Highly Ordered 2D-Assemblies of Phase-Segregated Block Molecules for Upconverted Linearly Polarized Emission

Martin H. C. van Son, Anton M. Berghuis, Fabian Eisenreich, Bas de Waal, Ghislaine Vantomme, Jaime Gómez Rivas, and E. W. Meijer*

This Communication is dedicated to the memory of Dr. John M. Warman of IRI Delft for his eminent contributions to physical chemistry

Materials based on the laminar ordering of self-assembled molecules have a unique potential for applications requiring efficient energy migration through densely packed chromophores. Here, employing molecular assemblies of coil–rod–coil block molecules for triplet–triplet annihilation upconversion (TTA-UC) based on triplet energy migration with linearly polarized emission is reported. By covalently attaching discrete-length oligodimethylsiloxane (oDMS) to 9,10-diphenylnanthracene (DPA), highly ordered 2D crystalline DPA sheets separated by oDMS layers are obtained. Transparent films of this material doped with small amounts of triplet sensitizer PtII octaethylporphyrin show air-stable TTA-UC under non-coherent excitation. Upon annealing, an increase in TTA-UC up to two orders of magnitude is observed originating from both an improved molecular ordering of DPA and an increased dispersion of the sensitizer. The molecular alignment in millimeter-sized domains leads to upconverted linearly polarized emission without alignment layers. By using a novel technique, upconversion imaging microscopy, the TTA-UC intensity is spatially resolved on a micrometer scale to visually demonstrate the importance of molecular dispersion of sensitizer molecules for efficient TTA-UC. The reported results are promising for anti-counterfeiting and 3D night-vision applications, but also exemplify the potential of discrete oligodimethylsiloxane functionalized chromophores for highly aligned and densely packed molecular materials.

M. H. C. van Son, Dr. F. Eisenreich, B. de Waal, Dr. G. Vantomme, Prof. E. W. Meijer*
Institute for Complex Molecular Systems and Laboratory of Macromolecular and Organic Chemistry Eindhoven University of Technology P.O. Box 513, Eindhoven, MB 5600, The Netherlands E-mail: e.w.meijer@tue.nl
A. M. Berghuis, Prof. J. Gómez Rivas
Department of Applied Physics and Institute for Photonic Integration Eindhoven University of Technology P.O. Box 513, Eindhoven, MB 5600, The Netherlands

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adma.202004775.

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Supporting Information. The required energy transfer processes for TTA-UC can only occur for certain sensitizer–annihilator pairs where all energetic requirements are met.5,9 TTA-UC utilizing aligned chromophores for fast exciton diffusion, known as triplet energy migration-based upconversion (TEM-UC), has the potential to outperform rigid systems5,9 where molecular diffusion is inherently low as in polymers (e.g., poly(methyl methacrylate))5,10 and organic glasses.11

Triplet energy migration-based photon upconversion has been realized in condensed amorphous systems,12 ordered self-assembled structures in liquid,13 gels,14 molecular crystals,15 and MOFs16 with various reviews written about this topic.5 In most of these approaches, the annihilator is functionalized with side-chains or ionic groups. This functionalization results in dense self-assembled structures in liquid or quasi-solid phases by exploiting solvophobic interactions, hydrogen bonding, and electrostatic interactions. These interactions are also used to bring the sensitizer in close proximity to the annihilator for
efficient Dexter-type energy transfer between both chromophoric units.\textsuperscript{[13a,15b,17]} Furthermore, self-assembly approaches in liquids have been shown to prevent unfavorable oxygen quenching of triplet excited states.\textsuperscript{[12a,13a,c]} For solid-state upconverting systems, self-assembly of soft annihilator crystals is a relatively unexplored but promising approach that could even lead to polarized upconverted emission.\textsuperscript{[13a,b,15a,18]} Until now, upconverted circularly polarized emission has been realized for chiral annihilators in solution.\textsuperscript{[19]} or dispersed in a liquid crystalline matrix.\textsuperscript{[20]} Upconverted linearly polarized emission has only been shown for aligned lanthanide crystals\textsuperscript{[7,23]} and for annihilator molecules dispersed in a liquid crystalline matrix.\textsuperscript{[22]} However, matrix-free upconverted linearly polarized emission in films from ordered annihilator molecules remains a challenge that, when solved, can find applications in optical storage, optical anti-counterfeiting, and 3D night vision.\textsuperscript{[7,8,21,23]}

To obtain ordered morphologies such as cylinders or lamellae in films, block copolymers and liquid crystals are most often used. In polymeric systems, phase segregation dictates the feature size and morphology. Phase segregation is influenced by the composition and immiscibility of its constituents as well as (post-)processing parameters such as solvent choice or thermal annealing. Recently, we developed block molecules that combine phase segregation with crystallization in discrete molecular weight molecules for highly ordered structures in bulk through functionalization with oligodimethylsiloxane (oDMS).\textsuperscript{[24]} These block molecules bridge the gap between block copolymers and liquid crystals.\textsuperscript{[24e]} By using “soft” oDMS of discrete lengths and “hard” crystalline molecular blocks, ordered lamellar structures with sub 10 nm spacings can be obtained.\textsuperscript{[24d,e]} Furthermore, functionalization with oDMS can result in the formation of millimeter-sized domains of ordered crystalline monolayers, which has been demonstrated with hydrazine derivatives.\textsuperscript{[24h]} The hydrazine block molecules could additionally be aligned, resulting in linearly polarized absorption.\textsuperscript{[24h]} The high degree of long-range order, large domain size, and polarized characteristics make oDMS block molecules promising for upconverted linearly polarized emission.

Here, we report on the synthesis as well as molecular and photophysical characterization of the benchmark TTA-UC annihilator 9,10-diphenylanthracene (DPA) functionalized with discrete-length oligodimethylsiloxane. We demonstrate air-stable TEM-UC through ordered annihilator molecules in films doped with triplet sensitizer Pt\textsuperscript{41} octaethylporphyrin (PtOEP). Topographic mapping of the upconverted emission intensity was used to study the effect of sensitizer aggregation. For the DPA derivative with the shortest oDMS chains, millimeter-sized domains with regular chromophore alignment were obtained during annealing and this block molecule is therefore studied for polarization-dependent absorption and upconverted emission.

The molecular structure and synthetic route of the 9,10-diphenylanthracene derivatives (Si\textsubscript{n})\textsubscript{2}DPA functionalized with discrete oligodimethylsiloxane chains with lengths of 7, 11, or 15 repeating units is shown in Scheme 1. The side-chains are attached at the periphery of the core to maintain the spectroscopic properties of unfunctionalized DPA.\textsuperscript{[18a,25]} as well as to allow the investigation of oDMS functionalization as a general approach for inducing nanoscale organization of block copolymer structures. The flexible nature of oDMS and the crystalline nature of DPA make these block molecules small coil–rod–coil structures of discrete molecular weight.

The first step in the (Si\textsubscript{15})\textsubscript{2}DPA synthesis is a Suzuki coupling to obtain 9,10-dianisylanthracene.\textsuperscript{[18a]} After deprotection of the methoxy groups with boron tribromide, the hydroxy groups were derivatized with a terminal alkyne spacer via Williamson ether synthesis. In the last step, Karstedt’s catalyst was used for the hydrosilylation of the terminal alkyne with hydride-functionalized discrete oDMS. The liquid oDMS chains were synthesized using a previously reported procedure.\textsuperscript{[24b]} The final products were purified with recycled GPC to yield (Si\textsubscript{6})\textsubscript{2}DPA, (Si\textsubscript{11})\textsubscript{2}DPA, and (Si\textsubscript{15})\textsubscript{2}DPA as light-yellow waxy compounds of which (Si\textsubscript{15})\textsubscript{2}DPA crystallized over time into a brittle light-yellow material.

![Scheme 1. Synthetic route of 9,10-difunctionalized anthracenes (Si\textsubscript{n})\textsubscript{2}DPA.](image-url)
solid. The purity of the block molecules was confirmed by $^1$H NMR, $^{13}$C NMR, and MALDI-TOF-MS (Figures S2–S6, Supporting Information).

Differential scanning calorimetry (DSC) and polarized optical microscopy (POM) were used to investigate the thermal properties of $(\text{Si}_n)_{2}\text{DPA}$. For all block molecules, a melting transition to the isotropic phase is observed between 47 and 80 °C (Figure 1a) that corresponds to a loss in birefringence observed with POM. As expected, the melting point decreases upon increasing the length of the flexible $\text{oDMS}$ side-chains (Table 1). The melting enthalpies of about $\approx 30–45$ kJ mol$^{-1}$ are similar to unfunctionalized DPA as well as DPA functionalized with alkyl chains and indicate crystallinity.[18a,26] The highest enthalpy with the sharpest transition, and thus strongest intermolecular interactions, is observed for $(\text{Si}_7)_{2}\text{DPA}$. For all block molecules, cooling from the isotropic phase restored the birefringence in micrometer-sized domains showing the reversibility of the thermal transitions (Figure S7, Supporting Information). Interestingly, upon slow cooling (1 °C min$^{-1}$), multiple crystalline domains with millimeter dimensions were obtained and can be observed by eye for $(\text{Si}_7)_{2}\text{DPA}$ and $(\text{Si}_{11})_{2}\text{DPA}$ (Figure 1b). On the contrary, faster cooling (10 °C min$^{-1}$) gave smaller domains due to an increased number of nucleation sites. Careful thermal treatment can thus induce regular chromophore alignment over large areas.

The nanoscale morphologies of the $(\text{Si}_n)_{2}\text{DPA}$ after annealing were examined using medium- and wide-angle X-ray scattering (MAXS and WAXS), respectively (Figure 1c). All block molecules show equally spaced reflection peaks from the principal scattering peak ($q^*$, $2q^*$, $3q^*$, …) indicating long-range lamellar ordering.[27] This ordering, schematically shown in Figure 1d, is the combined result of both crystallization of the DPA core and phase-segregation with the amorphous $\text{oDMS}$ leading to alternating layers of both molecular blocks.[24c] The observed increase in lamellar spacing, $d_{\text{lam}} = 2\pi/q^*$, from 3.2 to 5.7 nm for $(\text{Si}_7)_{2}\text{DPA}$ and $(\text{Si}_{15})_{2}\text{DPA}$, respectively, is explained

![Figure 1. Characterization of $(\text{Si}_n)_{2}\text{DPA}$. a) Differential scanning calorimetry traces of the second cycle of $(\text{Si}_7)_{2}\text{DPA}$ (black), $(\text{Si}_{11})_{2}\text{DPA}$ (orange), and $(\text{Si}_{15})_{2}\text{DPA}$ (blue) with 10 °C min$^{-1}$ showing melting and crystallization peaks (exothermic down). b) Optical photographs of annealed films of $(\text{Si}_7)_{2}\text{DPA}$ (left) and $(\text{Si}_{11})_{2}\text{DPA}$ (right) between two crossed linear polarizers showing domains with dimensions of 10 and 5 mm respectively obtained after annealing. c) Room-temperature X-ray scattering profiles for $(\text{Si}_7)_{2}\text{DPA}$ (black), $(\text{Si}_{11})_{2}\text{DPA}$ (orange), and $(\text{Si}_{15})_{2}\text{DPA}$ (blue) after annealing showing lamellar order. d) Schematic representation of the multilayer lamellar ordering of self-assembled 2D crystalline DPA sheets (blue) separated by the discrete-length side-chains (gray).](image_url)

Table 1. Molecular characterization data for the $\text{oDMS}$ functionalized DPA derivatives.

|             | $\lambda_{\text{abs, peak}}^{a)}$ [nm] | $\lambda_{\text{em, peak}}^{a)}$ [nm] | $\tau_{\text{solution, b)}$ [ns] | $\tau_{\text{Cast film, c)}$ [ns] | $\tau_{\text{PtOEP-doped Cast film, c)}$ [ns] | $T_{\text{melt}}, T_{\text{cryst}}$ [°C] | $\Delta H_{\text{m, d)}$ [kJ mol$^{-1}$] | $d_{\text{lam}}^{e)}$ [nm] |
|-------------|--------------------------------------|--------------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|----------------|
| DPA         | 357,375-396                          | 412,432                              | –                               | –                               | –                               | 247,172                         | 28.1                           | –               |
| $(\text{Si}_7)_{2}\text{DPA}$ | 360,378,398                        | 429                                  | 4.7                             | 4.3                             | 6.6                             | 80,68                           | 45.7                           | 3.2             |
| $(\text{Si}_{11})_{2}\text{DPA}$ | 360,379,399                        | 430                                  | 4.8                             | 5.6                             | 6                               | 59,40                           | 28.7                           | 4.3             |
| $(\text{Si}_{15})_{2}\text{DPA}$ | 360,378,399                        | 428                                  | 4.9                             | 5.6                             | 6.4                             | 47,31                           | 38.6                           | 5.7             |

$^{a)}$Recorded in $25 \times 10^{-6}$ m chloroform solution; $^{b)}$Fluorescence lifetimes at 440 nm under 400 nm excitation fitted to a single exponential decay; $^{c)}$Film doped with PtOEP (PtOEP:annihilator = 1:300); $^{d)}$Determined by DSC with 10 °C min$^{-1}$; $^{e)}$Lamellar domain spacing from SAXS data, calculated as $d_{\text{lam}} = 2\pi/q^*$.}

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Figure 2. Optical spectroscopy analysis. a) Absorption (full line) and emission (dotted line) spectra in 25 × 10⁻⁶ M CHCl₃ solutions of unfunctionalized DPA (green) and (Si₁₁)₂DPA (black). b) Fluorescence spectra of doped films (PTOEP:annihilator = 1:300) of (Si₁₁)₂DPA (black), (Si₇)₂DPA (orange), and (Si₁₅)₂DPA (blue) under direct excitation (λₑₓ = 350 nm, top) and under upconversion conditions through indirect excitation (λₑₓ = 532 nm, bottom) using a non-coherent light source. Inset shows a photographic image of (Si₁₁)₂DPA (PTOEP:annihilator = 1:300) under 532 nm laser irradiation with a 500 nm lowpass filter to remove reflected green light. Upconverted photoluminescence (UCPL) is observed by naked eye as a blue spot, here indicated with a red arrow.

by increased volumes of dMS resulting in larger distances between monolayers of the crystalline DPA cores. Interestingly, (Si₁₁)₂DPA displays pronounced spots in the 2D WAXS region indicating strong regular crystalline interactions of the DPA cores throughout the material (Figure S8, Supporting Information). In the WAXS region of (Si₁₁)₂DPA and (Si₁₅)₂DPA, the crystalline interactions are less pronounced than for (Si₇)₂DPA due to the increased contribution of the amorphous halo originating from the longer dMS chains. The high order and large domains observed for (Si₇)₂DPA make these materials promising for TEM-UC if the energetic requirements for upconversion are met. The optical properties are thus studied in solution and film. In 25 × 10⁻⁶ M chloroform solutions, the absorption and emission spectra are identical between the three (Si₇)₂DPA block molecules (Figure S9, Supporting information). In these spectra, the typical vibronic progression of unfunctionalized DPA is observed (Table 1 and Figure 2a), albeit less pronounced and slightly red-shifted (=15 nm) in emission. The spectra obtained for the drop-cast films of (Si₇)₂DPA are comparable to the solution spectra and differ only in relative intensities of the emission peaks at ≈425 nm and ≈444 nm. Although excimers have been reported for unfunctionalized DPA in bulk,[28] they are not observed in the drop-cast films as confirmed by comparable monoeponential fluorescence decays in solution and film (Table 1; Figure S10, Supporting Information). The absence of excimers is beneficial as they act as a loss channel for the overall upconversion efficiency.[30,29] In addition, the observed red-shifted emission increases the upconversion efficiency due to a smaller overlap with the absorption profile of PTOEP and corresponding lower reabsorption of upconverted light.[30] The fluorescence quantum yields in deoxygenated cyclohexane solution were determined to be 0.90, 0.95, and 0.93 for (Si₁₁)₂DPA, (Si₇)₂DPA, and (Si₁₅)₂DPA, respectively, relative to unfunctionalized DPA (Φ₅₁ = 0.97 in cyclohexane).[31] In thin film, slightly lower quantum yields (0.43, 0.46, and 0.49 for (Si₁₁)₂DPA, (Si₇)₂DPA, and (Si₁₅)₂DPA, respectively) are obtained as the high concentration in condensed film leads to reabsorption of the emitted light. These spectroscopic results prove that the (Si₇)₂DPA block molecules can be used as annihilator in solution as well as in films with PTOEP as sensitizer, provided PTOEP can be dispersed in the film.[35a]

To investigate the upconversion in films, deoxygenated solutions of (Si₁₁)₂DPA with =3 mol% PTOEP were drop-cast on glass slides and sealed under argon atmosphere. All films are transparent (Figure S11, Supporting Information) and displayed upconverted photoluminescence (UCPL) that is clearly visible by eye as blue emission upon 532 nm laser excitation (Figure 2b). The emission spectra under 532 nm excitation show the UCPL with maxima at 422 nm for both (Si₁₁)₂DPA and (Si₇)₂DPA and at 444 nm for (Si₇)₂DPA, identical to the spectra obtained for the doped (Si₁₁)₂DPA films under direct excitation of the DPA core with 350 nm light (Figure 2b). Residual PTOEP phosphorescence is observed even with low donor concentrations (PTOEP:annihilator = 1:10 000), indicating that the energy transfer from donor to annihilator is not complete (Figure S12, Supporting Information). Interestingly, the upconversion reported here is obtained with a non-coherent light source which is paramount for practical applications in photovoltaics.[32] Although non-coherent excitation has been shown for diffusion-based TTA-UC in flexible polymers,[5a,10b,33] this is the first time that non-coherent excitation is reported for TEM-UC (vide infra).

Before analyzing whether the upconversion is based on diffusion or triplet energy migration, the aggregation state of the PTOEP sensitizer is examined by absorption measurements and optical microscopy. Aggregated PTOEP reduces the efficiency of the triplet energy transfer processes and should thus be minimized.[35b] As comparable results were obtained for the three block molecules (Figure S13, Supporting Information), only the results of (Si₁₁)₂DPA are shown in Figure 3. The absorption spectrum of the drop-cast film displays a broad peak ranging from 530–560 nm with contributions of both molecularly dispersed PTOEP at 536 nm and aggregated PTOEP at 552 nm (blue line in Figure 3a).[35a] Aggregated PTOEP is observed by optical microscopy for various ratios PTOEP:annihilator (1:300, 1:600, 1:1000; Figure S14, Supporting Information) and likely occurs during the drop-casting process as the concentration increases during the overnight solvent evaporation.[15c,34] Optimization of the PTOEP concentration is not investigated for this study. After annealing
of the films, analysis by optical microscopy reveals two distinct regions of which the boundary is indicated by a red line (Figure 3b; Figure S13, Supporting Information). In the lower region, aggregated PtOEP is present as pink clusters while these aggregates are mainly absent in the upper region. The assignment of the pink solid as aggregated PtOEP is confirmed by significant absorption at 552 nm in this region (pink line in Figure 3a and Figure S13, Supporting Information). The upper region, where pink aggregates are mostly absent, absorbs only around 536 nm indicating molecularly dispersed PtOEP (orange line in Figure 3a and Figure S13, Supporting Information). Annealing can thus increase the molecular dispersion of PtOEP, although in some regions aggregates remain.

Additional information on the relation between PtOEP aggregation and UCPL intensity was obtained from spatially resolving the UCPL by correlating optical microscopy (OM) with upconversion imaging microscopy (UCIM) (Figure 4). By using UCIM, the UCPL intensity is spatially resolved with micrometer resolution in a region of 1.25 × 1.25 mm of doped (Si$_7$)$_2$DPA film, containing both aggregated and molecularly dispersed PtOEP. This novel technique gives a visual correlation between PtOEP aggregation and UCPL intensity with a magnification of two orders of magnitude higher than previously reported for a 0.4 × 0.5 mm$^2$ single crystal of DPA doped with PtOEP.$^{[15a]}$ In the OM and UCIM images of Figure 4, red and white lines respectively are drawn to indicate the grain boundary of the two crystalline regions identified by POM (Figure S15, Supporting Information). Upon superposition of the OM and UCIM images by visual comparison, a clear distinction can be made between both regions. The highest average UCPL intensity is obtained on the right side of the grain boundary where PtOEP is mostly dispersed. On the contrary, the average UCPL intensity on the left side of the grain boundary is lower due to the aggregation of PtOEP. This aggregation is visible in the OM image as dark aggregates and corresponds to regions in the UCIM image with a complete absence of UCPL (dark blue color). The results of the UCIM measurements show visually that even micrometer-sized PtOEP aggregates are detrimental for UCPL. Interestingly, also an absence of UCPL is observed in some regions where aggregation in the OM image is not visible. These features may be as small as the pixel size of the UCIM image (10 × 10 µm$^2$), which has similar dimensions as the excitation laser beam. The absence of UCPL from these small features may be the result of inhomogeneous PtOEP dispersion or defects in the DPA crystal lattice and illustrates the complexity in obtaining homogeneous upconverting solid materials.

By measuring the dependency of the excitation energy on the maximum UCPL, more information on the upconversion process is obtained. In all measurements, a linear correlation was found between the UCPL intensity and excitation energy, with slopes between 1.4 and 2.2 (Figure 3c; Figure S13, and Table S1, Supporting Information). These slopes indicate that besides triplet–triplet annihilation and upconverted emission, other deactivation channels are also present for the annihilator excited states.$^{[35]}$ For the annealed films (pink line) up to tenfold higher UCPL intensities are found compared with the drop-cast films (blue line). This is attributed to the increased chromophore alignment in the annealed films through which triplet energy migration can occur efficiently, proving TEM-UC in the studied system. TEM-UC is additionally shown by

Figure 3. PtOEP aggregation correlated with UCPL intensity of a (Si$_{11}$)$_2$DPA film (PtOEP:annihilator = 1:300). a) Normalized absorption spectra, b) optical microscopy image after annealing showing the boundary (red line) of regions with mostly dispersed PtOEP and mostly aggregated PtOEP. The PtOEP aggregates are observed as pink clusters and are mainly located at the bottom of the image. c) Power density dependence of UCPL intensity (laser excitation, $\lambda_{ex}$ = 532 nm). The blue line indicates the results before annealing and the pink and orange line after annealing. The pink line indicates regions with a large fraction of the PtOEP aggregated, while the orange line shows the results from regions with molecularly dispersed PtOEP. The PL intensity is integrated up to 500 nm.
shorter upconverted emission lifetimes after annealing as the enhanced triplet energy migration results in a higher probability for triplet–triplet annihilation (Figure S16 and Table S2, Supporting Information). Additionally, ≈20% shorter upconverted emission lifetimes are observed with higher excitation energies for the unannealed films of (Si7)2DPA and (Si15)2DPA. At higher excitation energy, more triplets are formed and therefore annihilation can occur more rapidly. The risetime of the UCPL intensity could be observed for the annealed film of (Si7)2DPA and maximum UCPL signal was measured after 12 µs (Figure S17, Supporting Information). As discussed in the previous paragraph, besides inducing chromophore alignment, annealing leads to an increase in PtOEP dispersion in some regions (orange line, Figure 3). The combination of increased chromophore alignment and better PtOEP dispersion leads to a remarkable 50- to 100-fold increase in UCPL intensity for (Si7)2DPA when compared with the drop-cast film.

Air-stability of the UCPL is expected for annealed films of (Si7)2DPA due to its dense chromophore packing, which has been shown to prevent oxygen quenching in liquid.[12,13] Time-dependent UCPL measurements were thus performed for drop-cast and annealed films of (Si7)2DPA prepared in air without prior deoxygenation of the solvent (Figure S18, Supporting Information). For the annealed film, a constant UCPL intensity was observed over the studied time-range. In contrast, the UCPL intensity of the drop-cast film showed a gradual decrease of ≈20–40% in the first 10–30 min attributed to the reaction of residual singlet oxygen with the DPA cores as confirmed by 1H NMR, and MALDI-TOF-MS.[46] After this initial decrease, the UCPL intensity remained constant for over a week. Measurements of the same films after 2 months showed a complete loss of upconverted emission while oxygen-free sealed films were stable for more than a year. These results indicate that molecular self-assembly is also an effective approach in condensed systems to minimize oxygen-related problems.

During the annealing of (Si7)2DPA, domain growth in two perpendicular directions was observed by polarized optical microscopy (Figure 5a) and resulted in millimeter-sized domains. The long-range ordering of the (Si7)2DPA crystals was confirmed by measuring the absorption intensity at 380 nm for one of the ≈20 mm2 single domains shown in Figure 1b while varying the orientation of the incoming linearly polarized light (Figure 5b). The maximum and minimum absorption intensities have a periodicity of 90 degrees as a result of chromophore alignment along crystallographic axes.[32] This confirms that the perpendicular alignment observed by POM occurs throughout the film. As a result of this perpendicular alignment, both the emission under direct excitation as well as the UCPL emission are linearily polarized (Figure 5c; Figure S19, Supporting Information). Although a higher polarization is required for practical applications, the reported approach based on organic coil–rod–coil block molecules serves as a first step for rare-earth-metal-free linearly polarized UCPL without the use of alignment layers.

In conclusion, 9,10-diphenylanthracene has been functionalized with discrete-length oligodimethylsiloxane to yield the three derivatives (Si7)2DPA, (Si15)2DPA, and (Si15)2DPA while retaining the required energy levels for TTA-UC in solution and bulk. The bulk morphology of these discrete coil–rod–coil block molecules consists of 2D monolayers of crystalline DPA chromophores separated by layers of amorphous DMS with spacings of 3–6 nm. Transparent films were prepared by drop-casting materials doped with ≈3 mol% PtOEP that show air-stable upconverted light emission (UCPL) of ≈440 nm under non-coherent excitation (λex = 532 nm). Annealing of these films leads to an increase in chromophore alignment and the corresponding increase in UCPL intensities proves that the reported TTA-UC relies on triplet energy migration through
ordered chromophores. Annealing additionally induces better molecular dispersion of PtOEP that, combined with the increase in chromophore alignment, leads up to a 100-fold increase in UCPL intensity when compared to the unannealed film. For films of (Si$_7$)$_2$DPA, millimeter-sized domains with regular alignment are obtained from which linearly polarized absorption and UCPL emission were observed. This is the first report of matrix-free polarized upconverted emission in organic films. The spatial dependence of the upconversion intensity as shown by upconversion imaging microscopy is a crucial factor to consider in upconversion research as displacements of only a few micrometers already can give different UCPL intensities. Future work may focus on the optimization of UCPL intensity by, for example, varying PtOEP concentrations or film thickness as well as investigating different sensitizer-annihilator pairs. The work presented here highlights the potential of nanophase-segregation with discrete-length DMS as a general approach for optoelectronic applications where dense chromophore packing and alignment are required in bulk, such as singlet fission\[39\] or nanoelectronics.\[1d,2a,40\]

**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.

**Keywords**

2D-assemblies, linearly polarized emission, photon upconversion, triplet energy migration, triplet–triplet annihilation

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Figure 5. Linear polarized properties resulting from perpendicular domain growth directions. a) Polarized optical microscopy image of (Si$_7$)$_2$DPA during slow cooling from the melt (0.05 °C min$^{-1}$) showing a preferential ± 90° angle in domain growth directions. The scale bar indicates 65 µm. b,c) Linear polarization-dependent absorption at 380 nm (b) and upconverted photoluminescence of 440 nm (c) with $\lambda_{ex} = 532$ nm for the ≈20 mm$^2$ domain of (Si$_7$)$_2$DPA (PtOEP:annihilator = 1:300) shown in the inset.
