Synthesis and Properties of Photoluminescent 1,4-Bis-(α-cyano-4-methoxystyryl)benzenes

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Abstract: 1,4-Bis-(α-cyano-4-methoxystyryl)benzene (1a) and 1,4-bis-(α-cyano-4-methoxystyryl)-2,5-dimethoxybenzene (1b) were synthesized by the Knoevenagel reaction of (4-methoxyphenyl)acetonitrile with terephthaldicarboxyaldehyde and 2,5-dimethoxy terephthaldicarboxyaldehyde, respectively. Both phenylene vinylene oligomers are highly photoluminescent, and the dimethoxy terephthaldicarboxyaldehyde, respectively. Both phenyl-vinylene vinylene oligomers are highly photoluminescent, and the comparison of the emission spectra of the crystalline solids with the ones of the corresponding low-viscosity molecular solutions reveals, particularly in case of 1b, an extremely large bathochromic shift. This effect is consistent with the formation of excimers that are characterized by low-bandgap emission. With the objective to control the emission characteristics of these dyes beyond the limiting states of molecular solution and crystalline solid, the investigation of their photophysical characteristics was extended to the liquid crystalline state and the isotropic melt, as well as to blends with isotactic polypropylene.

Key words: phenylene vinylene oligomer, photoluminescence, liquid crystal, excimer luminescence, Knoevenagel reaction, colour tuning

In the past decade, the potential use of π-conjugated semiconducting polymers in light-emitting diodes (LEDs) has attracted significant interest, since these materials may combine the processability and outstanding mechanical properties of polymers with the exceptional, readily tailored electronic and optical properties of functional organic molecules.1 Poly(p-phenylene vinylene)s (PPVs) represent the most extensively studied class of π-conjugated polymers, and numerous examples have demonstrated that their electronic properties can be tailored virtually at will by a judicious design of molecular and supramolecular architectures.1 In order to develop a fundamental understanding for the structure–property relation of PPVs, a number of well-defined low-molecular oligo(p-phenylene vinylene) (OPV) derivatives which comprise electron-withdrawing cyano-groups as part of the conjugated system have recently been investigated.2–5 These cyano-OPVs have served as model compounds for the corresponding PPV derivatives, in which the substitution has led to an increased electron affinity, concomitant with a bathochromic shift of the emission and a reduced barrier for electron injection into the polymer.6 In this context, a few cyano-OPVs have been reported, which feature emission characteristics that strongly depend on the state of matter. Bathochromic shifts of up to 100 nm have been reported when comparing the emission of the crystalline solid with the one of the corresponding low-viscosity molecular solution.2b,3d This effect has been explained with the strong π–π overlap encountered in the crystalline lattice of these molecules.2b,3d Because of the pronounced π–π interactions, multiple conjugated molecules adopt a ‘sandwich structure’ and arrange under cofacial π-stacking with distances of the planes of the conjugated systems of the order of 3–4 Å. This architecture leads to the formation of excimers, which usually exhibit strongly red-shifted fluorescence bands and long fluorescence lifetimes.7 Intrigued by the possibility to control the emission colour of a given PL dye over a wide range of the colour spectrum by merely tuning its supramolecular architecture, and with the technological potential of PL materials in mind,8 we have embarked to explore the possibility to access supramolecular structures of cyano-OPVs between the limiting states of highly crystalline solid and molecular solution. Our initial target structures were 1,4-bis-(α-cyano-4-methoxystyryl)benzene (1a)9 and 1,4-bis-(α-cyano-4-methoxystyryl)-2,5-dimethoxybenzene (1b) (Scheme 1). While few conclusive data are available for 1a,9 its structural analogy to a five-ring OPV considered in an earlier study,2b and the reported smectic liquid crystalline (LC) behaviour9c suggested that this molecule might be an attractive candidate for the present study. The introduction of two methoxy – in contrast to frequently employed hexyloxy2,3 – groups into the central ring was expected to substantially shift the emission spectrum to lower energies, while keeping the physico-chemical properties of this new dye similar to the ones of 1a.

Thus, 1a and 1b were synthesized through the Knoevenagel reaction of (4-methoxyphenyl)acetonitrile with terephthaldicarboxyaldehyde and 2,5-dimethoxy terephthaldicarboxyaldehyde, respectively (Scheme 1). Our experimental conditions essentially followed the procedures reported to be effective before,2,3 and relied on a mixture of THF and t-BuOH as the solvent, and minor amounts of n-Bu4NOH and anhydrous t-BuOK. Gratifyingly, 1a and 1b precipitated from the reaction mixture in high yield
The thermal properties of 1a and 1b were studied using differential scanning calorimetric (DSC) measurements at heating and cooling rates of 5 K/min, as well as polarized optical microscopy. Upon heating, the DSC trace of 1a displayed a weak (ΔH = 9.7 J/g) irreversible endothermic transition at 220 °C and reversible endothermic transitions at 245 °C (ΔH = 109.4 J/g) and around 281 °C (ΔH = 2.5 J/g) (Figure 1). As can be seen from the inset in Figure 1, the latter transition is superimposed by a weak reversible transition around 279.5 °C. The features of the DSC spectrum remained essentially unchanged in subsequent heating cycles, except that, as mentioned above, the transition at 220 °C disappeared, and the position of the peaks exhibited minor changes; for example, in the third heating scan the transitions, in °C, are K 237 S 274 N 279 I. A detailed investigation with polarization microscopy revealed no changes when passing 220 °C, suggesting that the transition observed by DSC at this temperature is most likely a crystal–crystal transition. Gratifyingly, all other transitions determined by DSC were also observed by optical microscopy, and the transition temperatures determined by these two methods were found to correlate well. Polarization microscopy revealed that 1a enters a birefringent, highly viscous, mobile state around 243 °C. The texture suggests the presence of a smectic mesophase, which is also consistent with the large ΔH associated with the transition and the spherulitic growth pattern observed upon cooling.10 Another transition to a highly mobile birefringent phase was observed around 272 °C, before the isotropic melt was entered around 278 °C (cf. Figure 2). The low viscosity and the Schlieren texture of the phase between 272 and 278 °C (DSC: 279.5–281 °C) points to a nematic phase in this extremely narrow temperature regime (Figure 2). Compound 1b, by contrast, displayed only one well-defined, reversible transition at 248 °C (ΔH = 101.2 J/g), which by means of polarization microscopy could be assigned to the crystalline–isotropic transition. Thus, it appears that the introduction of two methoxy groups into the central ring of the system reduces the molecular aspect ratio sufficiently to frustrate the onset of liquid crystallinity.

The 1,4-bis-(a-cyano-4-methoxystyryl)benzenes are bright yellow (1a) and orange (1b) strongly photoluminescent powders. The optical properties of these dyes were studied in detail by UV–Vis absorption and steady-state PL spectroscopy in different states of matter. Figure 3 shows the UV–Vis absorption spectra of both chromophores in CHCl₃ solution. Compound 1a displays an absorption band with a maximum at 389 nm and a weak shoulder around 290 nm. As expected, the introduction of the methoxy groups into the central ring caused a noticeable bathochromic shift in the absorption of 1b, which features a maximum at 436 nm and a pronounced shoulder around 365 nm.

PL spectra of 1a and 1b in solution and various solid states are shown in Figures 4 and 5. In solution, 1a shows an emission band that ranges from ca. 425 to 650 nm and exhibits two well-resolved maxima at 461 and 486 nm (Figure 4). In contrast to the absorption spectrum, the emission spectrum of the solution is clearly vibrationally structured, indicating a better planarization of the conjugated system in the emitting than in the electronic ground state.11 The ‘as-synthesized’, (semi)crystalline powder of 1a displays a much broader emission band than the solution with a maximum at 550 nm (Figure 4). The substantial red shift (64–89 nm) and the fact that the vibronic structure of the emission band has disappeared seem to suggest that the emission of this dye in the solid state is indeed predominantly governed by excimers rather than single-molecule emission. Interestingly, the PL spectrum of
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A drop-cast film of 1a represents an intermediate between the situation in solution and the solid state (Figure 4). The spectrum is fairly narrow and vibrationally structured, with maxima at 513 and 536 nm, indicating that in this case the contribution from a disordered fraction is dominant. This finding is consistent with the rapid solidification of this material, which was caused by the high vapour pressure of the casting solvent employed and the limited solubility of 1a, presumably leading to a poorly ordered solid state.

The solution PL spectrum of 1b shows similar features as the one of 1a (Figure 5). The emission band is slightly red-shifted when compared to 1a, with maxima at 506 and 538 nm. The emission spectrum of the ‘as-synthesized’, (semi)crystalline powder extends from ca. 530 to >800 nm and features a maximum around 644 nm. The fact that the spectrum of the crystalline material is broad and featureless, and the extraordinarily large bathochromic shift of 106–138 nm are again consistent with excimer formation in the crystalline lattice of this material. We have also produced a drop-cast film, and single crystals of 1b. The spectrum of the drop-cast film is rather similar to the one of the crystalline powder and displays a maximum at 654 nm. This finding seems to suggest that a rather efficient co-facial π-stacking of the chromophores is achieved, even if the dye is solidified from a rapidly evaporating solvent. Somewhat unexpectedly, the PL emission spectrum of the single crystals displays a maximum at 612 nm, thus, slightly blue-shifted compared to the spectra of the other solid samples of 1b investigated here. This results points to a less pronounced π–π overlap in the single crystal; a detailed investigation of the crystal structures of these solid samples is currently in progress and may reveal further insights.

Figure 2 Polarized optical microscopy images (crossed polarizers) of 1a in the smectic (left, T = 260 °C) and nematic (right, T = 275 °C) phase.

Figure 3 UV–Vis absorption spectra of 1a (solid line) and 1b (dotted line) in CHCl₃ solution.

Figure 4 PL emission spectra of 1a in solution (solid line), drop-cast film (dotted line) and crystalline powder (dashed line).
With the objective to control the emission characteristics of these dyes beyond the limiting states of molecular solution and crystalline solid, the investigation of their photophysical characteristics was extended to other states of matter. Since 1a displays liquid-crystalline behaviour, the investigation of the PL characteristics in the LC state suggested itself. As can be seen from Figure 6, the spectral characteristics of the emission are essentially unchanged when comparing spectra of the ‘as-synthesized’ powder recorded at 210 and 230 °C (i.e., at temperatures slightly below and above the solid–solid transition observed for this material, vide supra) with the one of the room-temperature sample (Figure 4). The emission maximum remains at 550 nm, but the high-temperature spectra are somewhat narrower than the room-temperature spectrum. The PL emission characteristics experience a significant change when the material enters the smectic mesophase (cf. Figure 6, spectrum recorded at 250 °C). The maximum of PL emission spectrum shifts to 511, concomitant with the fact that the intermolecular π–π interactions are substantially reduced and that emission from individual molecules is the dominant radiative process. Consistent with this interpretation, the emission characteristics of the sample remained essentially unchanged when entering the nematic mesophase and the isotropic melt, respectively (spectra recorded at 279 and 285 °C, cf. Figure 6). It should be noted that (although not reflected by Figure 6, which shows arbitrary PL intensities) the PL intensity of the mobile phases (> 230 °C) were reduced by a factor of ~25, when compared to the solid state.

Finally, we have also prepared thin films of blends of 1b and isotactic polypropylene (i-PP) by guest-diffusion, i.e., by swelling the i-PP films with solutions of the dye in CHCl3 of different concentrations and at different temperatures. Most interestingly, as is apparent from Figure 7, the PL spectra of the films thus obtained strongly depend on the diffusion conditions. Films that were dyed at low dye concentration and at room temperature exhibit an emission that is characteristic for single molecules, with maxima at 492 and 526 nm, and a weak shoulder at 569 nm. By contrast, films that were dyed at a higher dye concentration and at 60 °C feature an emission band that appears to be composed of a comparably small component associated with single molecule emission (with peaks at 492 and 530 nm), and a dominant component (with maximum at 644 nm) characteristic for the emission of aggregates. Thus, it appears that the extent of aggregation of the dyes in the polymer matrix, and therewith the intermolecular electronic interactions and photophysical characteristics of these blends, can indeed be conveniently controlled via the conditions applied to produce these materials.

In summary, we have shown that the 1,4-bis-(α-cyano-4-methoxystyryl)benzenes 1a and 1b can be synthesized in good yield and high purity by the Knoevenagel reaction of (4-methoxyphenyl)acetonitrile with terephthal dicarboxyaldehyde and 2,5-dimethoxy terephthal dicarboxyaldehyde, respectively. Both phenylene vinylene oligomers are photoluminescent and the comparison of the emission spectra of the crystalline solids with the ones of the corresponding low-viscosity molecular solutions reveals a remarkably large bathochromic shift, particularly in case of 1b. This effect is consistent with strong π–π overlap in the crystalline lattice of these molecules, which is associated with the formation of excimers that are responsible for low-bandgap emission. We have shown that the emission characteristics of these dyes can be readily and conveniently manipulated by controlling their supramolecular structure. In particular the possibility to shift the emission of 1b by about 150 nm by simply changing the conditions.

Figure 5 PL emission spectra of 1b in solution (solid line), single crystal (dash-dotted line), drop-cast film (dotted line) and crystalline powder (dashed line).

Figure 6 PL emission spectra of 1a as a function of temperature. Note that the Intensities have been scaled to optimally fit the graph; however, the absolute intensities of the mobile phases (> 230 °C) were reduced by a factor of ~25, when compared to the solid state.
Sing the i-PP films in a solution of i-PP (Polysciences, M_w = 220,000, M_n = 40,000) between two glass slides, and subsequent evaporation of the solvent under ambient conditions. Blend films of 1b in i-PP were prepared by guest-diffusion in analogy to the procedures reported before.12 Thus, a ca. 120 μm thick film of i-PP was produced by melt-pressing 500 mg of i-PP (Polysciences, M_w = 220,000, M_n = 40,000) between two Mylar® foils in a Carver laboratory press at a temperature of 180 °C and a pressure of 2 tons for 5 min, using a 120 μm spacer. Strips of ca. 7 × 1 cm of the resulting films were immersed in (a) a solution of 1b in CHCl_3 (ca. 10 mg/mL) for about 16 h at r.t., and (b) a solution of 1b in CHCl_3 (ca. 30 mg/mL) at 60 °C for about 3 h. The films were subsequently washed with CHCl_3 and dried at r.t. for 1 h.

1,4-Bis-(α-cyano-4-methoxystyryl)benzene (1a)
Terephthalidicarboxaldehyde (134.1 mg, 1.00 mmol) and (4-methoxyphenyl)acetonitrile (294.4 mg, 2.00 mmol) were dissolved in a mixture of t-BuOH (9 mL) and THF (3 mL) and the mixture was heated to 40–50 °C. t-BuOK (5.7 mg, 0.05 mmol) and Bu_4NOH (1 mL of a 1 M solution in MeOH) were added quickly, and an orange precipitate started to form immediately. The mixture was stirred for 15 min at 50 °C, cooled to r.t., and poured into acidified MeOH (50 mL containing 1 drop of concd H_2OAc). The precipitate was filtered off, excessively washed with MeOH, and dried in vacuo at 50 °C to yield 1a.

Yield: 351 mg (90%); yellow crystals.

^1H NMR: δ = 7.95 (s, 4 H, ArH), 7.64 (d, 3_J_HH = 8.9 Hz, 4 H, ArH), 7.44 (s, 2 H, CH=CCN), 6.98 (d, 3_J_HH = 8.9 Hz, 4 H, ArH), 3.86 (s, 6 H, OCH_3).
Anal. Calcd for C_{26}H_{20}N_{2}O_{2}: C, 79.57; H, 5.13; N, 7.13. Found: C, 79.51; H, 5.17; N, 7.10.

Figure 7 PL emission spectra of blend films of isotactic polypropylene and 1b. The films were prepared by guest-diffusion, by immersing the i-PP films in a solution of 1b in CHCl_3 (ca. 10 mg/mL) for about 16 h at r.t. (solid line), and a solution of 1b in CHCl_3 (ca. 30 mg/mL) at 60 °C for about 3 h (dotted line), respectively.

under which blends of the dye and an inert host material are prepared, is intriguing, and may find further technological exploitation. Clearly, measurements of the excited state life-times, and X-ray diffraction studies are desirable in order to provide unequivocal proof of the origin of the interesting behaviour documented here.

All chemicals were of highest commercial quality and were used as received. 2,5-Dimethoxy terephthallicarboxaldehyde was purchased from Ryan Scientific Inc., Isle of Palms, SC. ^1H NMR spectral data are expressed in ppm relative to internal TMS and were obtained on a Varian Gemini 200 MHz NMR spectrometer. Elemental analyses were carried out by Oneida Research Services Inc. DSC traces were recorded under nitrogen atmosphere on a Perkin Elmer DSC Pyris 1 at heating and cooling rates of 5 °C/min. UV–Vis absorption spectra were obtained on a Varian Elmer Lambda 800. PL spectra were measured on a SPEX Fluorolog 3 (Model FL3-12); all spectra were corrected for the spectral dispersion of the Xenon lamp, the instrument throughput, and the detector response. The excitation wavelength was 365 nm for solutions and 420 nm in case of solid-state samples. For the temperature-dependent PL experiments, a sample was heated between a microscope slide and a glass cover slip on a Gel Instrumente AG hotstage in connection of a Xenon lamp, the instrument throughput, and the detector response.

References


