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Triphenylene-Enchained Perfluorocyclobutyl Aryl Ether Polymers: A Modular Synthetic Route to Processable Thermoplastics Approaching Upper Limit T_g and Photostability

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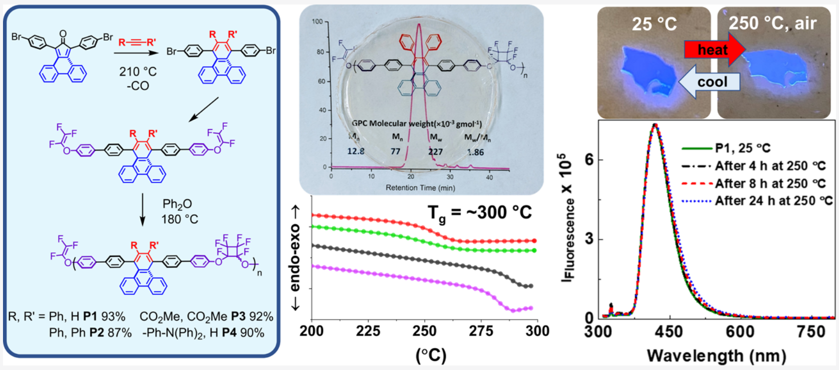

ABSTRACT: Triphenylene-containing trifluorovinyl ether monomers prepared from 2,3-disubstituted-*bis*-1,4-(*p*-bromophenyl)-triphenylene core building blocks undergo thermal step-growth polymerization (Ph_2O, 180 °C), affording perfluorocyclobutyl polymers with unprecedented glass-transition temperatures (up to 295 °C), excellent high thermal-oxidative stabilities, and solution processability. The modular synthetic route provides access to a series of triphenylene monomers from a common cyclopentadienone derivative and variably substituted alkynes, which polymerize thermally to solution-processable, tough, transparent films with bright blue solid-state photoluminescence (λ_{em} = ~400−470 nm). Conversion was monitored by ^{19}F NMR end-group analysis and gel permeation chromatography to reasonably high molecular weights (M_n = 45−93 kDa). Remarkably, photoemission persists at 250 °C in air for 24 h with negligible changes in absorbance and emission wavelengths after cooling to room temperature.

■ INTRODUCTION

Fluoropolymers are outstanding specialty materials due to their superb chemical inertness, thermal and oxidative stability, high gas permeability, and good dielectric properties.[1,2] In addition to traditional highly crystalline perfluorinated polymers, ongoing research in semi-fluorinated polymers has provided viable alternatives with improved processability, optical properties, and mechanical performance, further enabling emerging technologies such as separation membranes,[3] fuel cells,[4] and biomedical devices.[5] To expand material diversity, we have developed a platform of semi-fluorinated aryl ether polymers via step-growth polymerization of fluoroalkenes including perfluorocyclobutyl (PFCB),[6] fluorinated arylene vinylene ether (FAVE),[7] and perfluorocycloalkene (PFCA)[8] aromatic ether polymers.[9] Prepared by thermal cyclopolymerization of aromatic trifluorovinyl ether (TFVE) monomers, PFCB aryl ether-containing thermoplastic and thermosetting polymers, originally developed by The Dow Chemical Company,[10,11] represent the most successful family in this class due to their ease of synthesis and wide ranging structural variety.[12] Thermal [2 + 2] cycloaddition polymerization of aromatic TFVE groups does not require catalysts or initiators and proceeds free from mobile impurities, condensates, or other byproducts.[10,13] In addition, the TFVE group is highly tolerant to a wide variety of functional group transformations[14] including Grignard,[15] Suzuki,[16] and Sonogashira coupling[14] and Huisgen's 1,3-dipolar cycloadditions.[17,18]

Here, we report the first synthesis and polymerization of TFVE monomers (**M1−M4**) containing triphenylene cores (Figure 1), affording amorphous semi-fluorinated thermo-

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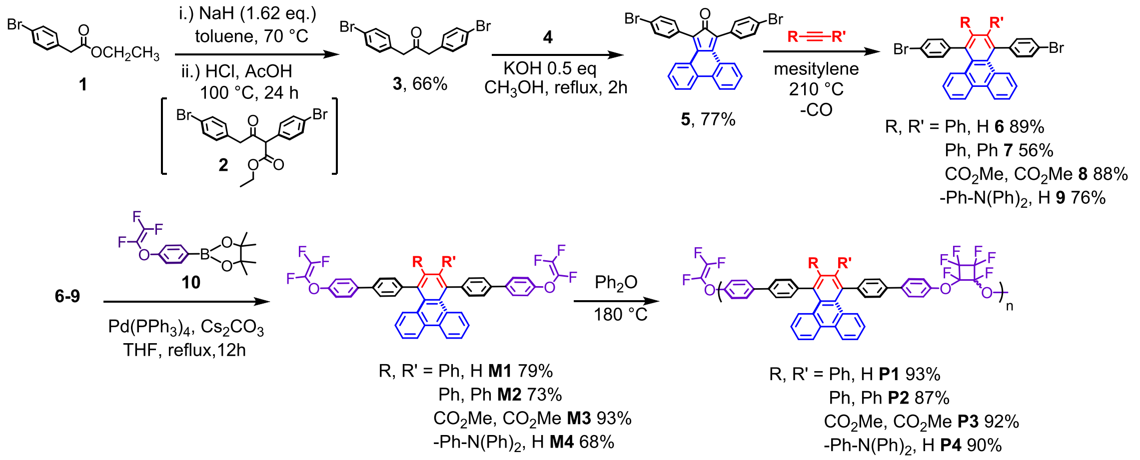

Figure 1. Modular synthesis of monomers **M1−M4** and polymers **P1−P4**.

plastics with unprecedented thermal performance ($T_g \sim 300$ °C) and solid-state emission after prolonged heating at 250 °C in air. Triphenylene is a well-studied blue light-emitting chromophore[19−23] and mesogen, which forms discotic liquid crystalline (LC) phases that act as one-dimensional charge carriers.[24] The triphenylene unit has been incorporated into star polymers to serve as a discotic core,[25] linear conjugated polymers by Suzuki cross-coupling,[22] and conjugated dendrimers by Diels−Alder reaction.[23] Triphenylene moieties have also been photocured by incorporating methacrylates[26] and copolymerized by the Sonogashira reaction.[27] Unfortunately, triphenylene derivatives typically lack solubility in common organic solvents, requiring the incorporation of alkyl or alkoxy groups. Moreover, solution polymerizations carried out by metal-catalyzed coupling strategies produced low monomer conversion and limited molecular weight, primarily due to solubility limits.[22]

Cyclopolymerization of TFVE monomers to stereo-random 1,2-disubstituted PFCB repeat units is famous for solubilizing extended aromatic cores such as triphenylene for both monomer and growing polymer. Previously reported accounts of PFCB polymers enchained with polycyclic aromatic hydrocarbons (PAHs) include hexabenzocoronene,[28] naphthalene,[29,30] and most recently, acenaphthoquinone[6] homo- and co-polymers. In addition, high aspect ratio penta-*p*-phenylene PFCB polymers have provided unique semi-fluorinated LC materials.[31] The broad synthetic versatility developed over many years has provided direction to prepare extreme PAH targets with controlled photonic properties and phase behavior. In addition to the largest PAH enchained in a PFCB thermoplastic, we present a straightforward modular synthesis to TFVE functional triphenylene monomers in a few steps from readily available starting materials.

■ RESULTS AND DISCUSSION

Monomer synthesis included preparation of the intermediate, 1,3-*bis*(4-bromophenyl)-2-propanone (**3**), via a modified literature procedure,[32] where Claisen self-condensation of ester **1** in the presence of NaH in anhydrous toluene at 70 °C produced the corresponding beta-keto ester (**2**). Non-isolated intermediate **2** was then hydrolyzed and decarboxylated under acidic conditions to obtain ketone **3** in 66% overall conversion from **1** to **3** (Figure 1). Knoevenagel condensation of **3** with 1,9-phenanthraquinone (**4**) gave key dibromo cyclopentadienone intermediate **5** in 77% yield. Triphenylene core formation was completed via a Diels−Alder/decarbonylation reaction of **5** with a variety of monosubstituted and disubstituted alkynes, providing a modular route to 2,3-disubstituted-*bis*-1,4-(*p*-bromophenyl)triphenylene building blocks. Thus, reacting **5** with phenylacetylene, diphenylacetylene, dimethyl acetylenedicarboxylate, and 4-ethynyl-*N*,*N*-diphenylaniline in mesitylene at 210 °C gave dibromo compounds (**6**−**9**) in 89, 56, 88, and 76% yields, respectively (Figure 1).

A commercial intermediate, *p*-bromo(trifluorovinyloxy)-benzene, was converted to the corresponding boronic ester (**10**) via a Suzuki−Miyaura cross-coupling reaction in 68% yield. It should be noted that several failed attempts were made to cross-couple **5** and boronic ester **10**, utilizing different conditions. Subsequent Suzuki−Miyaura cross-coupling of substituted dibromotriphenylenes **6**−**9** with **10** (Figure 1) successfully extended the π-system to give monomers **M1**−**M4** in moderate to good yields (68−93%). Interestingly, **M2** is a candidate for oxidative aromatization (Scholl reaction) to produce a TFVE containing coronene moiety as a future target.[28]

The structures of monomers **M1**−**M4** were determined by ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR, FTIR, and HR-MS, for which detailed data can be found in the SI. Single crystals of **M3** and **M4** suitable for X-ray structure analysis (Figure 2) were obtained by the ultra-slow evaporation of a 1:2 ratio of dichloromethane:hexane solution. The triphenylene cores are not planar but twisted, with torsional angles of 30° (**M3**) and 38° (**M4**). The bent phenanthrene moiety of the triphenylene core decreases the intermolecular $\pi-\pi$ stacking and enhances the solubility. The biphenyl moieties containing the TFVE groups exhibit a dihedral angle between the phenyl rings of 34−37°, typical of biphenyl groups. The distance between the

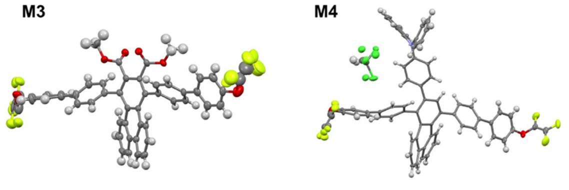

Figure 2. X-ray crystal structures of **M3** and **M4** illustrating twisted triphenylene cores.

TFVE end-groups is ~24.7 Å. Despite the strain in the triphenyl amine substituent of **M4**, the nitrogen's geometry is found to be nearly planar and compares well with the crystal structure of triphenylamine.[33]

The thermal [2 + 2] cyclopolymerizations of TFVE monomers **M1**−**M4** were observed by DSC (10 °C/min), whereby **M1** and **M4** gave sharp melting points (191 and 246 °C, respectively) beyond the known onset of exothermic TFVE polymerization (~150 °C) under these conditions (Figure 3 and see Figure S16 in the SI for more details).[13]

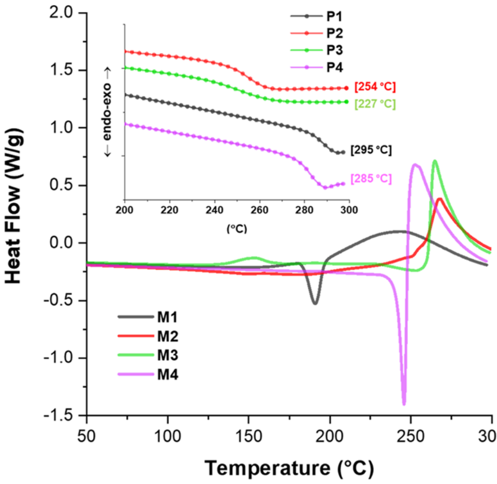

Figure 3. Monomers **M1**−**M4** melting and polymerization by DSC (10 °C/min in N_2) and reproducible glass transitions (T_g) from the fourth heating cycle for PFCB polymers **P1**−**P4** (inset).

Monomer **M3** does not exhibit a melting transition yet a clear exothermic event around 150 °C is evident, presumably due to a disorder−order transition and not an ester related reaction as the ester signals are intact in the IR spectrum of **P3** after polymerization at 180 °C (Figure S19). Due in part to these extraordinarily high melting monomers, exothermic polymerization events were not easily detected and did not follow the broad DSC profile observed for typical TFVE polymerization. Instead, a dramatic exotherm is detected immediately upon melting for **M3** and **M4**, resulting in a broad exothermic peak range (e.g., T_{exo} max = 242−268 °C, Table 1).

Larger-scale polymerization of monomers **M1**−**M4** was performed in diphenyl ether solutions at 180 °C for 24−48 h (Figure 1). Polymers **P1**−**P4** produced from neat monomers by DSC and from solution both gave the same T_g values of 295, 254, 227, and 285 °C, respectively, after the fourth heating cycle. These T_g values are the highest reported for any PFCB or triphenylene-based polymer.[24] They are among the highest reproducible glass-transition temperatures ever measured for any organic thermoplastic without degradation. With rare exception, organic thermoplastics undergo degradation and/or other reactions affecting properties like T_g when cycling to 300 °C. The T_g value for each was reproducible over subsequent heating cycles, and no further calorimetric events were detected. Molecular weight by gel permeation chromatography (GPC) and other spectroscopic data further confirms no significant changes in the polymer structure after heating.

Solution polymerizations were monitored by FTIR and ^{19}F NMR spectroscopy. A small but distinctive FTIR signal at 1832 cm^{-1} for **M1**−**M4** corresponds to the $—FC{=}CF_2$ stretching (Figure S19). After cyclopolymerization, this TFVE peak is diminished and a new characteristic band emerges at 960 cm^{-1}, attributed to the PFCB ring breathing mode.[13,15,34] Complete monomer and polymer ^1H NMR, ^{13}C NMR, and ^{19}F NMR characterizations are reported in the SI. The representative monomer, **M2**, and polymer, **P2**, ^{19}F NMR spectra are shown in Figure 4. Each fluorine on the TFVE group exhibits a dd at −119.6 (F_A, *trans* to O), −126.6 (F_M, *cis* to O), and −133.8 (F_X, *gem* to O) ppm, represented by an AMX pattern. Upon thermal polymerization, the well-resolved end-group signals diminish, while the cyclobutyl fluorine signals emerge as multiplets between −127 and −132 ppm for the stereo-random 1,2-disubstituted ring. Number-averaged molecular weight (M_n) data for **P1**−**P4** were calculated by quantitative integration of F_A vs cyclobutyl fluorine signals (Table 1) and gave M_n values ranging from 25 to 31 kDa. Conversion by ^{19}F NMR was also consistent with ^{13}C NMR data, where, for example, the vinyl carbons of **M2** exhibit a ddd pattern at 133.0 and 146.6 ppm. These patterns vanish upon their thermal polymerization to appear as sp^3 cyclobutyl carbons displaying a complex multiplet pattern from 105 to 116 ppm due to $^{13}C/^{19}F$ couplings (Figures S12 and S15). Moreover, the diastereomer ratio, expressed as *cis*/*trans* isomers, for the PFCB rings of **P1**−**P4** was estimated by integrating the corresponding *ipso* and *ortho* carbon signals under quantitative ^{13}C NMR conditions. As expected, the results were in agreement with previous measurements and with *ab initio* studies that predicted a near equal *cis*/*trans* isomer distribution.[35] GPC analysis of solution polymerized (Ph_2O, 180 °C) **P1**−**P4** in THF (relative to polystyrene) exhibited polydispersity indices that were characteristic of step-growth polymerization (Table 1).

Like other PFCB polymers, **P1**−**P3** are soluble in common organic solvents at room temperature, especially in aromatic,

Table 1. Selected Properties of Triphenylene PFCB Homopolymers P1−P4

					temp at 5% wt loss (°C)[b]		char yield 800 °C (%)[b]	molecular weight (kDa)			
								NMR[c]	GPC[d]		
entry	monomer T_m (°C)[a]	onset T_{exo} (°C)[a]	max T_{exo} (°C)[a]	T_g (°C)[a]	air	N_2	N_2	M_n	M_n	M_w	M_w/M_n
P1	191	166	244	295	459	508	73	29	45	191	1.6
P2	none	188	268	254	428	505	68	26	77	227	1.9
P3	252	250	265	227	513	523	62	27	93	428	1.9
P4	246	247	253	285	349	528	76	31	90	214	2.4

[a] DSC (10 °C/min) in nitrogen, onset upon melting, and T_g after the fourth heating cycle. [b] TGA at 10 °C/min in nitrogen and air from 0 to 800 °C. [c] Number average molecular weight of solution-polymerized (180 °C, Ph_2O) **P1**−**P4** determined by ^{19}F NMR end-group analysis. [d] Solution polymerized **P1**−**P4** vs polystyrene standards in THF.

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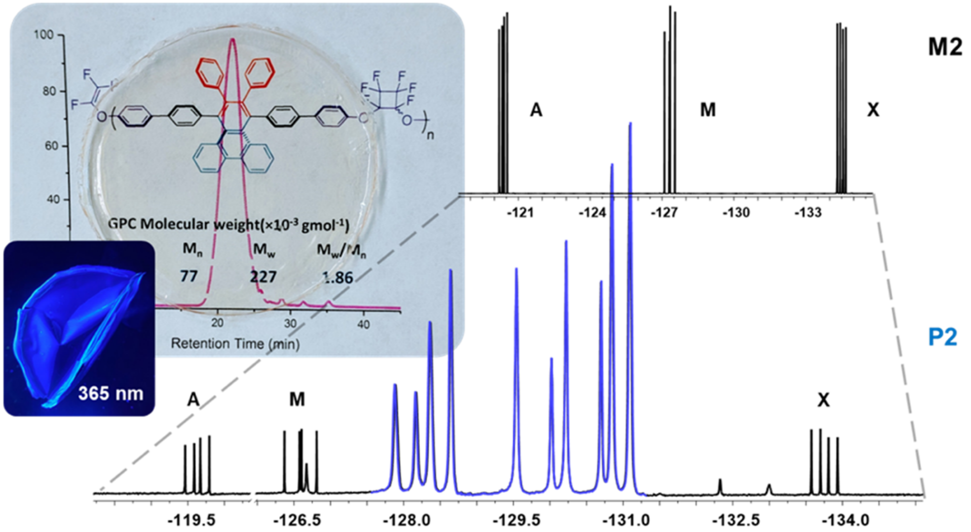

Figure 4. ^{19}F NMR ($CDCl_3$) spectra for **M2** and **P2** after 180 °C polymerization in Ph_2O and transparent **P2** film (left) with creased **P2** under UV radiation at 365 nm (inset).

chlorinated, ether, and formamide solvents. **P4**, however, is slightly less soluble and requires heating above room temperature to dissolve yet remains in solution after cooling. Tough, free-standing films that are creasable without tearing and optically transparent were obtained for **P1**−**P3** by solution casting from THF (see the inset in Figure 4 and Figure S17), while **P4** gave a slightly brittle film. Noteworthy is the remarkable toughness of these high T_g thermoplastics with large relatively inflexible aromatic cores. Surface hydrophobicities were probed by measuring **P1**−**P4** water contact angles using the sessile drop method and averaging (Figure 4 and Figure S23). Without spin-coating or surface modification, the free-standing films had hydrophobic surfaces with a highest contact angle of 92° (**P3**) and the lowest at 84° (**P1**). Surface morphologies of the solvent-cast films were investigated by atomic force microscopy (AFM). The films displayed a very low surface roughness over a 5 μm^2 area (Figure S24) as is consistent with the previous PFCB literature.[16,36] Thermal stabilities of **P1**−**P4** were evaluated in nitrogen and air by TGA (shown in Table 1and Figure S18). PFCB polymers **P1**−**P4** are exceptionally robust with TGA 5 wt % loss temperatures ranging from 349 to 523 °C in air and 508 to 528 °C in N_2. Upon heating to 800 °C in N_2, the polymers produce glassy carbon in relatively high yields ranging from 62 to 76% (Table 1 and Figure S18), as somewhat expected considering that triphenylene is a major component of a mesophase pitch, a known high carbon yielding material.[37]

The UV−vis absorption and fluorescence spectra for **M1**−**M4** were obtained in DCM (Figure S21), and all monomers exhibit absorption peaks at ∼230, ∼ 260, and ∼298 nm. Although the maximum absorption values (λ_{max}) of **M1**−**M4** were similar, the emission maxima (λ_{em}) for each monomer varied (λ_{em} = 414, 403, 417, and 473 nm). The UV−vis spectra of **P1**−**P4** were also obtained in THF (Figure 5) as well as in DCM (Table 2, except for insoluble **P4**). The initial photophysical properties reported here compare well with those obtained from previous studies on triphenylene-based molecules and polymers.[19,22] Similarly, a variety of chromophores have been functionalized with the TFVE moiety and copolymerized to PFCB polymers with predicted optical performance based on a combination of bare chromophore properties.[29,38,39]

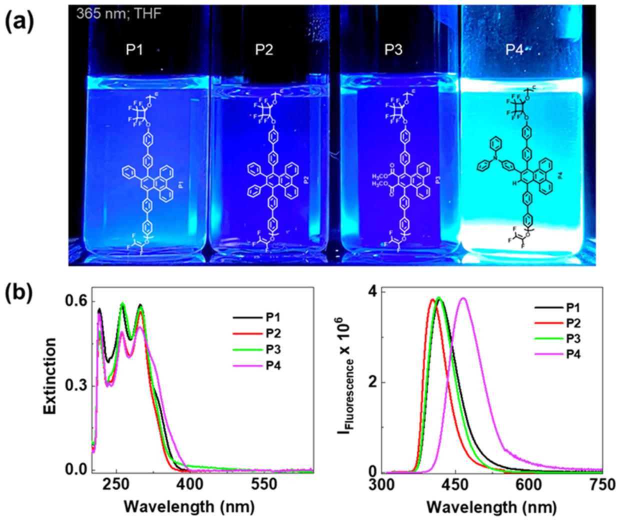

Figure 5. (a) **P1**−**P4** solutions irradiated at 365 nm and (b) overlay of the UV−vis extinction (left) and emission (right; normalized) spectra of **P1**−**P4** at equal concentrations in THF.

Table 2. UV−Vis Absorption and Fluorescence Emission of Polymers P1−P4 in THF and DCM

	THF[a]			DCM[b]	
polymer	λ_{abs} (nm)	λ_{em} (nm)[c]	$\varphi_{solution}$	λ_{abs} (nm)[b]	λ_{em} (nm)[c]
P1ssss	261, 298	417	0.19 ± 0.07	260, 290	395
P2	260, 298	399	0.26 ± 0.05	260, 290	418
P3	262, 298	413	0.19 ± 0.02	260, 290	399
P4	261, 298	467	0.47 ± 0.02	N/A[d]	N/A[d]

[a] Concentration = ∼7 × 10 $^{-6}$ M and temperature = 25 °C. [b] Concentration = ∼6.6 × 10^{-6} M and temperature = 25 °C. [c] Emission was obtained using the higher λ_{max} (e.g., ∼290 nm). [d] **P4** is not soluble in DCM. N/A = not applicable. Quantum yields were determined in THF (λ_{max} = 298 nm) relative to quinine sulfate in 0.1% H_2SO_4.

Fluorescence quantum yields, obtained in THF upon excitation at 298 nm and using quinine sulfate as a reference,[40] were 0.19, 0.26, 0.19, and 0.47 for **P1−P4**, respectively. As expected, these values are lower relative to triphenylene-based polymers with repeating units, ideally represented by complete conjugation[22] but are still much higher than those reported for lone triphenylene (~0.04−0.06).[19,41] Other unknown factors, such as the rigidity and planarity of the triphenylene core, or other cooperative effects induced by the electron withdrawing fluorocarbon PFCB ring, may play a role in determining the competitive rates between radiative and non-radiative decay. Although the absorption spectra for the monomers and polymers are similar, **P4** exhibits the largest Stokes shift and the highest quantum yield. These differences may be due to aggregation-induced emission since **P4** is the least soluble of the polymer series.

Upon further study, polymer films continued to emit blue light after heating to temperatures up to 250 °C in air for 4, 8, and 24 h (Figure 6a). As the films are heated in air, blue emission is maintained with slight specular attenuation throughout the heating cycle (Figure 6c). However, upon cooling and irradiating at 365 nm, the solid-state emission intensity appears to recover (Figure 6d). More importantly, the solution-based absorptions and emissions of the films showed negligible changes after heating in air at 250 °C for 24 h (Figure 6a). Therefore, thermal oxidative degradation that can dramatically alter the optical properties and commonly plagues π-conjugated systems is not observed here. Few organic polymers exhibit such persistent photostability above 200 °C for extended periods of time (e.g., 24 h) in air.[42]

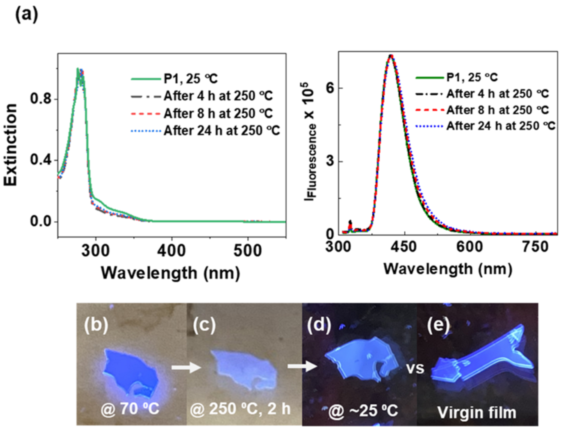

Figure 6. (a) Normalized UV−vis extinction (left) and emission (right; λ_{ex} = 298 nm) of **P1** in THF and **P1** in THF after heating at 250 °C for 4−24 h in air and then cooled to rt. Photographs of thumbnail size films of **P3** irradiated (λ_{ex} = 365 nm) and heated to (b) 70 °C in air, (c) 250 °C in air for 2 h, and then (d) cooled to ~25 °C in air compared to (e) a virgin **P3** film.

CONCLUSIONS

A modular synthetic preparation of triphenylene-containing TFVE monomers from simple building blocks and their thermal step-growth cyclopolymerization to PFCB-linked polymers were described. Knoevenagel condensation afforded a key dibromoaryl-cyclopentadienone intermediate for Diels−Alder decarbonylation with monosubstituted or disubstituted acetylenes. Catalyst-free and initiator-free thermal polymerization yielded four triphenylene-enchained PFCB aryl ether thermoplastics, exhibiting extremely high and reproducible glass-transition temperatures (T_g = 295 °C for **P1**) and thermal and oxidative stabilities. The polymers also demonstrated excellent solubility in common organic solvents, from which tough, creasable, transparent films were obtained. The new PFCB polymers are bright blue emitters with high-temperature photo-survivability in air at 250 °C for 24 h.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.1c01043.

Complete experimental methods, characterization of monomers and polymers (PDF)

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Notes

The authors declare no competing financial interest.
X-ray diffraction data can be found at https://www.ccdc.cam.ac.uk for **M3** (CCDC 2089914) and **M4** (CCDC 2089915).

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