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# Directed Functionalization Tailors the Polarized Emission and Waveguiding Properties of Anthracene-Based Molecular Crystals

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Supporting Information

ABSTRACT: Organic semiconducting crystals are characterized by anisotropic optical and electronic properties, which can be tailored by controlling the packing of the constituent molecules in the crystal unit cell. Here, the synthesis, structural characterization, and emission of anthracene derivatives are focused to correlate directed functionalization and optical properties. These compounds are easily and scalably prepared by standard synthesis techniques, and alterations in functional groups yield materials with either exclusive edge-to-face or face-to-face solid-state interactions. The resulting crystals feature either platelet or needle shapes, and the emission exhibits polarization ratios up to 5 at room temperature. In needle-shaped crystals, self-waveguiding of the



emission is also observed with propagation loss coefficients as low as 1.3 dB mm<sup>-1</sup>. Moreover, optical coupling between crossing crystalline microwires is found and characterized. The combination of optical anisotropy and emission self-waveguiding opens interesting routes for the exploitation of these active materials in photonic applications, including optical integrated circuits and microscale light sources.

# ■ INTRODUCTION

Tremendous progress in organic optoelectronics has been made possible by the improved control of the assembly and packing of molecules and polymers in amorphous and crystalline materials.<sup>1,2</sup> Indeed, most of the optical and electronic properties of organic compounds in the solid state are determined by the configurations of the individual molecular constituents at the nanoscale.<sup>3,4</sup> For instance, various approaches have been developed that aim at controlling the packing of organic building blocks in amorphous systems, through either by chemical functionalization and introduction of suitable moieties at the molecular level<sup>5</sup> or by engineering the processing steps leading to microand nanostructures, films, and electronic or optoelectronic devices.<sup>6,7</sup> In organic crystalline materials, intermolecular interactions can affect physicochemical properties even more tightly, leading to solid-state arrangements that can allow charge transport and emission to be enhanced compared to those of amorphous systems. Examples of improved properties include high charge-carrier mobility,8 polarized emission,9 superradiance,<sup>10</sup> and excitonic<sup>11-14</sup> and polaritonic<sup>15</sup> optical gain. Combining bright luminescence with high charge mobility, various organic crystals are appealing candidates for the development of next-generation photonic devices.<sup>16</sup> These comprise organic light-emitting diodes,<sup>17</sup> miniaturized optical waveguides, and a price optically pumped lasers, <sup>21,22</sup> including random lasers,<sup>23</sup> and photonic logic gates.<sup>24</sup> The performance and versatility of such devices and the fundamental features of compounds at their base can be further improved by molecular functionalization approaches, allowing for tuning the solidstate order of crystalline organics,<sup>25</sup> as well as the formation of intermolecular species such as excimers and exciplexes.<sup>26-28</sup>

The acenes, in particular, are highly susceptible to the tuning of a wide array of properties by appropriate functionalization. The optical gap is easily tuned by the addition of suitable functional groups,<sup>29-32</sup> and fluorescence quantum yield is dramatically enhanced by the incorporation of the dioxolane moiety.<sup>33</sup> Silylethyne functionalization leads to remarkable stabilization of acenes against reaction with oxygen,<sup>34</sup> and tuning of the solid-state order by this approach has led to materials with impressive charge transport properties.<sup>25,35</sup>

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Moreover, the packing of molecules in the solid state ultimately determines the crystal morphology. Organic single crystals have been grown in various shapes, such as nanowires,<sup>9,36</sup> microneedles,<sup>22,37</sup> and platelets.<sup>13,23</sup> Although the correlation between the morphology and optical properties in organic crystals is still poorly investigated, <sup>18,20,38</sup> for most optoelectronic and photonic applications, the shape taken by active crystalline materials is critically important. For instance, for directional optical waveguiding, needle-shaped crystals are preferred, since they provide effective transversal confinement of photons and almost unidirectional propagation of light.<sup>3</sup> Therefore, the possibility to control molecular packing and the resulting crystal shape are likely to enable the design and development of novel device architectures,<sup>39</sup> including net-works of almost one-dimensional (1D) organic singlecrystalline wires.<sup>21</sup> In these systems, the precise positioning of individual wires and their optical coupling would enable the realization of complex photonic circuits, where light generated locally can be transported over macroscopic distances. The intensity of light transported at millimeter to centimeter scales through these elongated crystals can be attenuated by selfabsorption of light and by scattering of photons by bulk or surface defects. For most organic single crystals, propagation losses are in the range of 30-270 dB mm<sup>-1</sup>.<sup>18-20</sup> Overall, controlling the propagation of light demands not only for unidirectional propagation but also for engineering the transport of photons over complex two-dimensional and three-dimensional circuits, built by interconnecting 1D crvstals.<sup>21,24</sup> To this aim, two or more individual elongated crystals can be joined to split(combine) light propagating in the individual structures in two(one) beams. Additional optical losses might arise at the regions where crystals overlap due to unmatched photon coupling, which also needs to be quantified and taken into account in network designing. In this framework, anthracene (ANT) constitutes a very promising system because it forms highly emissive crystals featuring superradiance<sup>40</sup> and amplified spontaneous emission.<sup>15</sup> The functionalization routes aimed at tuning anthracene's solidstate order and morphology are especially interesting in view of obtaining crystals with tailored microscopic morphology and emission properties.

Here, we report on three silylethyne-substituted anthracene single crystals (Figure 1) functionalized to adopt radically different solid-state arrangements. The synthesis and structure of 9,10-bis(triisopropylsilylethynyl)anthracene (TIPS ANT) have previously been reported, and the molecules adopt a strict



Figure 1. Molecular structures of TIPS ANT, TMS ANT, and F4 TMS ANT.

edge-to-face orientation in the solid state (Figure 2).<sup>26</sup> Offsetting the triisopropylsilyl groups of TIPS ANT to the



**Figure 2.** Crystal packing (highlighting the chromophores) for (a) TIPS ANT and (b) F4 TMS ANT. TIPS ANT shows completely isolated chromophores, whereas F4 TMS ANT is strongly  $\pi$ -stacked.

1,4 positions leads to a waxy compound that never forms crystals.<sup>26</sup> Reducing the size of the silyl group to methyl (i.e., 1,4-trimethylsilylethynyl anthracene, TMS ANT) yields a highly fibrous crystalline compound.

Structural similarity to the fluorinated derivative (described next) strongly supports a 1D alternating  $\pi$ -stacked structure. 1,2,3,4-Tetrafluoro-5,8-bis(trimethylsilylethynyl)anthracene (F4 TMS ANT) is prepared by silylethynylation<sup>41</sup> of 1,2,3,4-tetrafluoro-5,8-anthraquinone<sup>42</sup> (see the Supporting Information, including Figures S1–S5 for details). The fluorescence quantum yield of this compound in cyclohexane (based on a 9,10-diphenylanthracene standard) is 72%.

The different solid-state packing of the TIPS ANT and F4 TMS ANT derivatives leads to strikingly different crystal habits and optical properties. Highly polarized emission is collected from platelet-shaped TIPS ANT, whereas in needle-shaped TMS ANT and F4 TMS ANT crystals, efficient self-waveguiding of the emission is found with propagation losses as low as 1.3 dB mm<sup>-1</sup>. Moreover, optical coupling by evanescent field is found in crossing F4 TMS ANT needles, and their behavior as Y-splitters for light is characterized. These crystalline systems are therefore extremely versatile, and they can be used as the building blocks of complex optical networks.

# RESULTS AND DISCUSSION

**Crystal Structure.** According to our model to predict crystal packing in silvlethyne-functionalized acenes,<sup>25</sup> situations where the diameter of the silvl group is roughly the same as the length of the acene should lead to edge-to-face interactions in the crystal. The rules are supported by the structure of TIPS ANT (Figure 2a), where the acene chromophore of one molecule is completely surrounded by the hydrocarbon edges of adjacent molecules.

Switching to a smaller silyl group and offsetting that group away from the central acene position and adding fluorine substituents (Figure 2b) shift the crystal packing from edge-toface to  $\pi$ -stacked face-to-face, as observed for different families of compounds.<sup>27,43-46</sup> These disparate crystal packing motifs lead to substantial differences in many aspects of the molecular solids. First, we would expect to see no electronic coupling in TIPS ANT but strong intermolecular electronic coupling in F4 TMS ANT. These suppositions are borne out by the absorption spectra for these molecules (Figure 3). TIPS



**Figure 3.** Absorption spectra of TIPS ANT (a), TMS ANT (b), and F4 TMS ANT (c) in solution (solid lines) and in the solid state as single crystals (dashed lines). TIPS ANT and F4 TMS ANT are dissolved in hexane, and TMS ANT is dissolved in toluene.

ANT shows a small red shift (3 nm) between solution and solid-state absorption spectra, supporting the lack of solid-state interaction between chromophores exhibited by the crystals. F4 TMS ANT, in contrast, shows a dramatic red shift (in the range 15–20 nm) in absorption in single crystals (Figure 3) and thin-film form (Figure S6), confirming that the chromophores are electronically coupled in the crystal. The similar red shift observed for TMS ANT also supports a strongly  $\pi$ -stacked solid-state arrangement.

The dimensionality of the solid-state interactions also explains the shape of the resulting crystals (Figure 4). TIPS ANT shows strong edge-to-face interactions in two dimensions, with minimal intermolecular interaction in the third dimension (i.e., between the "ends" of the anthracene moieties). We would thus expect fast growth in two dimensions, leading to plate- or lath-shaped crystals. F4 TMS ANT shows very strong (dipolar) interactions in only one dimension ( $\pi$ -stacking) with very weak interactions in other dimensions.

Indeed, the molecules stack in a columnar arrangement with an average interplanar distance of 3.324 Å, pitch angle of 69.85°, and yaw angle of 69.01°.<sup>47</sup> We would thus expect this material to grow very quickly in one dimension and slowly in the others, leading to needle-shaped crystals (as observed).

Instead, an intermediate regime is expected for the nonfluorinated TMS ANT, which crystalizes in elongated microneedles with larger widths compared to those of the fluorinated F4 TMS ANT due to a decreased dipolar interaction in the  $\pi$ -stacking direction.

**Photoluminescence (PL) Properties.** The photoluminescence (PL) spectra of TIPS ANT, TMS ANT, and F4 TMS ANT are shown in Figure 5. The TIPS ANT emission (Figure 5a) peaks at about 502 nm and shows well-defined peaks at 511, 540, and 580 nm, together with a shoulder at higher energies ( $\lambda$  < 490 nm) indicative of a significantly self-absorbed transition. Instead, TMS ANT and F4 TMS ANT display a broad (full width at half-maximum, FWHM = 110 and 95 nm for TMS ANT and F4 TMS ANT, respectively) and featureless emission spectrum (Figure 5b,c) with peaks at about 538 and 559 nm, respectively. Such differences reflect



Figure 4. Relating strength of intermolecular interactions to the crystal shape. TIPS ANT (top panels) exhibits edge-to-face interactions in two dimensions and weaker edge-to-edge interactions in one dimension, leading to thin platelets. The double-headed arrows in the TIPS ANT structure (top) show the edge-to-face contacts between the trialkylsilyl groups and the aromatic faces, which prevent any solid-state coupling between chromophores. However, F4 TMS ANT (bottom) has strong interactions along the 1D  $\pi$ -stacking axis with minimal interactions along the other two axes, leading to thin needles. The double-headed arrow shown in the F4 TMS ANT (bottom panels) shows the strong, columnar  $\pi$ -stacking interaction between molecules, leading to strong electronic coupling in the solid state.



**Figure 5.** Polarized emission spectra of TIPS ANT (a), TMS ANT (b), and F4 TMS ANT (c), collected with the analyzer axis either parallel (continuous line) or perpendicular (dotted line) to the short axis of the crystal face. Insets: (a) bright-field micrograph of a TIPS ANT crystal and (b, c) confocal fluorescence micrographs of a TMS ANT and F4 TMS ANT crystal, respectively. Scale bars: 100  $\mu$ m (a, b) and 50  $\mu$ m (c). The horizontal arrows in the insets indicate the polarization axis of the excitation laser. (d–f) Spectral dependence of the ratio,  $r_{pol} = I_{//}/I_{\perp}$ , of the PL spectra collected by the analyzer with axis parallel ( $I_{//}$ ) and perpendicular ( $I_{\perp}$ ) to the short axis of the crystal. Here, crystals are excited with a laser polarization either parallel (continuous line) or perpendicular (dashed line) to the short crystal axis.



**Figure 6.** Emission intensity maps of TIPS ANT (a), TMS ANT (b), and F4 TMS ANT (c) as a function of wavelength and analyzer angle,  $\vartheta$ . 0° corresponds to the analyzer axis parallel to the short axis of the crystal face. The intensities shown in (a)–(c) are normalized to the maximum value measured at about 0°. Insets: molecular packing for (a) TIPS ANT and (c) F4 TMS ANT, as viewed from the crystal face. The short axis of the crystal faces is along the vertical direction. The black arrows mark the polarization direction of the emission. The red arrow in (a) highlights the dipole moment of a single molecule of anthracene. (d–f) Normalized emission intensity vs  $\vartheta$ , for TIPS ANT (d), TMS ANT (e), and F4 TMS ANT (f). The continuous lines are fits to data by a  $\cos^2(\vartheta)$  function.

the different molecular packing of the crystalline anthracene derivatives (Figure 2). In TIPS ANT, the very large TIPS groups, yielding edge-to-face interactions in the solid state and effectively isolating the chromophores in a matrix of the solubilizing appendage, allow the emission features of the isolated molecules to be almost preserved.

In contrast, the F4 TMS ANT spectrum, which is red-shifted by about 100 nm compared to the emission of the chromophore in solution (Figure S7), clearly indicates a highly delocalized excited state due to the strong coupling along the columnar  $\pi$ -stacking chromophores.<sup>46</sup> A similar behavior is observed for TMS ANT though with a smaller PL red shift associated with the lack of fluorination. Even more pronounced differences are highlighted by the crystal morphologies (insets in Figure 5a,b), as well as by the emission polarization properties. TIPS ANT luminescence is strongly polarized along the short axis of the crystal, featuring a polarization ratio ( $r_{pol}$ ) of the emission intensity polarized along the short side to that polarized along the long side of up to 5. The  $r_{\rm pol}$  spectral behavior evidences a strongly polarized transition at short wavelengths ( $\lambda < 490$  nm, Figure 5d), not well resolved in the emission spectrum due to self-absorption (Figure 5a). TMS-functionalized compounds feature emission polarized along a direction perpendicular to the needle length with values of  $r_{\rm pol}$  up to 4 (Figure 5e,f). Whereas the TMS ANT derivative features  $r_{\rm pol}$  values and spectral trends similar to those of TIPS ANT, fluorinating TMS ANT is found to decrease significantly  $r_{\rm pol}$  to values <2.

In addition, in TIPS ANT and F4 TMS ANT systems, the polarization ratio is slightly lowered for polarization of the excitation laser perpendicular to the short axis of the crystal face (Figure 5d,f), whereas in TMS ANT, the polarization ratio is instead enhanced upon using excitation polarization perpendicular to the needle short axis (Figure 5e). In these experiments, no significant spectral feature can be appreciated. Also, emission properties are found to be only weakly sensitive to the excitation configuration (Figure S8). Moreover, the intensity of the excitation light transmitted by the sample is a few percentage of the incident intensity, not depending on the incident polarization direction (Figure S9). Such residual excitation component transmitted through the thick (about 15  $\mu$ m) crystal can be related to scattering of laser photons not being involved in optical transitions.

The spectral behavior of the emission intensities of TIPS ANT, TMS ANT, and F4 TMS ANT vs the angle,  $\vartheta$ , defined by an analyzer polarization axis and the short crystal side is summarized in the maps shown in Figure 6a–c, respectively. Overall, the PL intensity is well described by the Malus law:  $I(\vartheta) = I_0 + I_1 \cos^2(\vartheta)$ , where  $I_0$  and  $I_1$  are constants and the  $\cos^2$  angular dependence highlights a well-behaved polarized emission (Figure 6d–f).

The found polarization properties can be rationalized considering the optical properties of the single chromophores and their packing into the crystalline samples. The optical transition dipole moment of anthracene chromophores is parallel to the short molecular axis, as schematized in the inset of Figure 6a.<sup>40</sup> In TIPS ANT, the crystal face (*ac* crystal plane) contains the transition dipole moments of the chromophores, which, due to the herringbone packing of the constituent molecules (inset of Figures 6a and S10a of the Supporting Information), form an angle of about 35° with respect to the short axis of the crystal face. As a consequence, the emission is expected to be mainly polarized along this axis, as observed. Moreover, the polarization ratio is enhanced for excitation polarization parallel to the short molecular axis due to more efficient coupling (i.e., absorption) with the anthracene transition dipole moments. In F4 TMS ANT, the transition dipole moments of the chromophores are almost oriented perpendicular to the long axis of the needles, which is the  $\pi$ stacking axis (inset of Figures 6c and S10b of the Supporting Information). Therefore, emission is mainly polarized perpendicularly to the long crystal axis and the polarization ratio is decreased compared to that of TIPS ANT due to the more delocalized excited state, which introduces an intermolecular component in the transition dipole moment of the emitting state.

**Waveguiding Analysis.** Organic light-emitting crystals generally feature refractive index values that are high enough to support waveguiding of visible light. When these crystals are deposited on quartz or similar substrates, an active optical waveguide is formed, in which photons emitted by the sample do not promptly couple to the free space but are instead efficiently directed toward the crystals edges through guided modes.<sup>2,48</sup> A coupling efficiency of the fluorescence to the modes of the waveguide formed by thiophene-based crystalline needles up to 40% was recently measured.<sup>49</sup> In a given crystal species, the particular packing of molecules in the unit cell may enhance or suppress waveguiding effects, thus leading to prevalent emission either from edges or from the exposed surface.<sup>18,48</sup> In TIPS ANT crystals, weak self-waveguiding of the emitted photons was observed. Instead, Figure 7a shows a fluorescence micrograph of F4 TMS ANT needles, where the bright crystal tips are a signature of fluorescence trapping and self-waveguiding.

We characterize these microscale, active waveguides by micro-photoluminescence ( $\mu$ -PL), exciting a specific sample region by a focused laser beam (Figure 7b). Emitted light then partly couples into the elongated crystals, propagates along the needle length, and then exits at the crystal tips. The divergence of the light beam emitted by the crystal tips is 28° (Figure S11), making these crystals ideal for coupling with standard optical lenses and fiber-optic systems.

Measuring the intensity emitted by the crystal tips as a function of the distance,  $d_1$  to the excited region allows propagation losses to be quantified. The results of this analysis are displayed in Figure 7c,d, showing an exponential decay of the intensity of the emission guided along the crystal longitudinal axis, with a characteristic optical loss coefficient on the order of 10-20 dB mm<sup>-1</sup>. Self-absorption of the emitted light, scattering from surface defects, and coupling of the guided modes into the underlying substrate are the main sources of losses in such microscale waveguides. Figure 7e shows propagation losses as a function of the wavelength, highlighting lower values in the range 550-650 nm, far from the low energy tail of the absorption band (Figure 3b), and down to 1.3 dB mm<sup>-1</sup>, which corresponds to an intensity decrease of the transported light of about 10% for a propagation length of 2 mm. Remarkably, the optical loss coefficient here is much lower than typical values measured in organic single-crystalline samples (30-270 dB mm<sup>-1</sup>),<sup>18-20,3</sup> and comparable to hybrid organic crystals that were specifically designed to decrease propagation losses by plasmonics.<sup>21</sup> A lower optical loss coefficient (about a factor 2) is measured for TMS ANT compared to that for F4 TMS ANT (Figure 7c,d). This might be attributed to photon scattering at eventual morphological defects, and to the significant coupling of photons into the supporting substrate, an effect that is expected to be more pronounced for F4 TMS ANT crystals due to their smaller size (see insets of Figure 5b,c). In both TMS ANT and F4 TMS ANT crystals, the large Stokes shift between the absorption and emission spectra (in the range 100-130 nm) allows the self-absorption contribution to be significantly lowered.

Furthermore, different needles can be optically coupled by means of evanescent light fields.<sup>50–54</sup> This effect is important in view of assembling photonic structures where light can propagate along complex paths, carrying information through signals transmitted across integrated functional units, microwires, etc. Figure 8 demonstrates optical coupling between two crossing F4 TMS ANT microwires. In this configuration, coupled crystals split the light that is optically excited in a single wire, i.e., they work as Y-splitters. The coupling efficiency (from A to C in Figure 8a) depends on the angle formed by the long axes of the two waveguides ( $\beta$  in Figure



**Figure 7.** (a) Fluorescence micrograph of F4 TMS ANT needleshaped crystals. Scale bar: 100  $\mu$ m. The bright spots at the needle tips are indicative of self-waveguiding of the emitted light. (b) Exemplary micro-photoluminescence ( $\mu$ -PL) micrograph for waveguiding characterization. Bright spots here correspond to fluorescence emitted at the directly excited region (central spot) and at the crystal tips following waveguiding (A and B spots). The length of the crystal is about 200  $\mu$ m. (c, d) Plot of the normalized, guided emission intensity vs *d* -schematized in (b), for TMS ANT (c) and F4 TMS ANT (d). The dashed line is a fit to data by the equation  $I(d)/I_0 =$  $\exp(-\alpha d)$ , where  $\alpha$  is the propagation loss coefficient. (e) Dependence of the propagation loss coefficient,  $\alpha$ , on the wavelength for a TMS ANT sample. Inset: examples of emission spectra of a TMS ANT sample vs *d*. From top to bottom: d = 0.45, 0.6, 0.75, 0.9, 1.0, 1.2 mm.

8a).<sup>24,50,51</sup> We measure a ratio,  $\Phi = I_C/I_B$ , of the intensity emitted at the tip of the wire that is not directly excited  $(I_C)$  to that at the tip of the excited wire  $(I_B)$  of about 0.2 for  $\beta = 30^\circ$ , decreasing to  $\Phi < 0.03$  for  $\beta > 40^\circ$ . These results are in agreement with evanescent optical coupling in micro- and nanowires, typically featuring a rapid decrease of  $\Phi$  for values of the cross angle  $(\beta)$  greater than  $30^\circ$ .<sup>50,51</sup> At variance with previous reports,<sup>54</sup> this analysis provides a quantitative evaluation of the coupling between overlapping crystals as a function of  $\beta$  and suggests that effective propagation along complex networks can be accomplished by designing and assembling arrays of coupled microwires with small intersection angles ( $\beta < 30^{\circ}$ ).

# CONCLUSIONS

Directed functionalization of anthracene derivatives is a very effective approach for tuning the solid-state order, imparting a particular crystal shape, and tailoring the optical and waveguiding properties of the crystalline samples. Using very large TIPS substituents isolates the anthracene chromophores, producing plate-shaped crystalline samples with bright emission and well-defined PL polarization. By laterally shifting the position of the substituents, the trimethylsilyl derivative, F4 TMS ANT, crystallizes instead as thin yellow needles, characterized by efficient self-waveguiding of the emission. These needle-shaped crystals can also be optically coupled and arranged in complex photonic splitters. Interestingly, the nonfluorinated trimethylsilyl derivative, TMS ANT, features both emission polarized along the needle length and waveguiding of the emission with low propagation losses, down to 1.3 dB mm<sup>-1</sup>. These results open interesting perspectives for an improved control of the emission and waveguiding properties of organic crystalline materials, which is relevant for various light sources and for transport of photons in complex circuits and networks. These would ultimately combine different organic, crystalline building blocks based on specific molecular systems that can be individually designed and properly functionalized to feature a determined morphology and specific optical properties.

# MATERIALS AND METHODS

Synthesis and Crystal Analysis. TIPS ANT is synthesized by literature methods,<sup>26</sup> and single crystals are grown from acetone. TMS ANT is synthesized according to literature precedent.<sup>55</sup> F4 TMS ANT is synthesized as described in the Supporting Information, and crystals are grown from 2-butanone. Single-crystal X-ray analysis of F4 TMS ANT is performed on a Bruker-Nonius X8 Proteum diffractometer using Cu K( $\alpha$ ) radiation. The structures are solved using SHELXS and refined using SHELXL from the SHELX-97 program package.<sup>5</sup> Molecular fragment editing, including the construction of suitable disorder models, is performed using the XP program of SHELXTL. The comparison between the solid-state structures of single crystals and films is carried out by a Bruker D8 Discover equipped with a Göbel mirror for Cu K $\alpha$  radiation, an Eulerian cradle, and a scintillation detector. For optical characterization, the crystalline samples are deposited on  $1 \times 1$  cm<sup>2</sup> quartz substrates. Absorption measurements are performed by a UV-visible spectrophotometer (Lambda 950, PerkinElmer).

**Microscopic Characterization.** Bright-field images are acquired by an inverted microscope (IX71, Olympus), illuminating samples by a W lamp. Fluorescence micrographs are collected by exciting with a Hg lamp through a 20× objective of another inverted microscope (Eclipse Ti, Nikon) and collecting emission maps by a charge-coupled device (CCD) detector (Digital Sight-U2, Nikon). Confocal fluorescence imaging is performed by an inverted microscope equipped with a laser scanning confocal head (A1R-MP, Nikon). To this aim, samples are excited by a laser diode ( $\lambda_{exc}$  = 408 nm) through a 20× objective, whereas the emitted light is collected by the same objective and measured by a spectral detection unit equipped with a multianode photomultiplier (Nikon).

**Photoluminescence Measurements and Polarized Excitation Spectroscopy.** Polarized emission spectra are acquired by exciting with a linearly polarized diode laser ( $\lambda_{exc} = 405 \text{ nm}$ ), which is focused onto the sample surface that is in contact with the quartz substrate, by a 10× objective. We carefully check the polarization state of the excitation laser before and after passing through the objective, finding no relevant difference. The vertically emitted light is then



**Figure 8.** (a–c) Optical coupling in crossing F4 TMS ANT crystals for different values of the cross angle,  $\beta$ , schematized in (a). Scale bars: 50  $\mu$ m. PL is excited by a focused laser beam (A spot, highlighted by the dashed circle). A fraction of the fluorescence is coupled into the crystal, guided along the arrow direction, and emitted by the crystal tip (B spot). Part of the waveguided emission is instead coupled into a second crystal nearby and then guided again as highlighted by the bright edge (C spot) of the needles that are not directly excited by the focused laser. The dashed lines indicate the crystal bodies.

collected by a spherical lens (f = 75 mm) coupled to an optical fiber and measured by a spectrometer (Ocean Optics USB4000). To analyze the polarization state of the emission, a polarization filter (analyzer) is mounted on a precision rotation stage between the sample and the collecting lens. For polarized excitation spectroscopy, crystals are excited by a laser, whose polarization can be precisely adjusted with respect to the sample axes using a  $\lambda/2$  waveplate mounted on a rotation stage. Here, the intensity transmitted by the sample is measured as a function of the angle ( $\vartheta_{exc}$ ) formed by the polarization axis of the excitation laser and the short crystal axis of the TIPS ANT samples, chosen as a reference.

**Waveguiding.** Waveguiding in crystals is investigated by a  $\mu$ -PL setup, comprising an inverted microscope (IX71, Olympus), a diode laser, and a CCD camera detector. The shape of the excitation laser beam ( $\lambda_{exc}$  = 405 nm) is optimized through lenses for an efficient coupling to the microscope objective and is then focused onto the sample–quartz interface through a 20× objective (NA = 0.5, Olympus). The laser spot diameter is in the range 20–30  $\mu$ m. The light emitted by the sample is imaged by a CCD camera, allowing fluorescence maps to be acquired with micrometer spatial resolution. The measurement of the intensity of the waveguided emission as a function of the distance, *d*, between the excitation spot and the crystal edge allows the loss coefficient to be quantitatively determined. This is accomplished through scanning the laser spot along the crystal length by means of precision mirrors and collecting fluorescence maps for each excitation position.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-ter.8b05361.

Material synthesis, crystallographic and optical properties of films, X-ray characterization, absorption and polarized photoluminescence, divergence of light beam emitted from crystals tips (PDF)

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# Notes

The authors declare no competing financial interest.

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