Alkyl length dependent mechanofluorochromism of AIE-based phenothiazinyl
fluorophenyl acrylonitrile derivatives

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Abstract

Four alkyl phenothiazinyl fluorophenyl acrylonitrile derivatives (**PhC3F**, **PhC6F**, **PhC10F**, and **PhC12F**) with different length of alkyl chains were synthesized in high yield. The compounds showed obvious aggregation-induced emission (AIE) and alkyl length dependent mechanofluorochromic (MFC) properties. **PhC3F** with propyl chain and **PhC12F** with dodecyl chain showed obvious and reversible MFC behaviours, while **PhC6F** with hexyl chain and **PhC10F** with decyl chain exhibited little MFC property. Small and wide-angle X-ray scattering indicated the MFC behaviour of **PhC3F** and **PhC12F** were attributed to the phase transformation from crystalline to amorphous state, while **PhC6F** maintained excellent crystalline performance before and after grinding, which was also evidenced by differential scanning calorimetry result. Quantum mechanical computations further revealed **PhC6F** had high molecular polarity, which greatly improved its crystalline performance, and made its original aggregated morphology hard to damage, then brought about little MFC diversification. **PhC10F** showed the highest molecular polarity and least MFC behaviour. We concluded that obvious MFC feature derived from appropriate crystalline performance, favourable molecular polarity and energy gap.

Keywords: Alkyl length dependent; Mechanofluorochromism; Aggregation-induced emission; Acrylonitrile derivatives; Molecular polarity; Phase transformation

1. Introduction

Mechanofluorochromic (MFC) materials have attracted great interest owing to their promising application in mechano-sensors, memory chips, and security inks [1-3]. MFC materials can alter their luminescent properties in response to external force stimuli by

changing molecular assembly structure at solid state [4-6]. The alkyl length can influence molecular conformations, and change intermolecular interactions and packing mode, thus bring about different MFC properties [7]. The first example about alkyl length effect on MFC behaviour is cyano-substituted oligo(phenylene vinylene) derivatives reported by Weder *et al.* in 2008 [8]. Another two reported example about alkyl length effect on MFC behaviour are difluoroboron β -diketonate derivatives by Fraser *et al.* and alkyl-containing pyrene-amides derivatives by Araki *et al.* in 2011 [9, 10]. However, the studies on the effects of alkyl length on MFC materials are rare owing to the scarcity of MFC materials [1].

After introduction of aggregation-induced emission (AIE) fluorophores into MFC materials, the amount of MFC materials and the research about alkyl length effect of MFC materials increased rapidly [7, 11-13]. In 2012, Chi and Xu *et al.* first studied the alkyl length effect on AIE based MFC materials, phenoxy-substituted divinylanthracene derivatives, demonstrating more significant MFC behaviour generated with increased alkyl length [14]. Soon after, several similar AIE based MFC divinylanthracene derivatives have also been synthesized and investigated, including 9,9-dialkylfluorene-2-yl-substituted [15], phenoxy-substituted [16], and *N*-alkylphenothiazin-3-yl-substituted compounds [17], all indicating proportional alkyl length dependent MFC properties. However, some analogous AIE based MFC divinylanthracene derivatives showed inverse alkyl-length dependent MFC behaviours, such as *N*-alkylcarbazol-3-yl and *N*-alkylindole-3-yl-substituted derivatives [18, 19]. In addition, other AIE based MFC derivatives with various molecular structures like 9,10-distyryl-2,6-bis(p-dialkylaminostyryl)-anthracene homologues and indene-1,3-dione-methylene-4H-pyran derivatives were also reported, showing proportional

alkyl length dependent MFC behaviours [20, 21].

Recently, we have reported three novel AIE-based phenothiazinyl tetraphenylethenyl acrylonitrile derivatives with donor-acceptor (D-A) conjugated structure [22]. These compounds with tetraphenylethene group showed obvious AIE and alkyl length dependent MFC nature. As the alkyl length increased, the MFC feature gradually disappeared. The change of MFC mechanism was attributed to the steric effect of tetraphenylethene and long alkyl group, which led to amorphous morphology in the original sample. However, systematic investigation on alkyl length-dependent MFC properties is still a challenging issue due to the following reasons: first, introduction of longer alkyl chains usually increases the steric effect and limits understanding the MFC mechanism through growth of single crystal [7]; second, the previous reported literatures about structural factors like D-A effect and steric effect to regulate the MFC properties are still rare and the mechanism is still unclear [23-25]. Therefore, development of novel MFC materials by fine-tuning appropriate D-A effect and steric effect, and to further understand the alkyl length-dependent MFC mechanism is very attractive and highly demanded [26, 27].

In this work, we designed and synthesized four phenothiazinyl fluorophenyl acrylonitrile derivatives with different alkyl length (**PhC3F**, **PhC6F**, **PhC10F**, and **PhC12F**, see Scheme 1). In comparison to the previous phenothiazinyl tetraphenylethenyl acrylonitrile derivatives [22], the introduction of fluorophenyl group instead of tetraphenylethenyl group provided more D-A effect and less steric effect, which gave rise to weakened AIE nature but more significant MFC property. The alkyl length dependent MFC mechanism were investigated by small and wide-angle X-ray scattering (SWAXS), differential scanning calorimetry (DSC),

and quantum mechanical computation. We speculated that obvious MFC feature was attributed to appropriate crystalline performance, favourable molecular polarity and energy gap of the as-prepared compounds.

<Scheme 1>

2. Experimental procedure

2.1 Materials and characterization

Phenothiazine, 1-bromopropane, 1-bromohexane, 1-bromodecane, 1-bromododecane, 4-fluorophenyl acetonitrile, potassium tert-butoxide, tetrabutylammonium hydroxide (0.8 M in methanol) were obtained from Alfa Aesar. All other agents and solvents were purchased from commercial sources and used directly without further purification. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. Ultra-pure water was used in the experiments. The THF/water mixed solvents with different water fractions were prepared by slowly adding distilled water into the THF solution of samples under ultrasound at room temperature. The ground samples were obtained by grinding the original samples using a mortar and pestle. The experiment of solvent vapours fuming treatment is carried out in a large beaker saturated with dichloromethane vapours for 5 min at room temperature.

^1H and ^{13}C NMR spectra were recorded on a JEOL 400 MHz spectrometer [CDCl_3 as solvent and tetramethylsilane (TMS) as the internal standard]. Standard FAB-MS was determined on ZAB-HS mass spectrometry. Fluorescence spectra were measured on FLS 920 lifetime and steady state spectrometer. UV-vis absorption spectra were recorded on a UV/Vis/NIR Perkin-Elmer lambda750 spectrometer (Waltham, MA, USA). 1D small and wide angle X-ray scattering (SWAXS) experiments were conducted with a SAXS instrument

(SAXSess, Anton Paar) containing Kratky block-collimation system. An image plate was used to record the scattering patterns from 5 to 35 nm⁻¹. Differential scanning calorimetry (DSC) curves were recorded on TA Instruments DSC Q2000 at a heating rate of 10 °C min⁻¹ under a N₂ atmosphere. X-ray crystallographic intensity data were collected at 110 K using a Bruker Smart 1000 CCD diffractometer equipped with a graphite-monochromated Enhance (Mo) X-ray source ($\lambda = 0.71073$ Å). The structures were solved by direct methods following difference Fourier syntheses and refined by the full-matrix leastsquares method against F_0^2 using the SHELXTL software. Cyclic voltammetry (CV) measurement was carried out on a Shanghai Chenhua electrochemical workstation CHI660C. All CV measurements were performed under an inert argon atmosphere with supporting electrolyte of 0.1 M tetrabutylammonium perchlorate in dichloromethane at a scan rate of 100 mV/s using ferrocene (Fc) as standard.

2.2 General procedure for PhCnF derivatives

A solution of **PhCnA** (1.00 mmol) and 4-fluorophenyl acetonitrile (3.00 mmol) in ethanol (20.0 mL) was stirred at room temperature. After adding tetrabutylammonium hydroxide solution (0.8 M, 5 drops), the mixture was refluxed for 2 h. The reaction mixture was cooled to room temperature and filtered, washed with ethanol for three times to afford the **PhCnF** derivatives. The intermediates of **PhC3A**, **PhC6A**, and **PhC12A** were synthesized according to the previous literature [12, 28, 29]. **PhC12F** was synthesized according to our recently reported literature [30]. ¹H NMR, ¹³C NMR spectra and mass spectra of **PhC3F**, **PhC6F**, and **PhC10F** were shown in Figs. S1-S9.

PhC3F (yield 92.1%). ¹H NMR (400 MHz, CDCl₃) δ : 1.02 (t, 3 H, J = 7.2 Hz), 1.75–1.93

(m, 2 H), 3.83 (t, 2 H, $J = 7.2$ Hz), 6.80–6.90 (m, 2 H), 6.93 (t, 1 H, $J = 7.2$ Hz), 7.04–7.21 (m, 4 H), 7.27 (s, 1 H), 7.53 (s, 1 H), 7.56–7.63 (m, 2 H), 7.78 (d, 1 H, $J = 8.4$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 161.78, 147.30, 143.87, 140.84, 130.97, 128.60, 128.48, 127.84, 127.71, 127.63, 127.61, 127.56, 124.93, 123.74, 118.44, 116.26, 116.04, 115.71, 115.23, 107.39, 49.52, 20.13, 11.36. MS (FAB) calcd. for $\text{C}_{24}\text{H}_{19}\text{FN}_2\text{S}$, 386, found 386.

PhC6F (95.0% yield). ^1H NMR (400 MHz, CDCl_3) δ : 0.87 (t, 3 H, $J = 6.8$ Hz), 1.22–1.37 (m, 4 H), 1.37–1.49 (m, 2 H), 1.73–1.87 (m, 2 H), 3.85 (t, 2 H, $J = 6.4$ Hz), 6.81–6.89 (m, 2 H), 6.93 (t, 1 H, $J = 7.2$ Hz), 7.03–7.18 (m, 4 H), 7.26 (s, 1 H), 7.53 (s, 1 H), 7.55–7.63 (m, 2 H), 7.79 (d, 1 H, $J = 8.4$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 161.83, 147.32, 143.88, 140.55, 131.08, 128.57, 128.52, 127.82, 127.71, 127.63, 127.60, 127.55, 124.89, 123.77, 123.18, 118.44, 116.26, 116.04, 115.56, 115.19, 107.53, 47.79, 31.52, 26.83, 26.68, 22.70, 13.96. MS (FAB) calcd. for $\text{C}_{27}\text{H}_{25}\text{FN}_2\text{S}$, 428, found 428.

PhC10F (90.2% yield). ^1H NMR (400 MHz, CDCl_3) δ : 0.88 (t, 3 H, $J = 5.6$ Hz), 1.20–1.38 (m, 12 H), 1.40–1.48 (m, 2 H), 1.76–1.86 (m, 2 H), 3.90 (s, 2 H), 6.80–7.00 (m, 3 H), 7.04–7.22 (m, 4 H), 7.26 (s, 1 H), 7.32–7.46 (m, 1 H), 7.51–7.67 (m, 2 H), 7.77–7.89 (m, 1 H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 163.96, 161.97, 147.25, 143.93, 140.76, 138.55, 131.22, 131.15, 131.02, 128.49, 127.77, 127.63, 127.57, 127.46, 125.31, 124.88, 124.14, 123.75, 123.10, 122.90, 118.33, 116.21, 116.16, 115.98, 115.60, 115.32, 115.13, 107.49, 47.76, 31.89, 29.54, 29.48, 29.28, 29.22, 26.88, 26.79, 22.68, 14.12. MS (FAB) calcd. for $\text{C}_{31}\text{H}_{33}\text{FN}_2\text{S}$, 484, found 484.

3. Results and discussion

Scheme 1 illustrates the synthetic routes of alkyl phenothiazinyl fluorophenyl acrylonitrile

via the Knoevenagel condensation reaction of alkyl phenothiazinyl aldehyde with 4-fluorophenyl acetonitrile. The reaction yield was higher than 90%. According to the characterization methods like ^1H NMR, ^{13}C NMR spectra, and mass spectrometry, successful synthesis of these compounds was confirmed with designed chemical structure.

Fig. 1a represents the molecular structures of **PhCnF** and the previous reported **PhCnP4** [22]. In comparison to the previous **PhCnP4** derivatives, the introduction of fluorophenyl group in **PhCnF** instead of tetraphenylethenyl group provided more D-A effect and less steric effect, which would cause changes of AIE features and MFC properties. To evaluate whether these conjugated organic molecules were AIE active, their emission behaviours in solvent-nonsolvent mixtures were determined. **PhCnF** are highly soluble in THF, but nonsoluble in water. Using THF/water as the mixed solvent and increasing the water fraction would cause these molecules to aggregate and change their emission spectra. Fig. 1b showed the PL emission spectra of **PhC3F** in THF/water solution with different water fractions. When the water fraction was $\leq 70\%$, the emission intensity decreased as the water fraction increased, accompanying with a red-shifted emission wavelength, indicating obvious twisted intramolecular charge transfer (TICT) effect. When the water fraction was $> 70\%$, the PL intensity increased as the water fraction rised, showing characteristic AIE effect. The insets intuitively showed the changes in fluorescent intensity and images of the compounds during different water fraction with a UV lamp of 365 nm. Similarly, the PL spectra of **PhC6F**, **PhC10F** and **PhC12F** all showed obvious TICT and AIE features (Figs. S10-S11). In comparison, although the previous reported **PhC3P4** also exhibited similar TICT and AIE features, its AIE effect was more significant with more intense emission at high water fraction

than that of **PhC3F** (Fig. 1c) [22]. This difference of AIE property could be attributed to the introduction of tetraphenylethenyl group, well known as a common AIE fluorogen, and promoting the AIE effect. Furthermore, The UV absorption and fluorescent emission spectra of the **PhCnF** derivatives in different solvents have been conducted and shown in Fig. S12-S13, the selected solvents include ACN (Acetonitrile), Cyclohexane, DCM (Dichloromethane), DMF, TCM (Trichloromethane), and Toluene. Lippert–Mataga plot of the relation between Stokes shift ($\nu_a - \nu_f$) with solvent polarity Δf for the **PhCnF** derivatives was also measured in Fig. S14. The above results demonstrated obvious solvent effect that the UV absorption and fluorescent emission spectra of the **PhCnF** derivatives red-shifted as the solvent polarity increased.

In addition, the UV–vis absorption spectra were conducted to further demonstrate the emergence of aggregates at high water fraction. When the water fraction was $\leq 70\%$, there were no significant differences for the absorption spectra of **PhC3F** (Fig. 1d). When the water fraction was $> 70\%$, there were apparent level-off tails in the absorption spectra, which could be owing to the light scattering effect [31]. This result indicated the formation of aggregates at high water fraction. Similar phenomena were observed in the UV–vis absorption spectra of **PhC6F**, **PhC10F** and **PhC12F** in THF/water solution (Fig. S15). It was also found that the absorption spectra of the compounds at high water fraction exhibited red-shifted absorption peaks and shapes, which might be due to the different aggregated morphologies formed by the compounds.

<Fig. 1>

To investigate whether **PhCnF** possess MFC property, we ground the original **PhCnF** in a

mortar with a pestle directly. It was found that, when grinding the original sample, the fluorescent colours of **PhC3F** and **PhC12F** were significantly changed from yellow to orange, and green to yellow, respectively (Fig. 2a and 2c). In comparison, the compound of **PhC6F** and **PhC10F** exhibited scarce MFC feature with almost unchanged orange fluorescence colour in both original and ground states (Fig. 2b and Fig. S16). This unique MFC phenomenon derived from alkyl phenothiazinyl fluorophenyl acrylonitrile exhibited unusual alkyl length dependence, which was not consistent with the previous literatures [14-19].

Solid-state FL spectra quantitatively depicted the MFC behaviours of alkyl phenothiazinyl fluorophenyl acrylonitrile derivatives under different states. Fig. 2a showed the maximum fluorescent wavelength of the original **PhC3F** was 567 nm, while the ground **PhC3F** red-shifted to 597 nm with a 30 nm spectral shift, indicating obvious MFC behaviour. Moreover, the ground **PhC3F** could easily recover to the original state by fuming with dichloromethane vapours for 5 min, proving excellent reversibility of the MFC process. On the contrast, the MFC behaviour of **PhC6F** was not obvious. When grinding the original **PhC6F**, the maximum fluorescent wavelength red-shifted from 580 nm to 590 nm with a 10 nm spectral shift, accompanying the increase of the shoulder peak located at 615 nm (Fig. 2b). **PhC10F** exhibited only 5 nm spectral shift when grinding its original sample (Fig. S16). Interestingly, **PhC12F** appear obvious MFC behaviour again, when ground, the maximum fluorescent wavelength red-shifted from 549 nm to 579 nm with a 30 nm spectral shift (Fig. 2c). This result reveals that **PhCnF** are alkyl length dependent MFC materials. Although the alkyl chains are unconjugated group and normally have no contribution for the optoelectronic properties, alkyl groups had played an important role in dominating the MFC behaviour in this

case. The reversibility of the MFC behaviours of **PhC3F** and **PhC12F** was further confirmed by multiple grinding and fuming cycles, which proved excellent reversibility as repeatable fluorescence switch (Fig. 2d).

<Fig. 2>

To gain an insight into the MFC behaviour of **PhCnF** and detect the change of aggregated state under external stimuli, SWAXS experiments were conducted to study the original, ground, and fumed samples. As shown in Fig. 3a, the sharp scattering peaks in the original **PhC3F** suggested its well-ordered microcrystalline structure. After grinding, the scattering peaks disappeared, indicating the microcrystalline structure was destroyed and transformed to amorphous structure. As expected, the fumed **PhC3F** led to the restoration of well-ordered microcrystalline structure with reappearance of sharp scattering peaks, which was consistent with the original **PhC3F**. The SWAXS result indicated that the MFC behaviour of **PhC3F** was attributed to the phase change from crystalline to amorphous state. In contrast, the SWAXS curves of both original and ground **PhC6F** were observed with obvious sharp scattering peaks, indicating the microcrystalline structure maintained well both before and after grinding, suggesting excellent crystalline performance of **PhC6F** (Fig. 3b). This result suggested that the observed unobvious MFC behaviour of **PhC6F** was attributed to the little change of aggregated state. The SWAXS curves of **PhC12F** in different states were similar to that of **PhC3F**, suggesting phase change from crystalline to amorphous state, which would cause obvious MFC behaviour (Fig. S17a). As compared to the previous reported **PhCnP4**, **PhCnF** had more D-A effect and less steric effect, thence, increased crystalline performances were achieved in these compounds, and significantly influenced their MFC properties.

<Fig. 3>

The crystalline performances of the as-synthesized compounds were further determined by DSC measurements. As shown in Fig. 3c, at the first heating procedure, the compounds exhibited obvious melting peak located at 125 °C, 119 °C, and 85 °C, for **PhC3F**, **PhC6F**, and **PhC12F**, respectively, which indicated good crystalline performance of the pristine samples as also evidenced by the SWAXS study. However, at the first cooling procedure (Fig. 3d), only the compound of **PhC6F** was observed with exothermic crystallization peak at 91 °C, demonstrating that **PhC6F** had excellent crystalline performance from molten state, while the other two compounds transformed from molten state to amorphous state according to the first cooling curves. This better crystalline performance of **PhC6F** than **PhC3F** and **PhC12F** is also consistent with the SWAXS result. The second heating process of DSC curves of the original samples in Fig. S17b suggested **PhC3F** and **PhC12F** maintained amorphous states after a heating and cooling cycle, in comparison, **PhC6F** showed restored crystalline state after the same cycle.

The SWAXS and DSC studies revealed the influence of crystalline performance of the compounds for the MFC properties. To more deeply understand the MFC mechanism in molecular level, we carried out quantum mechanical computations to obtain the optimized geometry of the compounds. The lowest energy spatial conformations were calculated with Gaussian 03 software [32]. Fig. 4 shows the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of **PhC3F**, **PhC6F**, **PhC10F**, and **PhC12F** after structural optimization by the density functional method at the B3LYP/6-31 G level. The optimized geometries show twist conformations with same dihedral angles of the phenothiazinyl group and the adjacent phenyl group, which is calculated as 54°. For the

electron cloud distributions in the HOMOs and LUMOs, obvious migrations of electron clouds are discovered from phenothiazinyl group to the cyano and fluorophenyl groups. The result indicated little difference of the migration of electron clouds among these compounds. Furthermore, the single-crystal structure of **PhC3F** was obtained and shown in Fig. S18 and Table S1, demonstrating the twist conformations of the compound with the dihedral angle of the phenothiazinyl group and the adjacent phenyl group was calculated as 40°.

<Fig. 4>

As little difference of the migration of electron clouds was found, we further carried out quantitative analysis of the electronic spectral data to explore the divergences of dipole moment and energy gap, and study their influence to the MFC property. As shown in Table 1, time-dependent density functional theory (TD-DFT) was carried out, and the dipole moments of the compounds were determined as 7.57, 7.80, 8.32, and 7.65 debye for **PhC3F**, **PhC6F**, **PhC10F**, and **PhC12F**, respectively, which indicated **PhC6F** and **PhC10F** had larger molecular polarity. The calculated energy gaps according to the difference of HOMO and LUMO for **PhC3F**, **PhC6F**, **PhC10F**, and **PhC12F** were 3.17, 3.11, 3.19, and 3.13 eV, respectively. The HOMOs were also obtained using the onset oxidation potentials from CV curves, which were consistent with the result of quantum chemical computations (Fig. S19). At the same time, the energy gaps calculated from UV-vis absorption spectra for **PhC3F**, **PhC6F**, and **PhC12F** were 2.58, 2.54, 2.47, and 2.61 eV, respectively. The results from quantum mechanical computations revealed that high molecular polarity would improved the crystalline performance of the compounds, and influenced the aggregated state at solid state, then brought out different MFC property.

<Table 1>

4. Conclusions

In summary, four alkyl phenothiazinyl fluorophenyl acrylonitrile derivatives (**PhC3F**, **PhC6F**, **PhC10F**, and **PhC12F**) were synthesized in high yield. The derivatives showed AIE feature and alkyl length dependent MFC property. **PhC3F** with short propyl chain and **PhC12F** with long dodecyl chain showed obvious MFC behaviours, while **PhC6F** with hexyl chain and **PhC10F** with decyl chain exhibited little MFC property. In comparison to the phenothiazinyl tetraphenylethenyl acrylonitrile derivatives in our previous literature [22], the compounds in this study showed more D-A effect and less steric effect, which exhibited weakened AIE nature but more significant MFC property. Quantum mechanical computations revealed that **PhC6F** had high molecular polarity, which highly improved the crystalline performance of the compound, and made the aggregated state of the pristine sample hard to damage, then generated little MFC diversification. The SWAXS and DSC data also proved the excellent crystalline performance of **PhC6F**. In addition, **PhC10F** showed the highest molecular polarity and least MFC behaviour. We concluded that obvious MFC feature was attributed to appropriate crystalline performance, favourable molecular polarity and energy gap. The study on alkyl length dependent MFC property of AIE-based phenothiazinyl fluorophenyl acrylonitrile derivatives in this work would provide a new way to prepare more various functional MFC materials.

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Appendix A. Supplementary material

Experimental section. Supplementary data related to this article can be found at <http://dx.doi.org/xxxx>

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Figure Captions

Scheme 1 Synthetic routes of **PhC3F**, **PhC6F**, **PhC10F**, and **PhC12F**.

Fig. 1 (a) Molecular structures of **PhCnF** and the previous reported **PhCnP4** [22]. PL spectra of (b) **PhC3F** and (c) **PhC3P4** at 10 μ M in THF/water solution with different water fractions. The insets are the curves of fluorescent intensity vs. water fraction and the emission images of the compounds in THF/water solution with a 365 nm UV lamp. (d) UV-vis absorption spectra of **PhC3F** at 10 μ M in THF/water solution with different water fractions.

Fig. 2 Normalized solid-state fluorescence spectra of (a) **PhC3F**, (b) **PhC6F**, and (c) **PhC12F** in original (-o), ground (-g), and fumed (-f) states. (d) Repeated fluorescence switch of **PhC3F** and **PhC12F** by grinding and fuming cycles. The insets show fluorescent images of original and ground samples under 365 nm UV light.

Fig. 3 SWAXS curves of (a) **PhC3F** and (b) **PhC6F** in original (-o), ground (-g), and fumed (-f) states. DSC curves of original samples of **PhC3F**, **PhC6F**, and **PhC12F**: (c) first heating and (d) first cooling.

Fig. 4 Optimized geometries, HOMOs and LUMOs of **PhC3F**, **PhC6F**, **PhC10F**, and **PhC12F** obtained by quantum mechanical computations.

Table 1 Electronic spectral data of **PhC3F**, **PhC6F**, **PhC10F**, and **PhC12F** calculated with TD-DFT at the B3LYP/6-31 G level.

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Compound	f^a	μ (debye) ^b	HOMO (eV)	LUMO (eV)	HOMO (eV) ^c	E_1 (eV) ^d	E_2 (eV) ^e
PhC3F	0.2618	7.57	-5.44	-2.27	-5.45	3.17	2.58
PhC6F	0.2560	7.80	-5.37	-2.26	-5.39	3.11	2.54
PhC10F	0.2883	8.32	-5.43	-2.24	-5.41	3.19	2.47
PhC12F	0.2527	7.65	-5.39	-2.26	-5.37	3.13	2.61

^a Oscillator strength. ^b Dipole moment. ^c obtained using the onset oxidation potentials from CV curves ^d Energy gap calculated from quantum chemical analysis. ^e Energy gap calculated from UV-vis absorption spectra