Homoconjugation in Light-Emitting Poly(Phenylene Methylene)s: Origin and Pressure-Enhanced Photoluminescence

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ABSTRACT

The surprising optical properties of the non- π -conjugated polymer poly(phenylene methylene) (PPM) and its derivatives—that is, absorption in the 350–450 nm and photoluminescence (PL) in the 400–600 nm spectral regions—have been attributed to chromophores formed by homoconjugation along the polymer chain. The enabling role of homoconjugation, however, was hitherto ascertained primarily by excluding alternative origins of luminescence. The present study offers direct evidence for homoconjugation by employing optical and vibrational spectroscopy to investigate the interplay between microstructure and solid-state optical properties of PPM and its derivative poly(2,4,6-trimethylphenylene methylene) (PTMPM). In particular, polarized Raman and PL spectroscopy of melt-drawn fibers reveal a preferentially perpendicular orientation of the phenylene rings relative to the fiber axis, while, simultaneously, a preferentially parallel orientation of the transition dipole moment. PL spectroscopy under applied hydrostatic pressure yields a nearly 4-fold increase in PL intensity at 8 GPa, together with a surprising absence of excimer emission. These characteristics, being highly atypical of conventional π -conjugated polymers, highlight the different origin of the optical properties of poly(phenylene methylene)s as well as unique opportunities for applications.

1. INTRODUCTION

Despite its simple chemical structure and the first reports of its synthesis dating back to 1853,¹ poly(phenylene methylene) (PPM) has only recently received attention as a promising multifunctional polymer with a unique range of physico-chemical and optical properties. The latest reports highlighted its high decomposition temperature (~ 470 °C under ambient atmosphere),² excellent resistance to oxidizing agents,³ attractive barrier properties and high hydrophobicity.⁴

With recent reports having disclosed robust, one-step synthesis for yielding high molar mass materials in large volume,^{5–8} and combined with its excellent processability,^{4,9} PPM and its derivatives are proposed for a variety of advanced applications in, e.g., corrosion-resistant coatings, plastic optical fibers and encapsulating laminates.^{4,9,10}

Arguably, the most remarkable characteristics of PPM are its optical properties, that is photoluminescence (PL) in the 400–600 nm spectral region, with solid-state PL quantum efficiency $\approx 41\%$ and PL lifetime >8 ns.^{2,11} These observations for PPM and its methyl-substituted derivatives^{2,11} are especially fascinating given the absence of direct π -conjugation along the polymer backbone due to an electronically ‘insulating’ methylene group separating adjacent phenylene groups. For instance, the structurally similar poly(*p*-xylylene) and polystyrene, in which phenylene groups are separated by ethylene and propylene groups respectively, do not show PL in the visible region.^{12,13} While prior reports have attributed these optical properties of PPM to a 9,10-diphenylanthracene-related impurity,¹⁴ a recent, detailed re-examination² proposed that, in fact, their origin is due to the occurrence of *homoconjugation* along the chain, i.e. through-space π -orbital overlap across adjacent repeat units enabled by a (near-)cofacial arrangement of adjacent phenylene rings.^{15–18} Poly(phenylene methylene)s would thus represent the first of the class of macromolecules with *homoconjugation-enabled* optical properties. To-date, however, homoconjugation in PPM was ascertained primarily by excluding alternative origins of the observed optical properties, such as π -conjugated impurities, aggregation-induced emission or any effects due to inter-chain π - π interactions.²

The present study sets out to establish direct evidence for homoconjugation in poly(phenylene methylene)s by employing optical and vibrational spectroscopy to examine the interplay between intra-chain order and photophysical properties. Both isotropic films and uniaxially-oriented fibers are analyzed to establish the relevance of molecular anisotropy. The effects of chain ensemble equilibration by thermal annealing are investigated, and pressure-dependent spectroscopy is used to compare the response of these materials with that of conventional π -conjugated light-emitting polymers. Owing to their unique combination of physical and optical properties, non- π -conjugated fluorophores are attracting renewed research interest in the field.^{18–20} Thus, given their high molecular flexibility and, therewith, superior solubility and processability, poly(phenylene methylene)s hold promise for applications requiring biocompatibility and ease of processing, as well as efficient luminescence in the visible spectral range.

2. EXPERIMENTAL

Materials. Poly(phenylene methylene) (PPM) and poly(2,4,6-trimethylphenylene methylene) (PTMPM) were synthesized and purified as described previously.^{2,5} Weight-average molar mass M_w and polydispersity index PDI were determined by gel permeation chromatography, the corresponding values being: $M_w = 35900 \text{ g mol}^{-1}$, PDI = 3.3 for PPM, and $M_w = 27300 \text{ g mol}^{-1}$, PDI = 6.1 for PTMPM. Toluene (>99.8%, Labkem) was used as received.

Sample preparation. Films of PPM and PTMPM were spin-coated from solutions in toluene (60 and 50 wt% respectively). Both solution and substrates were pre-heated on a hotplate at 95 °C immediately prior to deposition to produce relatively thick films ($20 \pm 3 \text{ }\mu\text{m}$ and $15 \pm 1 \text{ }\mu\text{m}$ for PPM and PTMPM respectively). Spin-coated films were then ‘equilibrated’ by thermal annealing

above the corresponding glass transition temperatures, T_g : under nitrogen atmosphere the films were placed onto a pre-heated hotplate at 150 °C for PPM ($T_g = 66$ °C) or 220 °C for PTMPM ($T_g = 147$ °C), annealed for 15 min, and cooled to room temperature at ~ 10 °C min⁻¹. Fibers of PPM and PTMPM (~ 50 – 100 μ m diameter) were manually drawn from the viscous melt at, respectively, 150 and 240 °C under ambient atmosphere at a rate of approximately 0.5 m s⁻¹.

Characterization. UV-Vis absorption spectra were recorded with a Shimadzu UV-2600 spectrophotometer equipped with an integrating sphere, allowing the absorption spectra to be corrected for reflection and scattering losses. Photoluminescence (PL) spectra were recorded in reflection using a Jobin Yvon Horiba Fluoromax-3 spectrofluorometer ($\lambda_{ex} = 380$ nm); standard reflection geometry was adopted for analysis of films while the back-reflection configuration was used for fiber samples to minimize the effects of excitation scattering. Film thicknesses were measured using a DektakXT profilometer (Bruker). Microscopy was performed using an Olympus BX51 instrument (images in Figure 2e and Figure 4a) and a Mantis Elite stereo-microscope (images in Figure 2c,d). Raman spectroscopy ($\lambda_{ex} = 785$ nm; incident power = 15–25 mW) was performed using a WITec Alpha300RA instrument, with the spectra recorded over $\sim 50 \times 50$ μ m² sample areas in scanning mode (integration time = 0.5 s per spectrum), followed by averaging of data from ~ 2500 points and subtraction of a polynomial background. No sample degradation was observed under the adopted conditions. Polarized Raman and PL spectra were recorded with both excitation and detection polarized collinearly (except for cross-polarized measurements), using constant excitation, detection and sensitivity settings throughout. In all cases, polarized Raman and PL spectra were corrected for the polarization preference of the imaging system²¹ which was determined *via* polarized measurements performed on, respectively, a silicon wafer and an in-plane

isotropic film of poly(9,9-dioctylfluorene); the latter exhibiting PL in the same spectral range as the studied polymers. IR spectra were recorded with a Jasco FT/IR-4700 spectrometer equipped with an attenuated total reflectance (ATR) cell.

Pressure-dependent spectroscopy. Photoluminescence and Raman scattering measurements were performed using a gasketed diamond anvil cell (DAC). 4:1 vol/vol methanol:ethanol solution (dried over molecular sieves; non-solvent for the studied polymers) was used as the pressure-transmitting medium to provide a uniform hydrostatic environment. Several ruby spheres were also added to measure pressure *via* the standard fluorescence calibration method.²² Spectra were collected at room temperature in backscattering configuration using a 20× long working distance objective (NA = 0.35) and a LabRam HR800 spectrometer equipped with a CCD detector. PL and Raman spectra were recorded with excitation at 405 and 785 nm, respectively, using continuous-wave diode lasers. Low laser power density ($<2.4 \text{ W cm}^{-2}$) was used for PL acquisition to avoid any simultaneous photodegradation of samples. Measurements were performed on the thermally-equilibrated film samples. In each case, care was taken to record spectra at the same spot on a sample, allowing the absolute changes in PL intensity to be monitored as a function of pressure.

3. RESULTS

This study focuses on PPM and its derivative poly(2,4,6-trimethylphenylene methylene) (PTMPM) (Figure 1a). The latter polymer is selected due to its enforced, precisely-defined meta-substitution pattern along the chain (as opposed to PPM which may feature combined para-, meta- and ortho- links)⁵ and, possibly as a result, a substantially higher solid-state absorption coefficient.² Comparison of the spectral characteristics of PPM and PTMPM furthermore allows for

establishing the generality of observations relating to homoconjugation, the proposed intra-chain structure for which is illustrated schematically in Figure 1b.

Figure 1. (a) Chemical structures of PPM (left) and PTMPM (right). (b) Schematic of a homoconjugated para-substituted PPM chain segment, illustrating π -orbital overlap between adjacent phenylene rings across the methylene bridges enabled by the particular chain conformation. Dihedral angle ϕ and C-C-C bending angle θ are also indicated.

Optical spectroscopy

Solution-processed polymer films typically feature chains in highly non-equilibrium conformations that are expanded relative to those present in the melt, resulting from vitrification occurring at non-zero solvent content.²³ The kinetic contribution to trapping non-equilibrium conformations also becomes more prominent when low-boiling-point solvents are used or, as in the present case, when both solutions and substrates are pre-heated prior to spin-coating.²⁴ Given the previously established importance of intra-chain order for enabling the optical properties of interest,² films were annealed above the respective glass transition temperatures of the polymers, T_g , to allow optimal relaxation of the chain ensemble to equilibrium conformations.²⁵

Spectroscopic manifestations of this will be analysed below. For the sake of clarity, thermally annealed films will be hereafter referred to as ‘equilibrated’.

Figure 2. Optical spectroscopy of PTMPM in the form of (a) ‘equilibrated’ films and (b) melt-drawn fibers, showing absorption and PL spectra (black and red lines respectively). The inset in (a) shows the change in absorption coefficient, α , for an as-spin-coated film (dashed grey line) and following equilibration by thermal annealing above T_g (solid black line). Also shown are representative micrographs of PTMPM samples taken under UV-light illumination at 365 nm: (c) as-spin-coated film, (d) equilibrated film and (e) fibers. Scale bars = 500 μm .

Absorption and photoluminescence (PL) spectra for equilibrated films and melt-drawn fibers of PTMPM are shown in Figure 2a,b. Absorption spectrum of films exhibits vibronic peaks at 346, 365, 383 and 404 nm, while the PL spectra feature a single vibronic progression with peaks at 414, 441 and 467 nm (vibronic spacing $\approx 1370 \text{ cm}^{-1}$). The high degree of vibronic resolution for both absorption and PL spectra rules out excimeric origin of emission, and indicates that the chromophores correspond to a well-defined chain conformation despite the high molecular flexibility expected from the chemical structure. The relatively low 0-0 PL vibronic intensity is ascribed to self-absorption, while a further contributing factor may be a partial intrachain H-aggregate character of a homoconjugated chain segment featuring near-cofacially oriented phenylene rings (Figure 1b), for which the relative 0-0 vibronic intensities would be attenuated,²⁶ as indeed observed for both absorption and PL spectra (Figure 2a). The corresponding spectra for melt-drawn fibers (Figure 2b) exhibit similar features, with a somewhat lower vibronic resolution in the absorption spectrum due to heterogeneities introduced by the inevitable variations in, e.g., strain-rate during manual fiber drawing.

As shown in the inset of Figure 2a, equilibration of PTMPM films by annealing above T_g leads to a substantial *increase* in the absorption coefficient ($\sim 40\%$ at 383 nm). Simultaneously, micrographs of the films (Figure 2c,d) show the emergence of macroscopic cracking which occurs in response to the internal mechanical stress accumulated within the inelastic macromolecular network upon cooling below T_g and is, therefore, indicative of pronounced *contraction* of polymer chains with reducing temperature.⁴ Taken together—and recalling that the occurrence of homoconjugation *a priori* necessitates a contracted or ‘folded’ chain conformation (Figure 1b)—these observations are thus attributed to an increase of the volume fraction of homoconjugated

chain segments following equilibration. It is relevant to note that alternative interpretations based on, for instance, microstructural changes cannot apply here given the absence of distinct spectral shifts following equilibration (cf. absorption data in the inset of Figure 2a), as well as the amorphous character of poly(phenylene methylene)s.²

The corresponding optical spectroscopy data for PPM (Figure S1) is consistent with the observations for PTMPM and previous reports,² albeit featuring a somewhat lower increase in absorption coefficient following equilibration (~20% at 387 nm). The latter can be rationalized by considering that PTMPM features a higher T_g (147 °C vs 66 °C for PPM)² resulting in a more pronounced trapping of non-equilibrium chain conformations in the as-spin-coated films, which is ameliorated by subsequent thermal equilibration.

Vibrational spectroscopy

Vibrational spectroscopy probes local molecular vibrations and is employed here as an established means of gaining insight into chain conformation and orientation.^{21,27–29} Raman and IR spectra for pristine and equilibrated PTMPM films are shown in Figure 3. Assignment of Raman vibrational modes (Table 1) was made by cross-reference with the related small-molecular compounds such as diphenylmethane (DPM; essentially the equivalent of a PPM dimer),³⁰ styrene,³¹ xylene,³² 1,3,5-trimethylbenzene³³ and toluene,³⁴ as well as atactic polystyrene³⁵ and poly(*p*-phenylene vinylene).³⁶

Figure 3. Raman and IR spectra (left and right ordinates respectively) recorded for PTMPM films: as-spin-coated (dotted black lines) and equilibrated (solid red lines). Spectra are normalized by the intensity of the peaks in the 2920–3060 cm^{-1} region (C–H and C–H₃ stretching vibrations; not shown here). The spectral positions of selected peaks are indicated.

As shown in Figure 3, equilibration of PTMPM by thermal annealing above T_g results in strong attenuation of selected Raman modes. Upon close inspection (Table 1) it is found that in all cases the attenuated modes correspond to various in-phase ring deformation vibrations (generally termed ‘ring breathing’²⁹ for small-molecular aromatic compounds). Most striking is the near-complete quenching of the Raman mode at 1004 cm^{-1} , which is typically the most intense Raman peak for mono-, meta- and 1,3,5-substituted benzene rings²⁹ such as those of DPM,³⁰ polystyrene³⁵ and *m*-xylene.³² (*N.B.* This mode is absent for para-substituted benzene rings as in, e.g., poly(*p*-phenylene vinylene).³⁶) Similarly, the IR spectra in Figure 3 also show equilibration-induced attenuation of

the ring deformation modes at 694 cm^{-1} (699 cm^{-1} for DPM; out-of-plane ring distortion/puckering) and 728 cm^{-1} (734 cm^{-1} for DPM; in-plane trigonal breathing mode).³⁰

The corresponding vibrational spectroscopy data for PPM films (Figure S2a) similarly reveals attenuation of selected ring deformation modes upon equilibration, albeit to a lesser extent than observed for PTMPM. The latter is in line with the above-noted lower increase of the absorption coefficient of PPM following equilibration and is ascribed to structural differences between the two materials, with PPM featuring a mixed, predominantly para- substituted pattern⁵ and therewith a more limited scope for intra-chain ordering than meta-substituted PTMPM.

The most plausible origin of the observed changes in the vibrational spectra following equilibration is considered to be an increased interaction between adjacent phenylene rings along the chain which, essentially, ‘freezes out’ ring deformation vibrations. Such interaction is likely to be enabled by a close proximity of adjacent phenylene rings in a cofacial-type arrangement. As an example, we note the previously reported attenuation of the pyridine ring breathing mode ($1001\text{--}1017\text{ cm}^{-1}$) observed by Raman and density functional theory (DFT) analysis when 4,4’-bipyridine was adsorbed by $\pi\text{-}\pi$ interactions onto poly(sodium 4-styrenesulfonate)-templated nanoparticles.³⁷ Elsewhere, attenuation/broadening of Raman modes is also commonly observed under the application of hydrostatic pressure which is attributed to enhanced intermolecular interactions and the associated increase in interatomic force constants.³⁸ It is emphasized that *chemical* changes (e.g. cross-linking) can be conclusively ruled out as an alternative origin of the observations in Figure 3 and Figure S2a in view of the above-noted high thermal stability of the studied polymers² and the thermal treatments having been performed under nitrogen atmosphere. For instance, the

occurrence of cross-linking would be manifested in reduced solid-state absorption coefficients and altered solubility for the materials – neither of which were observed (see, e.g., Figure S1 and Figure S2b for PPM).

Overall, the above-described spectroscopic manifestations of equilibrating a disordered chain ensemble by annealing above T_g highlight: (i) the optical properties being dependent on intra-chain conformational order, with (ii) said conformation(s) exhibiting a small separation between adjacent phenylene rings in a (near-)cofacial arrangement. Clearly, these features are consistent with the occurrence of homoconjugation in poly(phenylene methylene)s *via* the arrangement depicted in Figure 1b.

Table 1. Assignment of Raman modes for solid-state PPM and PTMPM. The asterisk (*) indicates modes the intensity of which is attenuated following equilibration by annealing above T_g .

Mode assignment	PPM (cm^{-1})	PTMPM (cm^{-1})
Ring $\nu(\text{C}-\text{C})$	1610	1602
	1582	1563
$\delta(\text{CH}_3)$	–	1456
$\delta(\text{CH}_2)$, scissoring	1433	1428
$\nu(\text{CH}_3)$, sym.	–	1380
$\nu(\text{C}-\text{C})$; $\rho(\text{C}-\text{H})$	–	1288
Ring deformation	–	1210 *
$\delta(\text{C}-\text{H})$, in-plane	1182	1186
Ring deformation; $\delta(\text{C}-\text{H})$	1030	1031 *
Ring deformation, trigonal	1003	1004 *
$\delta(\text{C}-\text{H})$, out-of-plane	843	–
Ring deformation, antisym.	786 *	786 *
Ring deformation	620	622 *

ν = stretching; δ = bending. See references in the text.

Polarized Raman and PL spectroscopy

Following the recent report of straightforward fabrication of PPM fibers by melt-drawing,⁹ PPM and PTMPM fibers were studied by polarized spectroscopy to further explore the interplay between intra-chain structure and photophysics, the nuances of which typically are obscured by molecular disorder in isotropic samples. Cross-polarized microscopy of the obtained fibers (inset of Figure 4a) indicates pronounced birefringence, confirming the anisotropic chain orientation which, with only rare exceptions,³⁹ is expected to be parallel to the fiber axis.

Figure 4. (a) Polarized Raman spectra recorded for a PPM fiber with excitation/detection polarization parallel (solid black line) and perpendicular (dotted red line) to the fiber axis. The differences in relative intensities of selected modes are highlighted. Upper inset shows cross-polarized optical micrographs of the fiber oriented vertically and at 45° (left and right images respectively; dotted lines highlight fiber position). Scale bars = 50 μm . Also shown in the lower inset are schematic (quasi-) top- and side-views of a uniaxially-oriented homoconjugated PPM chain segment within the fiber (for clarity, a para-substituted segment is shown). (b) Polarized PL spectra recorded for the same PPM fiber. Excitation/detection polarizations relative to the fiber axis are indicated; data are normalized by the maximum intensity of the parallel-polarized

spectrum. The shaded area highlights the spectral region for which PL self-absorption is prominent.

Polarized Raman spectra of PPM fibers recorded with polarizations parallel and perpendicular to the fiber axis are shown in Figure 4a. Interestingly, the vibrational modes associated with (substituted) phenylene ring vibrations (Table 1) exhibit substantially higher intensities in the *perpendicular*-polarized spectrum. Raman anisotropy $\langle r \rangle_R$ for a given mode was quantified as the ratio of maximum Raman intensities, I_R , obtained with polarizations parallel and perpendicular to the fiber axis ($\langle r \rangle_R = I_{R,\parallel}/I_{R,\perp}$). For the PPM fiber $\langle r \rangle_R = 0.82$ is obtained for the intense 1003 cm^{-1} ring deformation mode (known to be strongly polarized for DPM³⁰ and related compounds²⁹). Similar values ($\langle r \rangle_R = 0.76\text{--}0.89$) are recorded for the other resolvable modes, although their lower intensities, as well as varying depolarization ratios for different Raman modes, prevent a more detailed analysis. The corresponding data for the PTMPM fiber (Figure S3a) are fully consistent, exhibiting average $\langle r \rangle_R = 0.92$ for the four most intense modes – importantly, with the above-noted absence of the intense 1004 cm^{-1} ring deformation mode.

To confirm that the observations above are not due to any instrumental artefacts or effects of dielectric confinement, polarized Raman analysis was repeated on the same fibers following annealing above the respective T_g , leading to complete removal of chain-orientation-induced anisotropy (confirmed by cross-polarized microscopy; not shown here). The resulting spectra featured average $\langle r \rangle_R$ values of 1.04 and 0.98 for PPM and PTMPM respectively (Figure S4), which, within experimental error, are indicative of essentially isotropic materials. Hence, the

observation of $\langle r \rangle_R < 1$ for the Raman spectra of PPM and PTMPM fibers indicates preferentially *perpendicular* orientation of the phenylene rings relative to the chain axis.

Polarized PL spectroscopy was performed for the same fibers to investigate the interplay between molecular and optical anisotropy. The data for the PPM fiber (Figure 4b shows a distinct anisotropy (~ 1.2 and ~ 1.7 for the parallel/perpendicular spectral intensities at the 0-1 and 0-2 vibronic peaks respectively), with higher PL intensity for the *parallel*-polarized spectra indicating along-chain orientation of the transition dipole moment. (*N.B.* The relatively low values of PL anisotropy indicate a limited degree of chain orientation, which nevertheless is likely to be underestimated by this analysis given that (i) the fibers comprise undiluted material, allowing efficient PL depolarization by excitation energy transfer²¹ (see the cross-polarized spectrum in Figure 4b) which is further enhanced by (ii) high excess energy for excitation at 355 nm.)

Further information on the orientation of the transition dipole moment can be gathered from the relative differences in self-absorption for parallel- and perpendicular-polarized PL components. Comparison of thin and thick films (Figure S5) showed that PL of PPM up to ~ 470 nm is susceptible to attenuation by self-absorption, its impact being strongest for the S_1 - S_0 0-0 vibronic peak at ~ 419 nm. Hence, using the degree of self-absorption as a proxy for absorption coefficient, the lower intensity of the 0-0 vibronic in the parallel-polarized spectrum (Figure 4b) indicates higher absorption parallel to the fiber axis, thereby confirming that the transition dipole moment of PPM is oriented preferentially *parallel* to the chain axis. The corresponding data for the PTMPM fiber (Figure S3b) exhibits similar features, corroborating the analysis presented above.

Taken together—and considering that the relatively low degree of chain alignment in the fibers underestimates the respective anisotropy values—the observations above can be rationalized with reference to the schematic illustration of a homoconjugated chain segment shown in the inset of Figure 4a. The occurrence of homoconjugation across adjacent phenylene rings is understood to be critically dependent on the C–C–C bending angle θ (Figure 1b)² which preliminary DFT calculations have estimated to be substantially less than 90°. Hence, homoconjugated phenylene rings would have a larger projection *perpendicular to the extended chain axis* (proportional to $\cos \theta/2$), which leads to higher intensities for the perpendicular-polarized Raman spectra of the fibers. At the same time, chromophore formation by homoconjugation relies on electronic delocalization across phenylene rings along the chain, which in turn would imply a transition dipole moment orientation predominantly *parallel to the extended chain axis*. The latter is manifested by higher PL intensity for the parallel-polarized spectra of the fibers. We note that the occurrence of electronic delocalization along the chain in PPM is supported by the ‘classical’ PL redshift with the degree of polymerization reported previously.²

Pressure-dependent spectroscopy

The application of hydrostatic pressure provides the means for inducing a continuous variation of macromolecular conformation, as well as inter-chain interactions. Here pressure-dependent PL and Raman spectroscopy is used to study the response of poly(phenylene methylene)s to conformational confinement and compare it with that of conventional π -conjugated polymers, an excellent review of which can be found in ref. 38.

Figure 5. Pressure-dependent PL spectroscopy of a PTMPM film. (a) PL spectra recorded as a function of pressure P . (b) Integrated PL intensity, normalized by the value at ~0 GPa. (c) Spectral position of the ~2.44 eV PL peak (see corresponding marker in (a)). The solid grey line indicates

linear fit for $P \geq 4$ GPa; dashed grey line is a guide to the eye only. (d) Relative integrated spectral area, A_{PL} , for the ~ 2.83 eV PL peak (see corresponding marker in (a)). The direction of increasing self-absorption is indicated by the grey arrow. In all cases the values recorded during increasing and decreasing pressure cycles are designated by solid and open symbols, respectively.

Figure 5a–d presents the results of pressure-dependent PL spectroscopy for a PTMPM film. As shown by the spectra in Figure 5a, PL intensity is found to *increase* with applied pressure. Integrated PL intensity (1.6–2.6 eV; outside the self-absorption region) shows a linear increase with pressure up to ~ 4 GPa, followed by a sub-linear roll-off (Figure 5b), with PL enhancement reaching a factor of as much as 3.8 at 7.5 GPa. Integrating the entire spectrum (1.6–3 eV) yields a similar trend for PL intensity as a function of pressure, albeit with a more shallow slope (Figure S7). The variation of integrated PL intensity is fully reversible and the original PL is recovered upon release of pressure, signifying the absence of any phase transitions occurring under pressure. The corresponding data for a PPM film (see Table 2 and Figure S6) confirms the generality of pressure-induced PL enhancement for the poly(phenylene methylene)s studied.

By contrast, π -conjugated macromolecules invariably display strong PL attenuation under applied pressure, which is primarily attributed to increased intermolecular interactions leading to (i) formation of weakly-emissive charge-transfer or excimer states and (ii) increased exciton diffusion lengths resulting in more pronounced quenching at defect sites such as oxygen and residual catalyst.³⁸ For example, a factor of 10 *decrease* in PL intensity was reported for poly(*p*-phenylene vinylene) (PPV) at 10 GPa⁴⁰ and for poly(3-hexylthiophene) at 3.5 GPa.⁴¹ Hence, PL

enhancement with pressure for poly(phenylene methylene)s clearly signifies the different electronic and structural origin of their optical properties compared with that of conventional π -conjugated materials. While establishing the precise physical mechanism underlying PL enhancement undeniably requires further study, several plausible scenarios related to the occurrence homoconjugation will be outlined in *Discussion* below.

Turning attention now to relative spectral changes, PL spectra were fitted by a sum of Voigt peaks to track their evolution with applied pressure. In particular:

- (i) Spectral shifts are monitored by the position of the PL peak at ~ 2.44 eV (~ 508 nm; triangle marker in Figure 5a), located outside the self-absorption region.
- (ii) Relative measure of self-absorption (i.e. absorption by the sample) is provided by the integrated spectral area, A_{PL} , of the PL peak at ~ 2.83 eV (~ 438 nm; diamond marker in Figure 5a), normalized to the total integrated PL area. This analysis relies on the fact that this peak is located within the self-absorption region, as illustrated in Figure S5a. (*N.B.* Alternative origins of A_{PL} variation—e.g. changes in the Huang-Rhys parameter—can be largely disregarded here due to the amorphous character of the studied poly(phenylene methylene)s and invariance of their optical spectra with, e.g., temperature.² Figure S8 confirms that spectral areas of PL peaks located *outside* the self-absorption region show a correlated evolution with pressure – distinct to that of the 2.83 eV peak.)

The data for a PTMPM film (Figure 5c,d) reveals a complex evolution with pressure that can be divided into three distinct regions, indicated by dashed green lines in the figure:

- (1) 0–1 GPa: PL redshift by 3 nm, and reduced (self-)absorption (i.e. increased A_{PL});

- (2) 1–2.7 GPa: PL blueshift by 6 nm, and increased (self-)absorption (i.e. reduced A_{PL});
- (3) >2.7 GPa: continuous PL redshift and increasing (self-)absorption.

Regions (1) and (2) are attributed to conformational rearrangement proceeding through a combined variation the dihedral and C–C–C bending angles (Figure 1b), both of which are understood to be critical to homoconjugation and the corresponding bandgap energy in both PPM² and related compounds such as diphenylmethane.^{15,18} The conformation appears to stabilize for pressure >2.7 GPa (region (3)), above which PL redshifts continuously with a slope of ~ 3 meV GPa⁻¹ for both of the investigated poly(phenylene methylene)s (see Table 2 and Figure S6). By contrast, (semi-)flexible π -conjugated polymers typically display much higher slopes of PL redshift with pressure, e.g. 40 meV GPa⁻¹ for PPV⁴⁰ and 28–40 meV GPa⁻¹ for poly(9,9-bis(2-ethylhexyl)fluorene),⁴² which is primarily attributed to planarization of the conjugated backbone due to the resonance interaction.³⁸ Accounting only for inter-atomic bond contraction, and the resulting stabilization of the S₁ state, a smaller value of ~ 9 meV GPa⁻¹ was estimated for phenylene-based polymers.^{43–45} The latter value, in fact, closely matches those obtained for poly(phenylene methylene)s (Table 2). Therefore, the lack of planarization-related spectral shifts for poly(phenylene methylene)s is consistent with the occurrence of homoconjugation.

To further investigate bond contraction, pressure-dependent Raman spectroscopy was performed on an equilibrated PTMPM film, revealing the expected shift to higher energy of the 1602 and 1563 cm⁻¹ C–C stretching modes, the slope of which (~ 5 –8 cm⁻¹ GPa⁻¹ for $P < 2$ GPa; see Figure S9a) is indeed characteristic of aromatic polymers (~ 4 –10 cm⁻¹ GPa⁻¹).^{40,42} As shown in Figure S9b, the application of pressure does not lead to re-emergence of the Raman peaks that exhibited

equilibration-induced attenuation, which would otherwise signify a reducing volume fraction of homoconjugated chain segments. The results are therefore consistent with the observed monotonic increase of integrated PL intensity with pressure (Figure 5b).

Table 2. PL spectral shifts with applied pressure P , and pressure-induced PL enhancement for poly(phenylene methylene)s.

Material	PL shift with pressure ^{a)} meV GPa⁻¹ (<i>nm GPa⁻¹</i>)	PL intensity increase at 4 GPa ^{b)}
PTMPM	-4 (0.9)	3.2
PPM	-2 (0.5)	1.6

^{a)} From data for the ~2.44 eV PL peak for $P \geq 4$ GPa; ^{b)} from PL intensities integrated in the 1.6–2.6 eV region in Figure 5 and Figure S6

4. DISCUSSION

Certain aspects of the findings described above deserve further comment.

The first of these concerns the physical origin of pressure-induced PL emission enhancement observed for the poly(phenylene methylene)s. To the best of our knowledge, such observations for aromatic (macro-)molecules to-date have been reported only for small-molecules that support aggregation-induced emission (AIE), such as triphenylamine, the PL intensity of which doubles at 2 GPa.⁴⁶ However, AIE could be conclusively ruled out as the origin of the optical properties of PPM given its high PL quantum efficiency in both solution and solid-state (69% and 41% respectively).²

Hence, the first possibility may be that pressure-induced conformational confinement overcomes local steric barriers towards close-approaching arrangement of the phenylene rings along the chain and generates additional homoconjugated segments within the hitherto disordered parts of the chain ensemble. Increasing the volume fraction of homoconjugated chain segments accordingly would lead to higher PL intensity under constant photoexcitation conditions. However, formation of homoconjugated segments by, for instance, thermal annealing above T_g was shown to be *irreversible* both in this work (see Figure 2a and Figure 3) and previous reports² – that is, the spectroscopic signature of increased fraction of homoconjugated segments is retained following cooling to ambient temperature. Clearly, this is inconsistent with the observed *reversible* variation of PL intensity with pressure (see Figure 5b and Figure S6b). An alternative possibility may be related to an increase in oscillator strength and, therewith, absorption coefficient, with increasing pressure. Such increase in oscillator strength is indeed typically observed for π -conjugated polymers and is attributed to pressure-induced chain planarization.⁴⁷ Such interpretation, however, is unlikely to be applicable in the present case given that a *linear* PL intensity increase is observed up to ~4 GPa despite spectral shifts and variation of (self-)absorption occurring in the 0–2.7 GPa range for both PTMPM and PPM films (see Figure 5b–d and Figure S6b–d, respectively).

Hence, the origin of pressure-induced PL enhancement for poly(phenylene methylene)s is most likely related to an increase of T_g accompanying the application of hydrostatic pressure. A linear increase of T_g with pressure is well-documented for numerous polymers, such as natural rubber (80 °C increase at 0.5 GPa)⁴⁸ and polycarbonate (70 °C increase at 0.2 GPa),⁴⁹ albeit for a narrower range of pressures than employed in this work. Such increase of T_g would act to restrict

intramolecular motion such as the rotational degrees of freedom which, in turn, reduces non-radiative losses – that is, conceptually similar to the AIE mechanism. The interpretation above is therefore consistent with reversible variation of PL intensity with pressure, as well as the lower PL intensity increase at 4 GPa observed for PPM ($\times 1.6$; $T_g = 66\text{ }^{\circ}\text{C}$) compared with PTMPM ($\times 3.2$; $T_g = 147\text{ }^{\circ}\text{C}$) (see Table 2). The eventual roll-off of linear PL intensity increase with pressure for $P > 4\text{ GPa}$ is ascribed to an increasing contribution from opposing effects such enhanced exciton migration to quenching sites.

The second noteworthy feature of the presented pressure-dependent PL data for the poly(phenylene methylene)s is the remarkable absence of excimer emission at the highest pressures. As shown by Figure S10, the vibronic shape of PL spectra of PPM and PTMPM remains essentially unchanged up to 8 GPa (outside the self-absorption region), with no additional emission bands emerging. By comparison, polyfluorenes—a widely studied class of blue-emitting π -conjugated polymers—invariably display a loss of PL vibronic structure and emergence of a broad band centered at $\sim 2.3\text{ eV}$, already at pressures of $\sim 2\text{ GPa}$, that is generally attributed to the formation of excimers.^{42,50} The absence of corresponding excimer emission for poly(phenylene methylene)s is all the more surprising given their long solid-state PL lifetimes ($\sim 8.6\text{ ns}$ for PPM),² which should facilitate excitation transfer to energetically lower-lying excimers or oxidation-related defect sites. An exploration of whether this is related to the particular geometry of homoconjugation or the dynamics of excitation energy transfer presents a worthwhile avenue for future research given the detrimental effects of excimer emission on the efficiency and color purity of light-emitting devices.

Finally, previous reports² have noted the low absorption coefficients of poly(phenylene methylene)s (e.g., more than factor of 400 lower for PTMPM than for poly(9,9-dioctylfluorene)²⁴) and speculated whether it is intrinsic to homoconjugation or, instead, arises from a kinetically-trapped low fraction of homoconjugated chains segments within disordered solution-processed films. The spectroscopy data presented herein for equilibrated PTMPM films showing (near-)complete attenuation of ring-breathing Raman modes (Figure 3) and only a 1.4-fold increase in absorption coefficient (Figure 2a) supports the former explanation.

5. CONCLUSIONS

In summary, optical and vibrational spectroscopy were employed to study films and fibers of poly(phenylene methylene) and one of its methyl-substituted derivatives. The results highlighted a number of features that are indicative of the occurrence of homoconjugation, such as (preferentially) perpendicular orientation of phenylene rings and parallel orientation of the transition dipole relative to the extended chain axis within melt-drawn fibers. Pressure-dependent PL spectroscopy revealed an increase of PL intensity, as well as absence of excimer emission, for pressures up to 8 GPa – observations that are entirely contrary to those for conventional π -conjugated polymers. It is concluded that homoconjugation in poly(phenylene methylene)s is indeed substantiated, and yields a unique set of optical characteristics. Looking ahead, it would be of interest to study the excited state dynamics using transient spectroscopy methods, as well as exploring electroluminescent characteristics of poly(phenylene methylene)s and their blends with conventional π -conjugated materials.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge.

Additional optical and vibrational spectroscopy; polarized photoluminescence and Raman spectroscopy; pressure-dependent photoluminescence and Raman spectroscopy. (PDF)

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Notes

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