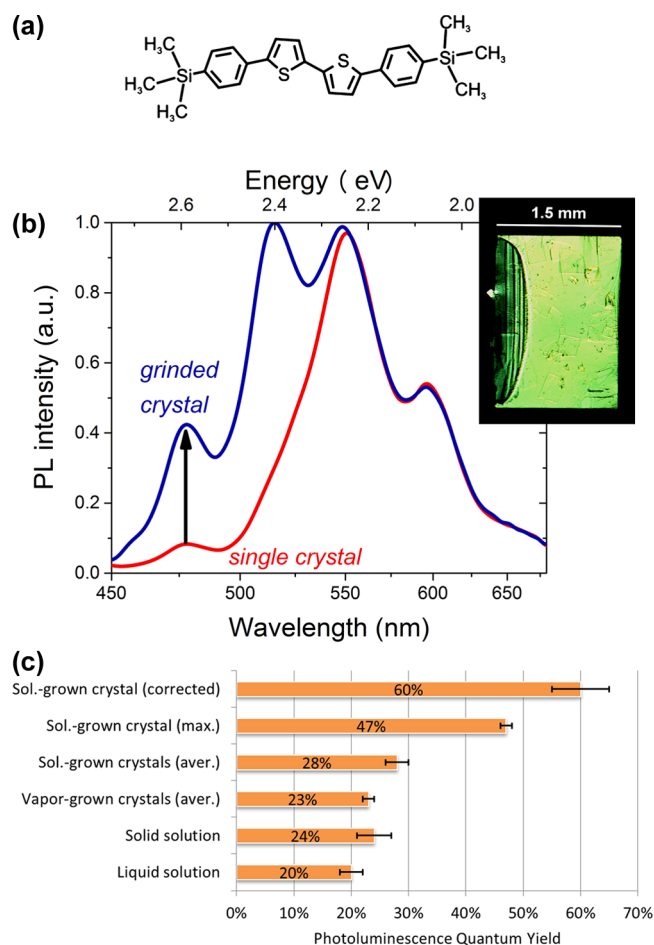


Figure 1. (a) Structural formula of studied thiophene-phenylene oligomer (TMS-PTTP-TMS). (b) PL spectra of a large (1.5×2.2 mm) solution-grown single crystal and its grinded sample. The spectra are normalized to the position of the low-energy sub-band at 600 nm. Inset shows a dark-field microphotograph of the solution-grown single crystal. (c) PL QY in solutions and single-crystal samples. The bars indicate standard deviations for the averaged PL QYs and the instrumental accuracy for the other data.

conjugated core (5,5'-diphenyl-2,2'-bithiophene, PTTP) and trimethylsilyl (TMS) terminal substituents to provide good solubility.

TMS-PTTP-TMS single crystals were grown by both solvent-antisolvent crystallization (SAC)¹³ and PVT¹⁴ methods for comparison. TMS-PTTP-TMS crystals grew in the shape of squarish plates with a lateral size of about 1–5 mm and a thickness from a half to a few μm . The X-ray diffraction, crystal structure, and atomic-force microscopy data for TMS-PTTP-TMS single crystals were reported earlier.¹³ The solution-grown crystals (inset, Figure 1b) had a very flat top facet (about one molecular step over $10 \times 10 \mu\text{m}$),¹⁵ whereas the vapor-grown ones had both facets with molecularly flat areas larger than $30 \times 30 \mu\text{m}$ (Figure S1). After the growth, the crystals were inspected with a polarizing optical microscope for cracks, aggregates, outgrowths, and ruptured edges; those having these defects were not selected for the further measurements.

Figure 1b shows normalized PL spectra of a large solution-grown single crystal (for PL spectra of other crystals, see Figure

S2a). To estimate the effect of PL reabsorption,¹⁵ we mechanically grinded the crystal in powder with a typical grain size of no more than 100 μm . Mechanical grinding dramatically reduces the PL reabsorption as shown for various aromatic hydrocarbon crystals.¹⁵ As evident from comparison of the PL spectra of as-grown and grinded crystals (Figure 1b), the high energy PL sub-bands (region >2.2 eV) in the grinded sample show much higher intensities due to strong reduction of PL reabsorption. The ratio between the integrated PL spectra of the as-grown and grinded crystals gives the fraction of reabsorbed PL as high as 30%. This value is used as a reabsorption correction factor for PL QY determination.

Figure 1c compares the PL QY in different TMS-PTTP-TMS samples. The averaged PL QY in sets of more than 20 crystals was $23 \pm 1\%$ for the vapor-grown crystals and $28 \pm 2\%$ for the solution-grown ones (for detailed statistics, see Figure S2b). The highest PL QY of the vapor-grown crystals did not exceed $35 \pm 1\%$, whereas it climbed up to $47 \pm 1\%$ for the solution-grown crystals. With the correction for reabsorption, the maximal PL QY of the solution-grown crystal reached impressive $60 \pm 5\%$.

Remarkably, the PL QY in single crystals exceeds that in dilute liquid solutions ($20 \pm 2\%$) by a factor of 3. To reveal the reason for PL QY increasing in crystals, we measured the PL QY in a solid solution (see Experimental Section). The PL spectra of the solid and liquid solutions are virtually the same except a 0.05 eV bathochromic shift in the latter (see Figure S2c). The measured PL QYs in the solid ($24 \pm 3\%$) and liquid ($20 \pm 2\%$) solutions are very close indicating that hindered molecular motions in the solid solution do not result in a noticeable increase in PL QY. Therefore, the reason for high PL of the TPCOs in the crystalline phase is mainly associated with intermolecular interactions in the closely packed ordered arrangement.

To elaborate on this point further, Figure 2 compares PL kinetics of TMS-PTTP-TMS in solutions and a typical solution-grown single crystal. The PL lifetime in the crystal is longer by approximately a factor of 2.5–3 than that in the solutions, in full accordance with the corresponding increase in PL QY (Figure 1c).

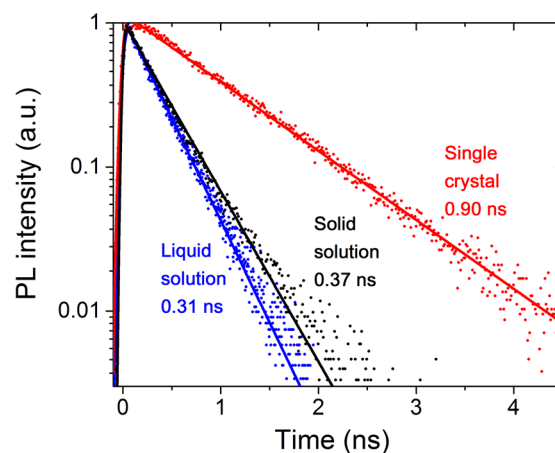


Figure 2. PL kinetics in TMS-PTTP-TMS dilute THF solution (blue), solid solution (black), and single crystal (red). The kinetics were recorded at the PL maxima of 460 nm in the solutions and 550 nm in the crystal. The lines are monoexponential fits convoluted with an apparatus response, and the numbers are the corresponding decay times, τ (see eq S1).

Table 1 summarizes the PL parameters for TMS-PTTP-TMS samples whose PL kinetics are presented in Figure 2. The

Table 1. PL Parameters for TMS-PTTP-TMS Samples

| sample | PL QY (%) | τ (ns) | k (ns ⁻¹) ^a | Γ (ns ⁻¹) ^b |
|-----------------|---------------------|-------------|--------------------------------------|---|
| liquid solution | 20 ± 2 | 0.31 ± 0.02 | 2.6 ± 0.2 | 0.65 ± 0.08 |
| solid solution | 24 ± 3 | 0.37 ± 0.03 | 2.1 ± 0.2 | 0.7 ± 0.1 |
| single crystal | 60 ± 5 ^c | 0.90 ± 0.05 | 0.4 ± 0.1 | 0.6 ± 0.1 |

^aRate constants of nonradiative decay. ^bRate constants of radiative decay. ^cReabsorption corrected.

approximately equal radiative rates, Γ , in solution and single crystal point out to the very close values of the transition dipole moments of individual and closely packed molecules. According to the X-ray data, the crystalline packing of TMS-PTTP-TMS molecules corresponds to a herringbone structure within closely packed molecular layers with the parallel long molecular axes in the layers.¹³ Molecules in the layers are inclined by a 41-degree angle against the basal plane (Figure S3) so that coupling between their dipole transition moments corresponds to J-aggregation,¹⁶ which is known to result in high luminescence. Tentatively, high PL observed in the TMS-PTTP-TMS crystals could be assigned to J-aggregation; however, its quantitative analysis needs to go beyond the point dipole approximation as the TMS-PTTP-TMS dipole (conjugation) length is a few times longer than the intermolecular distance (Figure S3). Note that J-aggregation is rarely observed in herringbone packing of rod-shape conjugated oligomers, which usually form low-emissive H-aggregates.¹⁷ Therefore, TMS-PTTP-TMS crystals are a notable example of the system where the herringbone packing of conjugated molecules is compatible with very high luminescence.^{18,19} The luminescence efficiency is greatly enhanced in the crystal evidently as a result of suppression of the radiationless relaxation channel (Table 1).

To explore charge transport in TMS-PTTP-TMS single crystals, top-contact top-gate OFETs were fabricated (Figure S4). As far as we are aware, these are the first reported top-gate TPCO devices. Figure 3 demonstrates current–voltage characteristics for a device based on a solution-grown single crystal. The device exhibits *p*-type OFET behavior with virtually text-book output characteristics (Figure 3a) showing negligible contact effects and clear linear and saturation regions. The hole mobility as high as $0.091 \pm 0.003 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was calculated from the transfer characteristics in the linear regime (Figure 3b) using eq 1 (Experimental Section). The linear regime is known to provide more reliable mobility values of a material in OFET

measurements than the saturation regime.²⁰ In the latter, the hole mobility calculated from the transfer characteristic (Figure S5a) was $0.077 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ using eq 2 (Experimental Section), which was close to that in the linear regime.

To compare charge transport properties of solution- and vapor-grown single crystals, we calculated the charge mobility in the linear and saturation regimes for a series of three devices based on both solution- and vapor-grown single crystals (Table S2). A typical transfer characteristic for a vapor-grown single crystal OFET is shown in Figure S5b. The averaged mobilities for the vapor-grown single crystals are similar to the solution-grown ones both in the linear and saturation regimes. Note that the top-electrode OFET configuration allowed us to decrease contact effects as follows from the virtually linear output characteristics at near zero voltage in Figure 3a. The clear contact effects are typically observed for TPCO crystals in OFETs fabricated in the staggered configuration (the data for bottom-gate top-contact OFETs are given in the Supporting Information).²¹ Therefore, solution processing can provide TPCO single crystals with the same charge mobility as potentially cleaner vapor processing. The hole mobility for TMS-PTTP-TMS single crystals is the highest value reported for single crystals grown from short TPCOs containing no more than four conjugated rings, and it is in the range reported for longer TPCOs.²²

The negative threshold voltages in TMS-PTTP-TMS single-crystal OFETs in the top-electrode configuration varied in the range 15–55 V. Partially, this variation is due to various thickness of the gate dielectric. Although these threshold voltages are higher than those reported for other TPCO single-crystal OFETs operating in the staggered configuration,²² this is mainly due to the lower capacitance of our top dielectric so that the threshold charge density for TMS-PTTP-TMS and other TPCO are comparable (see Table S3).²² Therefore, our data show that the solution-grown TPCO single crystals demonstrate virtually the same electrical performance as the vapor-grown crystals.

In summary, we have demonstrated TPCO single crystals with record PL QY reaching 60%. The brightest PL was observed in solution-grown TPCO single crystals as compared with the vapor-grown ones. We have shown that the outstanding PL properties of TMS-PTTP-TMS single crystals are mainly associated with suppression of the radiationless relaxation channel in the closely packed geometry. Both solution- and vapor-grown TMS-PTTP-TMS single crystals show virtually identical performance in OFET. Comparing the vapor- and solution-grown TPCO single crystals, we conclude that solution processing seems a more promising approach to

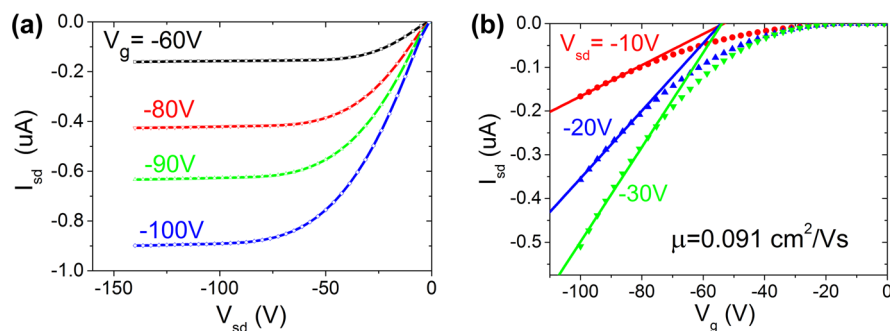


Figure 3. (a) Output and (b) transfer characteristics of OFET based on a solution-grown single crystal.

fabricate high-grade TPCO single crystals for organic optoelectronics. This highlights the high potential of solution-processing semiconducting organic crystals as an industrial platform for organic electronics.

■ EXPERIMENTAL SECTION

TPCO Synthesis. 5,5'-bis(4-trimethylsilyl-phenyl-1-yl)-2,2'-bithiophene (TMS-PTTP-TMS) was synthesized and purified according to the procedure reported elsewhere.¹³

Crystal Growth. The SAC-method was reported elsewhere.¹³ In PVT-method, TMS-PTTP-TMS was sublimated from the solid phase and transported by helium laminar flux to the growing zone in a glass tube of 2 cm in diameter. The crystal growth time was 5–8 h. After the growth, the crystals were transferred on glass substrates. For the OFET samples, the flattest crystal facet was identified with an optical microscope and used further for charge-transport studies.

TPCO Solid Solutions. TPCO solid solution was prepared by coextrusion (Micro Compounder, DACA Instruments) of Paraloid B-72 (Rohm and Haas) with TMS-PTTP-TMS molecules at 180 °C. The rotation speed of the extruder was slowly raised from the initial 90 r min⁻¹ to the final 360 r min⁻¹. After 5 min of mixing the composition obtained was released through a round die to make extrudate rods. Films with TPCO concentrations of 0.02 g L⁻¹ and a thickness of 420 μm were prepared by hot-pressing of the extrudate rods at 150 °C and 5 MPa using a hydraulic press apparatus (Specas Atlas Manual 15T) with heated plates.

Photoluminescence Quantum Yield (PL QY). The PL QY in solid samples was measured using a homemade 5 cm-diameter integrating sphere, whose internal surface was covered with MgO. The optical output of the integrating sphere was coupled to a spectrometer (InVia, Renishaw). To calibrate the spectral sensitivity of the spectrometer, the sphere illuminated by an incandescent lamp was coupled to a calibrated spectrometer (S100, Solar Laser Systems; calibrated at the All-Russian Research Institute for Optical and Physical Measurements). PL in TPCO samples on glass substrates was excited by radiation of a semiconductor laser at a wavelength of 405 nm. The optical response of the glass substrates and sample holders was separately checked for not contributing to the measurement. The PL QY was measured by the method described in ref.²³ Typical raw spectra of a TMS-PTTP-TMS sample recorded in the integrating sphere are shown in Figure S2d. The PL spectrum of TMS-PTTP-TMS liquid solution in tetrahydrofuran (THF) at a concentration from 1 × 10⁻⁸ to 1 × 10⁻⁵ mol l⁻¹ was measured using a homemade spectrofluorimeter, and the PL QY was determined by using five fluorescence standards with the known PL QY (*p*-terphenyl, phenylphenyloxazole, anthracene, 1,4-bis-(5-phenyloxazole-2)benzene, and rhodamine 6G), whose PL spectra were recorded in optically dilute solutions.²⁴ The PL QY in THF solution was calculated as the mean value from the experimental data for each of the five standards.

Photoluminescence Kinetics. PL kinetics were measured using a streak camera (C5680, Hamamatsu) combined with a polychromator. The PL was excited at a wavelength of 400 nm by short pulses (100 fs duration at 1.9 MHz repetition rate) on a doubled Ti:sapphire laser output. The apparatus function was ~30 ps for the 5 ns base. The kinetics were fitted by an exponential function convoluted with the Gaussian-shaped instrument response (see eq S1).

Organic Field-Effect Transistors. Single-crystal OFET samples were fabricated using the top-contact top-gate configuration according to the procedure reported elsewhere.²⁵ The schematic structure of the devices is presented in Figure S4a. The electrodes were painted by colloidal graphite paint (PELCO, TED PELLA) as shown in Figure S4b. The OFET channel width and length were measured using an optical microscope. As a top dielectric layer, parylene was deposited from [2,2]paracyclophane (Chemical Point) as described elsewhere,²⁶ its thickness was measured using an atomic-force microscope (Integra-Spectra, NT-MDT). OFET current–voltage characteristics were recorded using a source-meter instrument (Keithley 2636A) at dark conditions, ambient atmosphere, and room temperature. The voltage sweep rate was 0.5 V s⁻¹. Both linear and saturation modes were used

for the determination of field-effect mobility of OFET samples. The source-drain current (I_{sd}) in the linear and saturation regimes was fitted according to eqs 1 and 2, correspondingly²⁰

$$I_{sd} = \frac{W}{L} \mu_{lin} C (V_g - V_{th}) V_{sd} \quad (1)$$

$$I_{sd}^{1/2} = \left(\frac{W}{2L} \mu_{sat} C \right)^{1/2} (V_g - V_{th}) \quad (2)$$

Here, C is the capacitance per unit area of the insulating layer; W and L are the channel width and length; μ_{sat} and μ_{lin} are the carrier mobilities in the saturation and linear regimes; V_g , V_{th} and V_{sd} are the gate, threshold, and source–drain voltages, respectively.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b11967.

Microscopy images for vapor-grown TMS-PTTP-TMS crystals, PL spectra of TMS-PTTP-TMS crystals and solutions, detailed statistics on PL QY in solution- and vapor-grown crystals, typical raw spectra for PL QY calculations, fit equation for PL kinetics, scheme and optical image of top-contact top-gate OFET, current–voltage characteristics of solution- and vapor-grown single-crystal OFET devices with different geometries, and parameters of single-crystal OFETs (PDF)

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

TPCO, thiophene-phenylene co-oligomers
 PL, photoluminescence
 PL QY, photoluminescence quantum yield
 SAC, solvent-antisolvent crystallization
 PVT, physical vapor transport
 OFET, organic field-effect transistor

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