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Direct laser writing of poly(phenylene vinylene)
on poly(barrelene)

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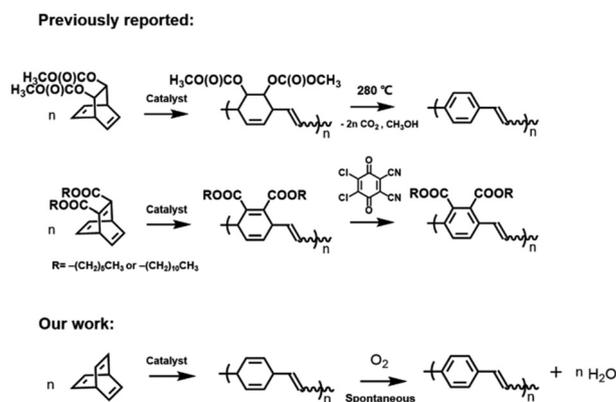# Direct laser writing of poly(phenylene vinylene) on poly(barrelene)†

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The ring-opening metathesis polymerization of barrelene (bicyclo[2.2.2]octa-2,5,7-triene) is described. The monomer was synthesized using an optimized route and characterized, for the first time, using X-ray diffraction analysis of a coordination complex. The solubility of poly(barrelene) was found to correlate with the ratio of *cis* to *trans* exocyclic vinylenes in the polymer backbone. Copolymers of barrelene and norbornene were also prepared and used to obtain robust films. The barrelene-containing polymers underwent spontaneous dehydrogenation under air or upon being subjected to laser pulses to afford poly(phenylene vinylene). A series of well-defined patterns with micrometer dimensions were created by direct laser writing on films of poly(barrelene-*co*-norbornene) and visualized by the fluorescence of the conjugated polymer that formed upon irradiation.

Conjugated polymers[1–3] have been used in a wide range of electronic[4,5] and optical applications[6–8] due to their abilities to form films and exhibit high electrical conductivities upon oxidative or reductive doping.[9] Although poly(acetylene)[10–13] is the prototypical example, significant attention has been directed toward poly(phenylene vinylene) (PPV) because of its low optical band gap, large nonlinear optical response, and emissive characteristics. While these properties poise PPV for use in applications that range from light-emitting diodes to photovoltaic devices,[6,14,15] the material is typically intractable and therefore challenging to process which mandates the need for functionalized polymeric precursors in conjunction with a post-polymerization modification scheme to enhance solubility.[16] The precursors are typically synthesized using step-growth[16–21] or chain-growth polymerization methodologies,[22,23] and then heated or chemically-treated to promote transformation. For example, as summarized in Scheme 1, Grubbs reported that the ring-opening metathesis polymerization (ROMP) of a bis(carboxylate) functionalized bicyclo[2.2.2]octadiene followed by a thermally-induced elimination at an elevated temperature (280 °C) affords PPV.[24] Substituted PPVs have been obtained in similar manner by treating polymers

obtained *via* ROMP[25,26] with relatively harsh oxidants (*e.g.*, 2,3-dichloro-5,6-dicyanoquinone; DDQ).

A new approach to PPV was envisioned through the ROMP of "barrelene" (bicyclo[2.2.2]octa-2,5,7-triene) (**1**). The corresponding polymer, which is formally a copolymer that consists of alternating 1,4-cyclohexadienyl and vinylene repeat units, should be prone to aromatization *via* dehydrogenation and thus may transform to PPV under relatively mild conditions. The realization of such a feature combined with the emissive characteristic of PPV was expected to enable the use of poly(barrelene) in laser machining, direct laser writing (DLW) and other contemporary patterning technologies that create micro- or nanometer sized objects in a manner that does not require masks, inks or developing agents.[27–29] While metallic nano-clusters are often utilized as substrates in such applications,

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Scheme 1 Selected examples of routes that have been used to synthesize PPV.

metal-free materials are appealing alternatives from economic and fundamental perspectives. Substrates that afford conjugated polymers, particularly those that luminesce, are especially attractive because they should facilitate access to novel types of high precision optical devices, including displays, sensors, and waveguides. For example, Mendonça described the synthesis of spatially resolved PPV by applying laser pulses to films of poly(xylyliden tetrahydrothiophenium chloride).[30] Photon absorption was shown to result in a photothermal reaction that facilitated the elimination of reactive byproducts, including sulfonium leaving groups and hydrochloric acid, and afforded PPV with a higher conjugation length than analogues prepared using conventional thermal-based approaches.

Herein the ROMP of barrelene is described. The solubility of the resulting polymer was found to depend on its geometry with the *cis* form exhibiting a higher solubility in organic solvents than its *trans* isomer. Copolymers of barrelene and norbornene were also synthesized and used to create robust films. Exposure of the polymers to air was found to result in spontaneous dehydrogenation and afforded PPV. The transformation was also facilitated using laser pulses and DLW on films of poly(barrelene-*co*-norbornene) afforded precisely defined fluorescent patterns with micrometer-sized dimensions.

The requisite monomer (**1**) has a storied history. It was first called "klovosene" (after a Greek word for bird-cage) by Hine in 1955.[31] However, Zimmerman coined the term "barrelene" after synthesizing the molecule in 1960 because its molecular orbitals resembled the shape of a wooden barrel.[32] The π-system features Möbius topology and was initially hypothesized to result in a new type of aromaticity.[33] However, transannular interactions lead to overlap of sets of p-orbitals with mismatched signs[33] and thus minimizes any stabilization

from such an arrangement.[33] Indeed, barrelene reacts in a manner typical of alkenes: it readily undergoes additions with bromine or hydrogen[33] and is prone to epoxidation.[34]

As summarized in Fig. 1a, barrelene (**1**) was synthesized according to modifications of literature reports.[35,36] Heating a mixture of benzene oxide (**2**)[36] and *cis*-1,2-bis(phenylsulfonyl) ethylene at 80 °C in toluene afforded the corresponding cyclo-adduct after 24 h. Subsequent reduction with WCl_6 and *n*-butyllithium (*n*-BuLi) in THF afforded **4**, which was desulfurized with sodium amalgam to afford **1**.[35] Spectroscopic data recorded for the product agreed with literature reports.[33,35] A representative ^{1}H NMR spectrum is shown in Fig. 1b.

Although barrelene has been known for decades, the structure of the compound has been determined using only spectroscopic techniques. It was reasoned that a solid-state structure may be obtained through the formation of a coordination complex. Analogous to methodology used to form $[Rh(norbornadiene)Cl]_2$,[37,38] mixing excess barrelene and di-μ-chlorotetraethylene dirhodium(ɪ) in CH_2Cl_2 afforded $[Rh(barrelene)Cl]_2$ (**5**) (Fig. 1c). Crystals were obtained by slowly evaporating a mixture of CH_2Cl_2 and hexane (1 : 1 v/v) that was saturated with **5**. As shown in Fig. 1d, X-ray diffraction analysis of the crystals revealed that each Rh(ɪ) atom was chelated by a molecule of barrelene and interconnected *via* chloride bridges. The average distance between the carbon atoms in the alkenes coordinated to the Rh atoms was measured to be 1.3965 ± 0.010 Å, consistent with the value reported for [Rh(norbornadiene)Cl]_2 (1.396 ± 0.003 Å).[38] The average bond lengths of the non-coordinated alkenes were measured to be relatively short (1.316 ± 0.001 Å) due to the lack of π-backbonding interactions. To the best of our knowledge, this is first example of an organometallic complex that contains barrelene and provides unambiguous solid-state structural elucidation of the compound.
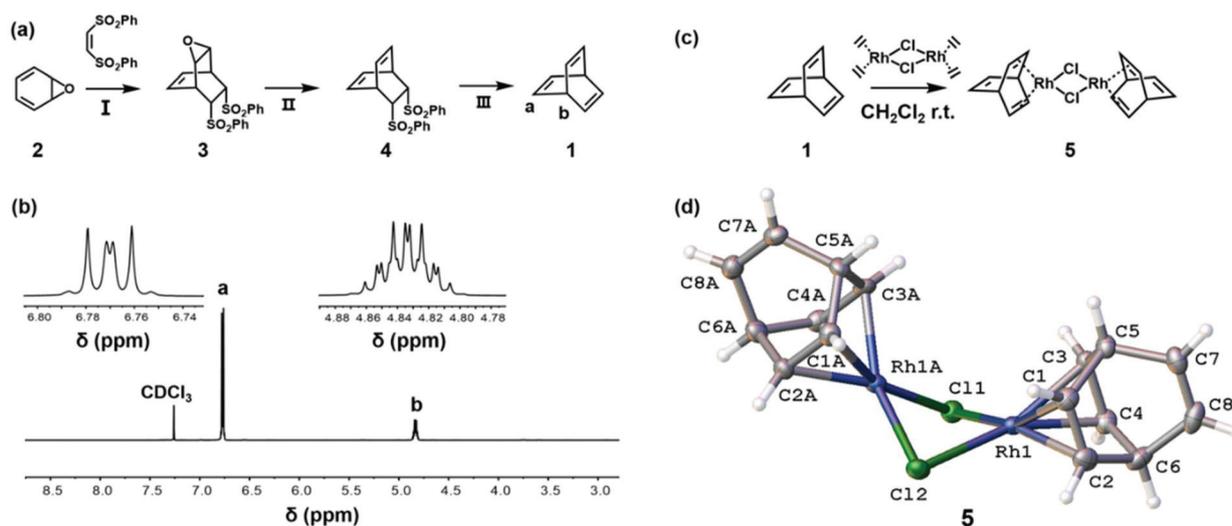

Fig. 1 (a) Synthesis of barrelene (**1**). I: toluene, 80 °C, 24 h. II: WCl_6/*n*-BuLi, r.t., 24 h. III: Na amalgam, KH_2PO_4, methanol, r.t., 24 h. (b) ^{1}H NMR spectrum recorded of barrelene in $CDCl_3$. (c) Synthesis of $[Rh(barrelene)Cl]_2$ (**5**). (d) Single crystal X-ray diffraction analysis of **5**. The thermal displacement ellipsoids shown were drawn at the 50% probability level. Selected distances (Å): C1–C2, 1.387(7); C3–C4, 1.385(6); C7–C8, 1.317(7); C1A–C2A, 1.409 (6); C3A–C4A, 1.405(6); C7A–C8A, 1.318(7). Selected angles (°): C1–C5–C7, 109.2(4); C3–C5–C7, 108.4(3); C1–C5–C3, 97.9(3).
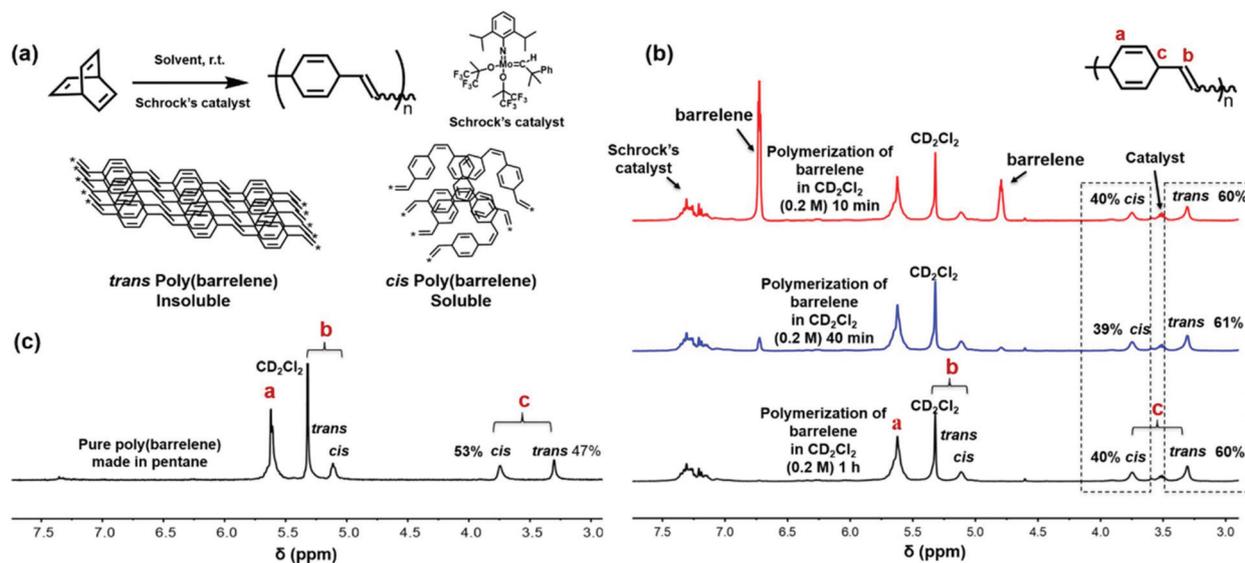
Fig. 2 (a) ROMP of barrelene. Polymerization in CH_2Cl_2 afforded polymers that were rich in *trans* exocyclic vinylenes whereas polymerization in pentane afforded polymers that were rich in *cis* exocyclic vinylenes. The different geometries may facilitate or impede chain stacking *vis-à-vis* solubility. (b) ^1H NMR spectra recorded for the ROMP of barrelene in CD_2Cl_2 over time (indicated). (c) ^1H NMR spectra recorded in CD_2Cl_2 for a poly(barrelene) that was synthesized in pentane.

As summarized in Fig. 2a, barrelene was polymerized using Schrock's catalyst, 2,6-diisopropylphenylimidoneophylidene molybdenum(VI) bis(hexafluoro-*t*-butoxide).[39] Treatment of a solution of **1** in CH_2Cl_2 ($[1]_0 = 1.0$ M) with the catalyst ($[1]_0/[cat.]_0 = 50$) at ambient temperature and under an atmosphere of nitrogen afforded an insoluble product after 5 min. Similar results were obtained when the initial monomer concentration was decreased (0.2 M) and when different solvents (*e.g.*, CH_2Cl_2, $CHCl_3$, or THF) were used. To gain additional insight, a polymerization reaction ($[1]_0/[cat.]_0 = 50$, $[1]_0 = 0.2$ M, CD_2Cl_2) was monitored using ^1H NMR spectroscopy. As shown in Fig. 2b, barrelene appeared to convert to a polymer consistent with the expected structure over time; however, the ratio of the signals assigned to the catalyst and the signals assigned to the soluble product remained constant after normalization (4.6 : 1.0), even as the reaction proceeded which indicated that the polymer began to precipitate once a certain molecular weight threshold was reached. Inspection of the NMR data also revealed that the exocyclic vinylene content in the polymer that formed was approximately 60% *trans*. Thus, it was reasoned that the insoluble products may due to the relatively high *trans* alkene content, which facilitates stacking of the polymer chains and reduces solubility.

Since greater than 50% of the exocyclic vinylenes in the polymer backbone were observed to be *trans*, it was surmised that the catalyst facilitates the conversion of the *cis* forms of the units to their thermodynamically more stable *trans* isomers. To potentially form a polymer with a relatively high *cis* alkene content, the polymerization reaction was conducted in pentane as it was envisioned that this would be a poor solvent for the polymer and thus would facilitate precipitation prior to isomerization. Performing the ROMP in pentane using

the aforementioned conditions ($[1]_0/[cat.]_0 = 50$, $[1]_0 = 0.2$ M) resulted in the rapid formation of a precipitate, which was subsequently collected in a 75% yield based on the structure of poly(**1**). The polymer was found to be soluble in organic solvents (*e.g.*, THF, CH_2Cl_2 and $CHCl_3$) and featured a relatively high exocyclic *cis* vinylene content (53%) as determined by ^1H NMR spectroscopy in CD_2Cl_2 (Fig. 2c). The number average molecular weight (M_n) and polydispersity index ($Đ$) of the polymer were measured to be 2400 Da and 2.0, respectively, by size exclusion chromatography (SEC) (Fig. S19†).

Exposure of poly(barrelene) to air had marked effects on its chemical and physical properties. For example, the solubility of the material appeared to gradually decrease upon exposure to air and was accompanied by color changes to yellow and then brown. In addition, while freshly prepared polymer was non-emissive, a green emission was observed when aerated CH_2Cl_2 solutions of the material were excited with UV light (λ_{ex} = 365 nm) over several days. The observations prompted us to hypothesize that poly(barrelene) was undergoing spontaneous oxidation to PPV. To test the hypothesis, UV-vis spectra were recorded for freshly prepared poly(barrelene) and after the material was exposed to aerated CH_2Cl_2 for 1 month. As shown in Fig. 3a, the UV/vis spectrum recorded for the latter exhibited an absorbance profile with a local maximum (λ_{max}) of 339 nm. The product was also found to fluoresce with a maximum at 463 nm (λ_{ex} = 365 nm) as determined by spectrofluorimetry. For comparison, PPVs have been reported to absorb and emit over the ranges of 400–442 nm and 489–588 nm, respectively, under similar conditions.[26] Other spectroscopic and crystallography data were also consistent with the formation of PPV. As shown in Fig. 3b, FT-IR analysis revealed that the oxidized product displayed signals at 1696 cm^{-1}, 1515 cm^{-1} and
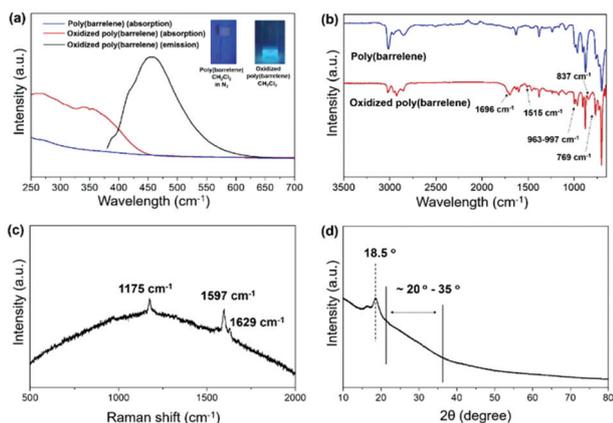
Fig. 3 (a) UV-vis and photoluminescence spectra recorded for freshly prepared poly(barrelene) and poly(barrelene) after being exposed to aerated CH_2Cl_2 for 1 month (oxidized poly(barrelene)). (b) IR spectrum of poly(barrelene) and oxidized poly(barrelene). (c) Raman and (d) powder XRD spectrum spectra recorded for oxidized poly(barrelene).

Fig. 4 (a) Copolymerization of 6 and 1 and subsequent oxidation. (b) ^{1}H NMR spectrum recorded for poly(6-co-1) (6 : 1 = 6.3) in CDCl$_3$. (c) Zoomed region of ^{1}H NMR spectra (CDCl$_3$) recorded for freshly prepared poly(6-co-1) (6 : 1 = 6.3) (top) and after exposure of the copolymer to aerated CH_2Cl_2 for three (3) weeks (bottom) (legend: f, cis vinylene; g, trans vinylene).

837 cm^{-1} which were diagnostic of aryl C=C, C–C, and C–H stretching modes.[40,41] Signals were also observed at 962–997 cm^{-1} and 769 cm^{-1}, and in accord with the *trans*- and *cis*-vinylene C–H out-of-plane bending modes, respectively, of PPV. Likewise, as shown in Fig. 3c, the salient Raman signals recorded at 1175 cm^{-1}, 1597 cm^{-1} and 1629 cm^{-1} matched literature reports for PPV.[30,42] A powder X-ray diffraction analysis revealed that the oxidized product was highly crystalline,[43] as indicated by the strong signal observed at 18.5°, and the broad signal recorded between 20° and 35° was agreement with literature data for PPV (Fig. 3d).[41]

To increase the stability of the barrelene-containing polymers and to facilitate the use of barrelene in optical applications (see below), a series of copolymers of 1 and a relatively inert monomer (norbornene) were synthesized. Solutions of norbornene (6) and 1 ([6]$_0$/[1]$_0$ = 6 or 15, [6 + 1]$_0$ = 0.4 M) in CH_2Cl_2 were independently treated with catalyst ([6 + 1]$_0$/[cat.]$_0$ = 300) for 2 h at ambient temperature under an atmosphere of N$_2$ gas. The polymerization reactions were subsequently quenched after 2 h with methanol, and then the resulting product mixtures were poured into cold methanol. The precipitated solids were collected, dissolved in CH_2Cl_2, and reprecipitated from pentane to obtain products that were isolated in high yield (89–91%) based on the structures of the corresponding copolymers (7) (Fig. 4a). Analysis of 7 by ^{1}H NMR spectroscopy revealed that the ratio of repeat units (6-to-1) ranged from 6.3 (Fig. 4b) to 15.7 (Fig. S16†) and depended on the monomer feed. The formation of a copolymer was further confirmed by SEC as monomodal distributions of chains were observed (Đ = 1.39–1.43; M_n = 48.1–46.4 kDa) (Table S1†). Although the copolymer containing a relatively high barrelene content (6 : 1 = 6.3) was found to be soluble in THF, CH_2Cl_2, and CHCl$_3$, the corresponding solutions slowly became gelatinous and ultimately insoluble when exposed to air.[44] For example, signals at 6.4 ppm, 7.1–7.2 ppm, and 7.2–7.4 ppm were identified in the ^{1}H NMR spectrum recorded for a copoly-
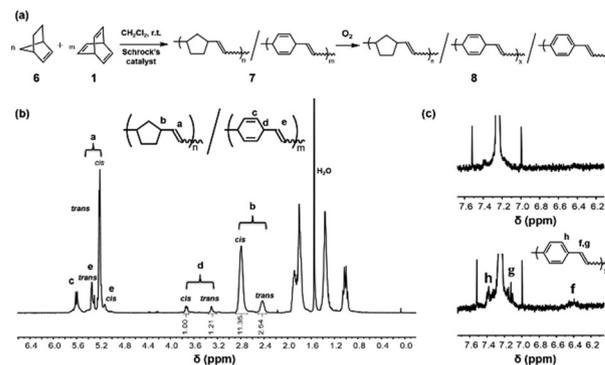
mer that was stored for three weeks in an aerated solution of CH_2Cl_2. The signals were diagnostic of the *cis* and *trans* vinylenes as well as the aryl groups in PPV,[45] respectively (Fig. 4c), and the molar ratio of 6 : 1 was found to increase (Fig. S14†). The reduced solubility was attributed to the generation of PPV followed by the physical cross-linking of the conjugated segments via π–π stacking interactions.

Compared to a freshly prepared copolymer of norbornene and barrelene, the UV/vis data recorded for the material after it was exposed to aerated CH_2Cl_2 for one month featured a bathochromic absorption at 365 nm (Fig. 5a and b). To drive the oxidation reaction, 7 was treated with DDQ (2.0 equiv. with respect to the barrelene repeat unit) in CH_2Cl_2 (8.0 mg of copolymer per mL of solvent) for 5 h at room temperature. The UV/vis spectrum recorded for the DDQ-treated copolymer exhibited a strong absorbance at 390 nm which agreed with spectroscopic data reported for PPV.[46] The oxidizing conditions also caused the copolymer to fluoresce. For comparison, the material obtained after exposing copolymer 7 to aerated CH_2Cl_2 for one month exhibited an emission maximum ($\lambda_{em, max}$) at 460 nm in CH_2Cl_2 (λ_{ex} = 365 nm) whereas the DDQ-treated material emitted at 473 nm. Collectively, these data indicated that the barrelene units in the copolymers converted to PPV upon exposure to oxidizing conditions and that stronger oxidants enhanced the conjugation length of the resultant PPV.[47]

Compared to poly(barrelene), the oxidation of poly(barrelene-co-norbornene) was found to be relatively slow in the solid-state at room temperature which may be due to the inert co-monomer (norbornene). No significant differences were observed in the ^{1}H NMR and Raman spectra recorded for the copolymer after it was stored in air for two months at room temperature (Fig. S15 and S20†). However, heating a film of the copolymer to 120 °C in the air for 10 min caused the material to change to yellow, and the resulting product appeared fluorescent (λ_{em} = 461 nm; λ_{ex} = 365 nm) in the solid-state (Fig. 5c). A series of thermal measurements indicated
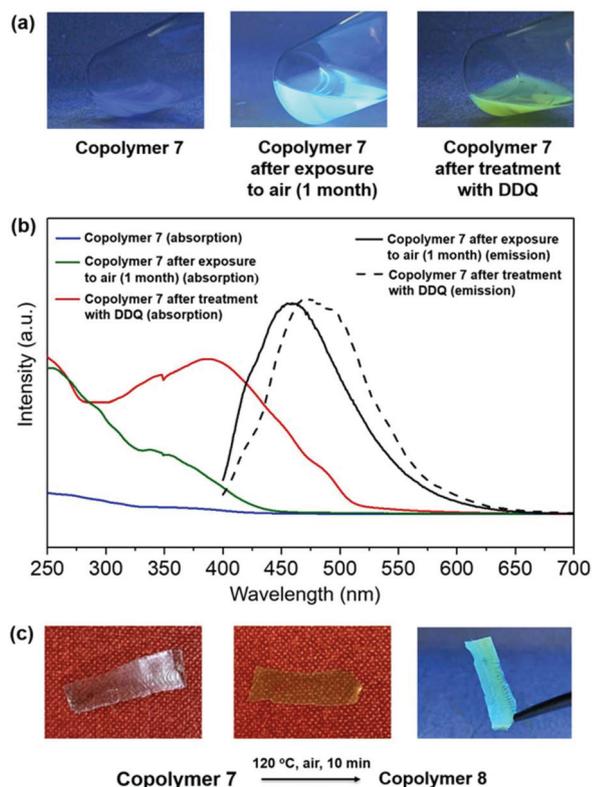
Fig. 5 (a) Photographs of CH_2Cl_2 solutions of copolymer **7** (**6**:**1** = 6.3) under different conditions (indicated). (b) UV-vis and photoluminescence spectra recorded for **7** under different conditions (indicated, λ_{ex} = 365 nm). (c) Heating a film of **7** in air at 120 °C resulted in a color change (from colorless to yellow) and the formation of a fluorescent material.

Fig. 6 (a) Schematic of DLW on a film of copolymer **7** (**6**:**1** = 15.7) (inset) Laser induced oxidation of poly(barrelene) to PPV. (b) Examples of patterns that were written. Photographs were taken under visible light (left) and UV-light (λ_{ex} = 488 nm; right). (c and d) Raman spectra recorded for the areas indicated in blue or red (see insets) of a film that was subjected to DLW. The films were prepared by drop-casting a solution of poly(barrelene-*co*-norbornene) (200 mg) in CH_2Cl_2 (4 mL) into a PTFE mold.

that the copolymer exhibited an exothermic reaction upon being heating to 100 °C, presumably due to oxidation (dehydrogenation), yet did not experience significant mass loss until approximately 400 °C (under N_2) (Fig. S17 and S18†).

Since exposure of the aforementioned copolymer to elevated temperatures resulted in an optical response, the potential of using the material in DLW applications was explored using a laser capture microdissection (LCM) system (Fig. 6a).[48] A 400 nm diameter laser beam at a wavelength of 355 nm was used to write on substrates that consisted of the copolymer at speeds of approximately 350 μm s^{-1}. As shown in Fig. 6b, irradiated areas were found to be fluorescent and the high precision of the laser enabled relatively complex patterns with micrometer-sized dimensions to be written within minutes (Videos S1 and S2†). To determine if the laser facilitated the oxidation of copolymer, the dark and fluorescent regions were investigated by Raman spectroscopy. As shown in Fig. 6c and d, the dark regions exhibited signals that were consistent with poly(barrelene-*co*-norbornene) whereas signals consistent with PPV and in accord with the data described above were observed in the fluorescent regions.

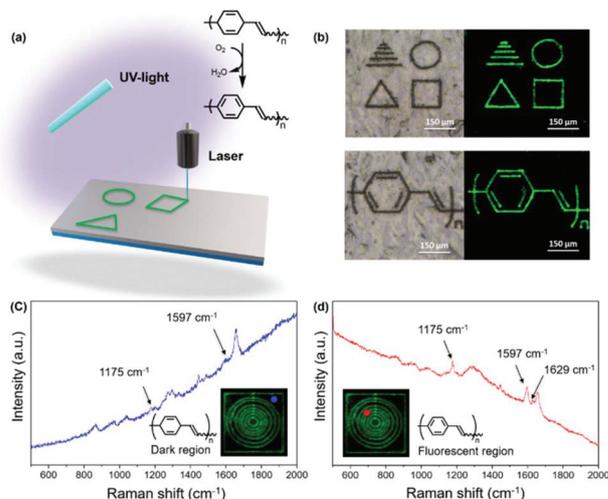In conclusion, barrelene (bicyclo[2.2.2]octa-2,5,7-triene) was synthesized using modifications of previously reported routes and characterized, for the first time, by X-ray diffraction analysis of a coordination complex. The homopolymerization of barrelene as well as the copolymerization of barrelene and norbornene using ROMP is also described. The solubility of the barrelene homopolymers was found to depend on the *cis* to *trans* ratio of alkenes in its backbone. The homo- and copolymers underwent spontaneous dehydrogenation under air to afford PPV, as determined using a range of spectroscopic techniques. Direct laser writing of the barrelene-containing copolymers was achieved and resulted in thermal aromatization within seconds. An intrinsic advantage of this polymer chemistry is that the monomer could be incorporated into other macromolecular scaffolds and at varying compositions, and thus render a broad range of materials suitable for use in laser machining and contemporary lithography applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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