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A Thermo- and Mechanoresponsive Cyano-Substituted Oligo(*p-phenylene vinylene) Derivative with Five Emissive States*

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Abstract: Multiresponsive materials that display predefined photoluminescence color changes upon exposure to different stimuli are attractive candidates for advanced sensing schemes. Herein, we report a cyano-substituted oligo(*p*-phenylene vinylene) (cyano-OPV) derivative that forms five different solvent-free solid-state molecular assemblies, luminescence properties of which change upon thermal and mechanical stimulation. Single-crystal X-ray structural analysis suggested that tolyl groups introduced at the termini of solubilizing side-chains of the cyano-OPV play a pivotal role in its solid-state arrangement. Viewed more broadly, this report shows that the introduction of competing intermolecular interactions into excimer-forming chromophores is a promising design strategy for multicolored thermo- and mechanoresponsive luminescent materials.

Stimuli-responsive luminescent materials, which change their emission color in response to external stimuli, such as light, a temperature change, exposure to solvent vapor, or mechanical treatment, currently attract much attention and are potentially useful for applications that range from sensors to data storage.[1–4] Especially the number of reports on compounds, luminescence properties of which can be changed mechanically, has surged during the last decade.[3] Because the emission characteristics of molecular materials can strongly depend on molecular conformation and electronic interactions between neighboring molecules, materials in which the molecular arrangement can be influenced by mechanical treatment are likely to display mechanoresponsive luminescent (MRL) behavior.[3] This design approach permits creating MRL materials that can exhibit more than two emission colors.[3c,d] Indeed, several multicolored MRL materials have been reported based on this general strategy or a combination thereof with other approaches, such as the scission of covalent bonds.[5,6] Although most MRL materials display two or three emissive states, there are few reports in which up to four emission colors were reported. Herein, we report a cyano-substituted oligo(*p*-phenylene vinylene) (cyano-OPV) derivative (**1**, Figure 1) as the first MRL material, the emission of which can be switched between five different emissive states. Cyano-OPV derivatives have a strong tendency to form excimers[9] in the solid state and often exhibit a high emission quantum yield, which makes them attractive for mechano-sensing.[10–12] As was demonstrated during our investigation of other cyano-OPV derivatives,[10–13] their self-assembly is governed by π–π stacking of the cyano-OPV cores on the one hand and by van der Waals interactions among auxiliary substituents on the other. Two-color MRL behavior was achieved by balancing these competing interactions, which caused the formation of two (meta)stable polymorphs.[11e] This general concept has also been used to induce (meta)stable assembly states in a few other MRL materials.[3d, 5a,i,7,8] We show herein that the introduction of tolyl groups, which we expected to complicate intermolecular interactions on account of steric (repulsion) and π–π (attraction) in-

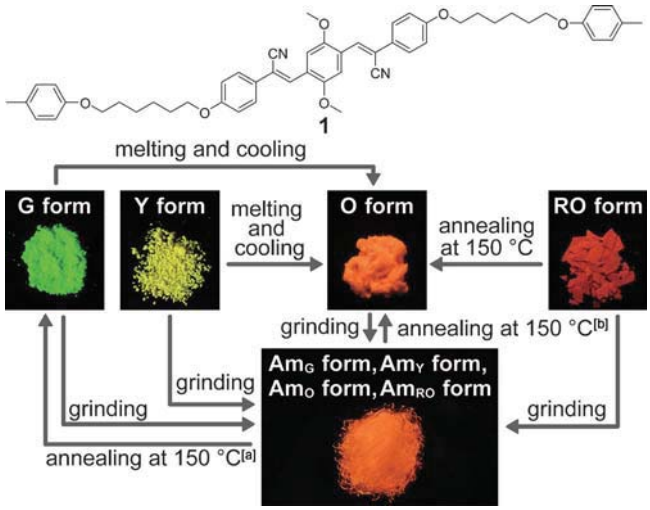

Figure 1. Molecular structure of cyano-substituted oligo(*p*-phenylene vinylene) derivative **1** and images presenting the photoluminescence color observed for the five molecular assembled states (G, Y, O, RO, and Am forms). Arrows indicate possible conversions by the indicated treatments. Images were taken under irradiation with UV light ($\lambda = 365$ nm) at room temperature. [a] Only for Am_G form. [b] Only for Am_O and Am_{RO} forms.

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teractions, at the termini of solubilizing side chains of a previously investigated cyano-OPV core,[10–13] leads to an MRL material (**1**) with five different (meta)stable assembly states, which translate in as many different emission colors. Taken more broadly, our results show that the introduction of competing intermolecular interactions into excimer-forming chromophores is a promising design strategy for multicolored stimuli-responsive luminescent materials.

Compound **1** forms four different polymorphs[14] (G, Y, O, and RO forms), which can be accessed by crystallization or precipitation from solution and exhibit green, yellow, orange, or red-orange emission upon excitation with ultraviolet (UV) light (Figure 1).[15] The G form was obtained by slow solvent evaporation from a dichloromethane solution of **1**. The Y and O forms were prepared by crystallization from toluene/methanol (9:1) and 1,4-dioxane, respectively. The RO form was accessed by precipitating **1** from a concentrated $CHCl_3$ solution into methanol. Thermogravimetric analyses showed no or only very minor weight losses below 200 °C, and indicated that no solvent molecules are included in any of the polymorphs (Figure S1 in the Supporting Information). The RO form could be converted into the O form through annealing at 150 °C, that is, below the melting temperature of 178 °C (see below), whereas melting and cooling were required to convert the G and the Y forms into the O form. Mechanical grinding of all polymorphs promoted the conversion to largely amorphous states, which display orange emission; as the origin of the amorphous form matters (see below) Am_G, Am_Y, Am_O, and Am_{RO} forms are differentiated. Annealing the amorphous forms at 150 °C for ten minutes caused crystallization; interestingly, the state formed depended on the history of the sample, which suggests that nucleation through residual crystals is at play. Thus, annealing of the Am_G form restored the G form, whereas annealing of the Am_O or Am_{RO} form gave the O form. In the case of the Am_Y form, yellow-green emission was observed after annealing, likely due to the formation of two polymorphs.

Powder X-ray diffraction (XRD) experiments confirmed that the G, Y, O, and RO forms are all crystalline, and that their molecular packing is different (Figure 2). The XRD patterns of the G, Y, and O forms feature many sharp peaks, indicating the formation of well-ordered structures. In contrast, only two intense, rather broad peaks can be discerned in the diffraction pattern of the RO form, suggesting a moderate level of order and a small crystallite size. This is consistent with the fact that the RO form was obtained by rapid precipitation. As was mentioned before, annealing the RO form at 150 °C causes the photoluminescence to change from reddish orange to an orange that is reminiscent of the O form (Figure 1); indeed, a transformation to the O form is evident from a comparison of the XRD patterns (Figure S2 in the Supporting Information). Differential scanning calorimetry (DSC) showed traces of the RO form with two exothermic peaks around 100 °C, thus, providing further evidence for the conclusion that the transformation occurs through a solid–solid phase transition (Figure S3 in the Supporting Information). The first DSC heating curves of the G, Y, and O form showed no such peaks, but reveal only melting transitions between 179 and 183 °C.

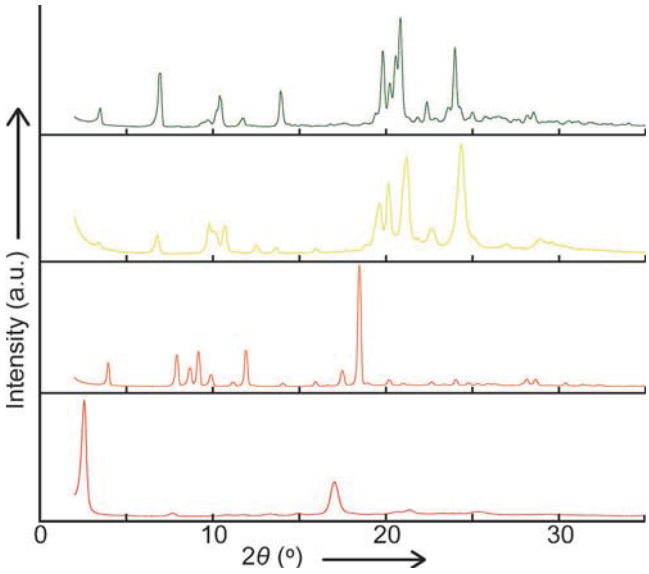

Figure 2. Powder X-ray diffraction patterns of the G (green line), Y (yellow line), O (orange line), and RO forms (red line) of **1**. All data were acquired at room temperature. Samples were prepared by crystallization or precipitation as detailed in the text.

Crystals of sufficient quality for single-crystal X-ray structure analysis could only be grown in the O form. The analysis showed that in this case, the cyano-OPV core of compound **1** is almost planar, and π-stacked structures, in which the electron-rich central phenyl group interfaces with the electron-deficient cyano-substituted ethylene moieties of the adjacent molecules can be observed (Figure 3 a and b). A similar structure has been reported for a cyano-OPV derivative featuring methoxy groups instead of the tolyloxyalkoxy moiety as peripheral substituents.[11e] The methoxy-substituted cyano-OPV also exhibited orange emission (associated with static excimers, see below), and its solid-state emission characteristics are similar to the O form of compound **1**. Figure 3 c and d shows that the peripheral tails interdigitate each other so that two tolyloxy groups "sandwich" the outer rings of the cyano-OPV core, although their orientation is orthogonal to the latter. All cyano-OPVs known to us,[10–13] with the same core and general chemical substitution pattern (i.e., two alkyloxy groups attached to the central phenyl ring, and one to each of the peripheral rings) display similar orange red emission in the solid state, which reflects very similar assemblies that promote excimer emission. Although the detailed structures remain unresolved, such excimer emission is absent in the G and Y forms, suggesting that the bulkiness and/or conjugated nature of lateral tolyl rings play an important role, because they make other polymorphs accessible, unlike longer alkyl chains.[11e]

The powder X-ray diffraction patterns of samples of the G, Y, O, and RO forms that had been ground at room temperature showed no unambiguous peaks (Figure S4 in the Supporting Information), confirming that mechanical treatment always leads to an orange light emitting amorphous state. However, the diffractograms acquired after annealing the ground samples for ten minutes at 150 °C displayed several sharp peaks

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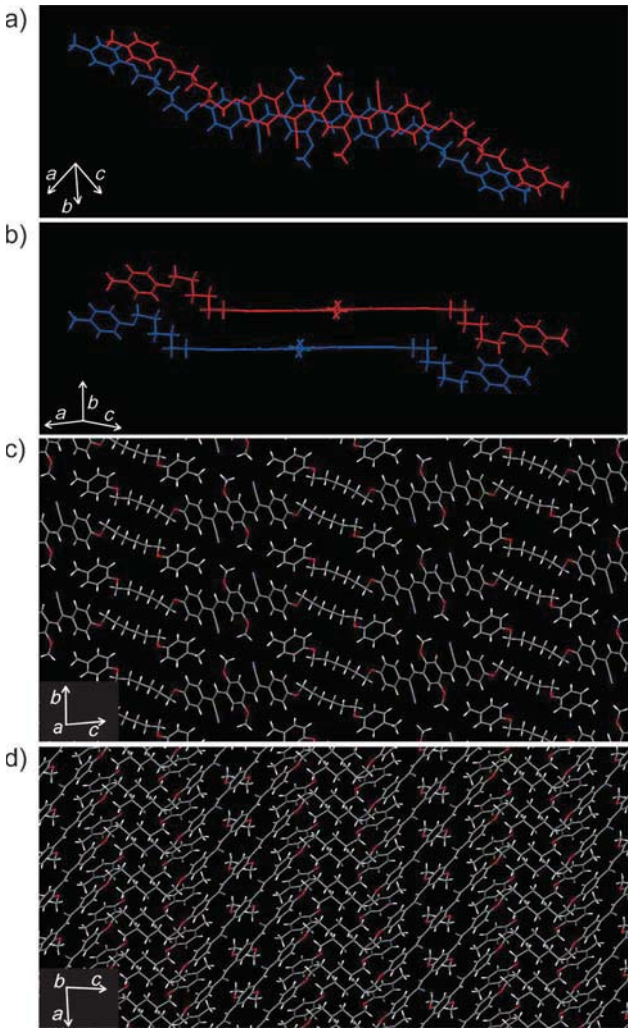

Figure 3. Crystal structure of compound **1** in the O form. a,b) Two adjacent molecules form π-stacked structures. c) Crystal structure viewed along the *a* axis. d) Crystal structure viewed along the *b* axis.

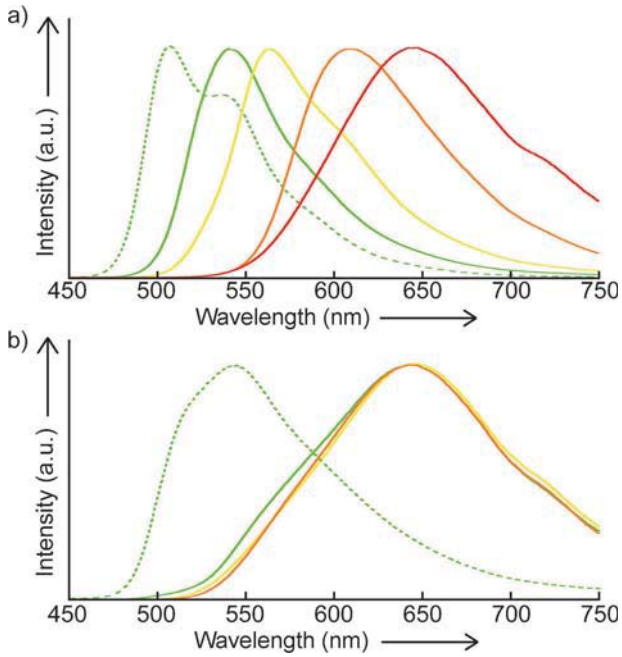

Figure 4. a) Photoluminescence spectra of a chloroform solution of **1** ($1 \cdot 10^{-5}$ M; green dashed line) and the solid G (green solid line), Y (yellow solid line), O (orange solid line), and RO forms (red solid line). b) Photoluminescence spectra of ground samples prepared from the same solid forms (solid lines) and of the annealed Am_G form (green dashed line); $\lambda_{ex} = 400$ nm. All spectra were recorded at room temperature.

(Figure S4 in the Supporting Information). Several peaks indicative of the G form can be discerned in the XRD patterns of the annealed Am_G and Am_Y forms, respectively. The DSC trace showed a melting transition that is indicative of the G form, but there were no crystallization peaks; this is consistent with a crystallization process that occurs over a broad temperature range (Figure S5a in the Supporting Information). Indeed, a broad exothermic peak can be detected around 90 °C in a DSC spectrum recorded with a higher heating rate (60 °C min^{-1}; Figure S5b in the Supporting Information). On the other hand, annealing the Am_O or Am_{RO} forms gave samples XRD patterns of which correspond to the O form. The XRD data thus confirm the structures inferred from the emission colors (see above) and that nucleation effects associated with residual crystals of the original form are at play.

The photophysical properties of cyano-OPV **1** were investigated in solution and the solid state. The absorption spectrum of a dilute chloroform solution ($1 \cdot 10^{-5}$ M; Figure S6 in the Supporting Information) displayed a band with a maximum at 435 nm and a shoulder around 365 nm. The emission spectrum of the solution showed peaks at 507 and 537 nm and a shoulder around 570 nm (Figure 4a). The fluorescence lifetime was 1.4 ns (Figure S7 in the Supporting Information). These parameters are identical to those of other cyano-OPV derivatives having the same luminescent core[10] and reflect emission from well-individualized monomer states. The emission spectrum of the solid G form is slightly redshifted and displays only one peak centered at 540 nm. Its width at half maximum is comparable to that of the band observed in chloroform solution and the lifetime (4.0, 6.9 ns; Figure S7 in the Supporting Information) remains short. Thus, the data point to monomer emission. Green monomer emission in a crystalline state has not been observed for any cyano-OPV with a similar core before, and appears to be directly related to the crystal structure promoted by the substituents used in **1**. By contrast, the emission band of the O form centered at 610 nm is broader and without structure, and the emission lifetime is increased to 26 ns. Taking also the π-stacked structure observed for the O form and the fact that all similar cyano-OPV derivatives show the same features into account,[10–13] we conclude that the O form is related to excimer emission from ground-state aggregates. The emission spectrum of the RO form showed the broadest band of the four crystalline samples, with a maximum at 647 nm. The emission of this form also displays the longest lifetime (33 ns; Figure S7 in the Supporting Information) of all forms of **1**. Given that the RO form displays the lowest degree of order of all crystalline forms, we speculate that some of the chromophores form ground-state aggregates, in which electronic interactions among the central rings and the electron-

withdrawing cyano groups, lead to even more stabilized excimers. Often, molecular materials that contain the emitting species in states associated with different bandgaps show emission characteristics that are associated with the lowest-energy state, if energy transfer processes are effective. In the case of the RO form, the fact that no higher-energy bands are observed suggests very efficient energy transfer to these low-bandgap sites. The thermal treatment-induced redshift of the emission band also supports this hypothesis. As was mentioned before, annealing the RO form at 150 °C causes a transformation to the O form, as was confirmed by comparison of the emission spectra (Figure S8 in the Supporting Information).

Finally, the Y form displays an emission spectrum that resembles the one of the G form, but its maximum is redshifted to 564 nm, and the curve seems to display a hint of a shoulder around 605 nm, that is, at the wavelength at which the O form displays an emission maximum. The fluorescence lifetime (11 ns, Figure S7 in the Supporting Information) is between those of the G and the O form. On account of the resemblance of the powder XRD patterns of the G and Y forms, we suspect that the molecular packings are similar. Thus, we interpret the emission to arise mainly from monomeric species, although some excimer-like interactions and/or exciton coupling may be also at play. Although no unambiguous conclusion can be drawn, it is clear that the yellow emission is not simply due to a combination of the emissive species that constitute the G and O forms.

The emission spectra of ground samples (Am_G, Am_Y, Am_O, and Am_{RO} forms) are virtually all identical (Figure 4b), irrespective of the form from which they were obtained. The spectra showed the broadest emission band of all samples, stretching from approximately 500 to above 750 nm, with maxima between 640 and 645 nm. The optical characteristics reflect the (perhaps random) formation of a few assemblies that are comparable to those responsive for the emission in the RO form, but on account of the large degree of disorder (and perhaps a low content of these low-energy sites) energy transfer is not complete, so that a higher-energy shoulder is observed. The emission spectra of annealed ground samples (Figures 4b and S9 in the Supporting Information) confirmed the conclusions drawn from the visual evaluation of their emission characteristics, the XRD data, and the DSC traces (see above). In the case of the G, Y, and O forms, the spectra largely mirror those of the original forms, whereas in the case of the RO form, a transformation to the more stable O form was observed. This is consistent with small amounts of the original crystals that remain in the largely (but apparently not completely) amorphous forms after grinding, though the emission bands ascribed to the original crystalline phases were not observed, likely due to energy transfer, which causes almost identical emission bands from the amorphous fractions (Figure 4b). After annealing, the remaining original crystals function as seed crystals that nucleate the formation of different crystal structures, which in turn lead to different emission colors.

The exposure of the Am_G form to dichloromethane vapor leads to a significant blueshift of the emission spectrum (Figure S10 in the Supporting Information). However, complete conversion to G form could not be achieved, even when the sample was exposed to solvent vapors for one day, perhaps on account of diffusion limitations. No pronounced blueshift was observed when Am_O and Am_{RO} forms were exposed to dichloromethane, suggesting that nucleation-driven crystallization is similar to thermal treatment of the amorphous forms.

Finally, it is remarkable that in all forms, the cyano-OPV **1** is highly emissive. Interestingly, the photoluminescence quantum yields of the G (0.60), Y (0.50), and O forms (0.64) are even higher than in dilute chloroform solution (0.40), reflecting the absence of non-emissive low-energy states and suggesting that the well-ordered molecular structures suppress non-radiative decay processes associated with rotation or twisting. Only the RO form displays a somewhat lower quantum efficiency of 0.22.

In conclusion, we have modified a known cyano-OPV core with peripheral tolyloxyalkoxy groups, which bestow the resulting compound **1** with the ability to crystallize in four polymorphs and also adopt an amorphous state. The five states exhibit different emission colors that cover a significant part of the visible spectrum. We demonstrated that conversion between (some of) these states is possible through exposure to heat, solvent vapors, or mechanical treatment. Our study clearly indicates that creating competition between different types of intermolecular interactions is a promising approach to create materials with a rich morphological and stimuli-responsive luminescence behavior.

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Keywords: materials science · mechanoresponsive luminescence · sensors · supramolecular chemistry · thermoresponsive luminescence

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[15] Detailed procedures that describe the preparation of all forms are provided in the Supporting Information.

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