Halogen effect on mechanofluorochromic properties of alkyl phenothiazinyl phenylacrylonitrile derivatives

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Abstract

Three novel alkyl phenothiazinyl phenylacrylonitrile derivatives (**C12F**, **C12Cl**, and **C12Br**) with different halogen end groups (fluorine, chlorine, and bromine) were synthesized with ultra-high yield (> 90%) and successfully confirmed according to standard spectroscopic methods. All these compounds were demonstrated with apparent twisted intramolecular charge transfer (TICT) and aggregation-induced emission (AIE) features. The halogen effect rendered them different electronic donor-acceptor behaviours, and gave birth to peculiar different mechanofluorochromic properties. The fluorine-substituted compound (**C12F**) showed obvious red-shifted mechanofluorochromic feature, while almost no mechanofluorochromic characteristic existed in the chlorine- (**C12Cl**) and bromine-substituted (**C12Br**) compounds. The mechanofluorochromic mechanism of **C12F** was investigated and attributed to the phase transformation from crystalline to amorphous state between the original and ground samples, **easy crystallinity of the compound**, straight conformation of alkyl chain, **higher energy gap**, and significant decrease of weighted mean lifetime. Moreover, **C12F** showed reversible mechanofluorochromic behaviour and reproducibility by annealing the ground sample, making it promising dual responsive and smart fluorescent materials for fluorescence switches and mechanosensors. The discussion of halogen effect on mechanofluorochromic properties in this work would provide a new way to adjust the fluorescent feature of mechanofluorochromic materials.

Keywords: Aggregation-induced emission; Mechanofluorochromic property; Halogen effect; Alkyl phenothiazinyl phenylacrylonitrile derivative; Crystalline-amorphous phase transformation;

1. Introduction

Mechanofluorochromic materials have attracted great interest in mechanosensors, fluorescence switches, and data storage applications in the past decade due to superior high efficiency and reproducibility [1-3]. However, mechanofluorochromic materials dependent on changes in molecular arrangement and packing are still rare ascribed to the lack of clear structure-property relationship of mechanofluorochromic materials [4-6]. Another problem that limit the development of these materials is the fluorescent quenching phenomenon in many planar conjugated molecules [7, 8]. On the contrary, aggregation-induced emission (AIE) materials with anti-quenching feature have been developed with various architectures and utilized for chemosensor and bioimaging applications [9-12]. More importantly, many AIE compounds have been demonstrated with mechanofluorochromic feature, which would open up a new path to fabricate more and more mechanofluorochromic compounds [13-18].

Based on the previous work, deeply understanding the structure-property relationship is of great importance to investigate the mechanofluorochromic mechanism, which will further broaden the area of mechanofluorochromic materials. Some recent design strategies have demonstrated the structure adjustment could directly affect the performance of mechanofluorochromic materials, and provided some aids to better understand their structure-property relationship [1]. In 2011, Harima *et al.* reported heteropolycyclic fluorescent dyes with donor-acceptor (D-A) π -conjugated structure showed mechanofluorochromism, and the degrees of mechanofluorochromism were dependent on the electron-accepting ability of acceptor, steric sizes of the substituents, and intermolecular π - π

interaction [19]. Other D-A associated mechanofluorochromic systems have been studied by Yagai's group, Wei's group, and Wang's group [20-22]. Alkoxy (alkyl) length is another important structural factor affecting mechanofluorochromism, which has been studied by Xu and Chi's group, indicating the mechanofluorochromism of 9,10-distyrylanthracene derivatives was more obvious when the length of alkoxy group increased [23]. The Yang's group also reported alkyl length-dependent solid-state fluorescence properties of 9,10-bis[(N-alkylcarbazol-3-yl)vinyl]anthracenes under various external stimuli, demonstrating the opposite phenomenon that the shorter the N-alkyl chain, the more remarkable the mechanofluorochromic behaviour [24]. In 2012, Xu and Chi's group reported the influence of carbazolyl groups on mechanofluorochromic properties of the distyrylanthracene derivatives, proving more obvious mechanofluorochromism with the increase of carbazolyl groups [25]. Most recently, Fraser's group examined the effect of halide substituted group to the mechanochromic luminescence of difluoroboron β -diketonate compounds, suggesting no obvious different mechanofluorochromism among the fluorine, chlorine, and bromine substituted compounds [26]. However, systematic investigation of halogen effect to mechanofluorochromic materials is still highly rare. Therefore, adjusting the mechanofluorochromic property of these smart materials through halogen effect is of great scientific interest and highly demanded.

In this work, we have designed and facilely synthesized three new alkyl phenothiazinyl phenylacrylonitrile derivatives with different halogen end groups (**C12F**, **C12Cl**, and **C12Br**, see Scheme 1), which endowed them with different electronic donor-acceptor effects. The AIE features were firstly demonstrated in THF/water mixed solvents. Then, solid

photoluminescence (PL) spectra were studied to explore their unique and interesting mechanofluorochromic properties. Finally, small and wide-angle X-ray scattering (SWAXS), quantum mechanical computations, and time-resolved emission-decay behaviours were conducted to understand their mechanofluorochromic features. The results demonstrated that introduction of halogen effect could endow the as-prepared compounds with peculiar and different mechanofluorochromic properties.

<Scheme 1>

2. Experimental procedure

2.1 Materials and characterization

Phenothiazine, 1-bromododecane, potassium tert-butoxide, 4-fluorophenyl acetonitrile, 4-chlorophenyl acetonitrile, 4-bromophenyl acetonitrile, tetrabutylammonium hydroxide (0.8 M in methanol) were purchased from Alfa Aesar and used as received. 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 annealing experiments were done on a hot-stage with an automatic temperature control system for 5 min with the annealing temperatures of 70 °C, 60 °C and 50 °C for **C12F**, **C12Cl**, and **C12Br**, respectively.

¹H NMR and ¹³C NMR spectra were measured on a JEOL 400 MHz spectrometer [CDCl₃ as solvent and tetramethylsilane (TMS) as the internal standard]. Standard FAB-MS was

obtained on ZAB-HS mass spectrometry. 1D small and wide angle X-ray scattering (SWAXS) experiments were carried out 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. Fluorescence spectra and life time were measured on FLS 920 lifetime and steady state spectrometer. The fluorescence quantum yield values (Φ_F) of the compounds in solution were estimated using quinine sulfate in 0.1 N H₂SO₄ (Φ_F = 54.6%) as standard. The fluorescent quantum yield for the solid samples were measured on a MK-301 EL/PL Measurement Program (Bunkoukeiki Co., Ltd, Japan) equipped with an integrating sphere and a CCD spectrometer (Andor Tech, CCD-6685). Differential scanning calorimetry (DSC) curves were performed on TA Instruments DSC Q2000 at a heating rate of 10 °C min⁻¹ under N₂ atmosphere.

2.2 Syntheses of C12F, C12Cl, and C12Br

Synthetic routes of the compounds **C12F**, **C12Cl**, and **C12Br** were showed in Scheme 1. The intermediate of **C12A** was synthesized according to the previous literature [27-29].

Synthesis of **C12F**. A solution of **C12A** (0.395 g, 1.00 mmol) and 4-fluorophenyl acetonitrile (0.405 g, 3.00 mmol) in ethanol (20.0 mL) was stirred at room temperature. Then tetrabutylammonium hydroxide solution (TBAH, 0.8 M, 5 drops) was added and the mixture was heated to reflux for 2 h. The reaction mixture was cooled to room temperature and filtered, washed with ethanol for three times to afford **C12F** (0.490 g, yield 95.7%). ¹H NMR (400 MHz, CDCl₃) δ : 0.86 (t, 3 H, J = 6.8 Hz), 1.13–1.36 (m, 16 H), 1.36–1.48 (m, 2 H), 1.73–1.86 (m, 2 H), 3.85 (t, 2 H, J = 6.8 Hz), 6.75–6.89 (m, 2 H), 6.93 (t, 1 H, J = 7.2 Hz), 7.01–7.19 (m, 4 H), 7.26 (s, 1 H), 7.53 (s, 1 H), 7.54–7.64 (m, 2 H), 7.79 (d, 1 H, J = 8.8 Hz).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 164.26, 161.78, 147.31, 144.00, 140.84, 131.07, 131.04, 128.58, 128.51, 127.81, 127.71, 127.62, 127.60, 127.55, 124.89, 123.77, 123.18, 118.44, 116.26, 116.04, 115.67, 115.19, 107.51, 47.84, 31.94, 30.02, 29.87, 29.73, 29.65, 29.63, 29.32, 26.84, 22.80, 14.24. MS (FAB) calcd. for $\text{C}_{33}\text{H}_{37}\text{FN}_2\text{S}$, 512, found 512.

The synthetic routes of **C12Cl** and **C12Br** were similar to that of **C12F**.

C12Cl (93.2% yield). ^1H NMR (400 MHz, CDCl_3) δ : 0.86 (t, 3 H, $J = 6.8$ Hz), 1.14–1.36 (m, 16 H), 1.36–1.48 (m, 2 H), 1.73–1.87 (m, 2 H), 3.85 (t, 2 H, $J = 7.2$ Hz), 6.80–6.89 (m, 2 H), 6.93 (t, 1 H, $J = 7.2$ Hz), 7.04–7.19 (m, 2 H), 7.31 (s, 1 H), 7.38 (d, 2 H, $J = 8.4$ Hz), 7.47–7.61 (m, 3 H), 7.79 (d, 1 H, $J = 8.4$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 147.46, 144.10, 141.19, 134.77, 133.39, 129.28, 128.75, 128.61, 127.69, 127.60, 127.57, 127.05, 125.78, 124.88, 123.72, 123.22, 118.26, 115.68, 115.18, 107.31, 47.68, 32.02, 29.73, 29.65, 29.63, 29.46, 29.32, 26.97, 26.84, 22.80, 14.25. MS (FAB) calcd. for $\text{C}_{33}\text{H}_{37}\text{ClN}_2\text{S}$, 528, found 528.

C12Br (97.6% yield). ^1H NMR (400 MHz, CDCl_3) δ : 0.86 (t, 3 H, $J = 6.8$ Hz), 1.15–1.36 (m, 16 H), 1.37–1.48 (m, 2 H), 1.73–1.87 (m, 2 H), 3.85 (t, 2 H, $J = 7.2$ Hz), 6.80–6.89 (m, 2 H), 6.93 (t, 1 H, $J = 7.2$ Hz), 7.05–7.18 (m, 2 H), 7.32 (s, 1 H), 7.45–7.51 (m, 2 H), 7.51–7.59 (m, 3 H), 7.80 (d, 1 H, $J = 8.8$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 147.48, 143.82, 141.22, 133.86, 132.23, 128.78, 128.62, 127.67, 127.59, 127.57, 127.30, 124.86, 123.70, 123.13, 122.93, 118.20, 115.69, 115.18, 107.05, 47.87, 32.02, 29.73, 29.65, 29.63, 29.46, 29.32, 26.97, 26.83, 22.80, 14.26. MS (FAB) calcd. for $\text{C}_{33}\text{H}_{37}\text{BrN}_2\text{S}$, 572, found 572.

3. Results and discussion

The fluorogens of **C12F**, **C12Cl**, and **C12Br** were prepared with ultra-high yields of

93.2–97.6% following the synthetic routes shown in Scheme 1. Their structures were characterized and confirmed by standard spectroscopic methods including mass spectrometry, ^1H NMR and ^{13}C NMR spectra. The AIE performance of cyano-substituted diarylethene has been previously demonstrated by Park *et al* [30]. To determine whether the compounds are AIE-active, the PL emission spectra of their diluted mixtures were investigated using THF/water mixed solvents with different water fractions (Fig. 1). Similar fluorescence characteristic could be found in these compounds, that is including twisted intramolecular charge transfer (TICT) and AIE features. The TICT section was featured with a red-shifted emission colour and a decreased emission intensity with increasing solvent polarity, which could be found as the water fraction was $\leq 60\%$. When the water fraction is higher than 60%, the AIE feature is prominent.

<Fig. 1>

The UV–vis absorption spectra of the as-prepared compounds in the THF/water mixed solvents (10 μM) are shown in Fig. 2. The spectral curves were significantly changed when the water fraction was higher than 60%. The entire absorption spectra started to increase, indicating the formation of organic nanoparticles. The light scattering of the nanoparticles in the mixed solvents caused decrease of light transmission in the solvents and led to level-off tail in the visible region of the absorption spectra. The UV–vis results were well-consistent with AIE phenomena of the compounds, which were caused by molecular aggregation.

<Fig. 2>

Many AIE compounds have been demonstrated with mechanofluorochromic feature,

therefore, we ground the compounds directly, and found the fluorescent colour of **C12F** was significantly changed from green to yellow (Fig. 3a), which revealed obvious red-shifted mechanofluorochromic feature. However, the compounds of **C12Cl** and **C12Br** exhibited no mechanofluorochromic performance at all, as both original samples and ground samples appeared orange fluorescence (Fig. 3b, 3c). This interesting and different mechanofluorochromic property based on alkyl phenothiazinyl phenylacrylonitrile derivative was not consistent with the previous report by Fraser's group [26]. Therefore, a series of characterization methods including solid FL spectra, SWAXS, quantum mechanical computations, and time-resolved emission-decay behaviours have been determined to reveal the mechanofluorochromism.

<Fig. 3>

To quantitatively study the fluorescent wavelength changes of these alkyl phenothiazinyl phenylacrylonitrile derivatives among different states, solid-state FL spectra were conducted. As shown in Fig. 3A, the maximum fluorescent emission wavelength of the original **C12F** sample was located at 549 nm. When it was ground, the emission wavelength was red-shifted to 579 nm, which gained a 30 nm red-shift of wavelength. Meanwhile, this ground sample could easily recover to the original luminescence by annealing on a hot plate at 70 °C for 5 min (Fig. 3a), demonstrating excellent reproducibility of the synthesized mechanofluorochromic compound. On the contrast, the compounds of **C12Cl** and **C12Br** showed little change of mechanofluorochromic wavelength. When grinding the original compounds of **C12Cl** and **C12Br**, only 7 nm and 6 nm red-shift of emission wavelength were detected, respectively, although they were also demonstrated excellent reversibility by

grinding and annealing (Fig. 3b, 3c). The reversibility of mechano-fluorescence of the synthesized compounds was confirmed by grinding and annealing cycles, which indicated excellent reversibility as repeated fluorescence switch (Fig. 3d). The above result evidenced that halogen effect could significantly affect the mechanofluorochromic properties of alkyl phenothiazinyl phenylacrylonitrile derivatives. The fluorescence quantum yields of **C12F**, **C12Cl**, and **C12Br** in solution and the solid-state before and after grinding have been determined to quantitatively study the fluorescent intensity of the synthesized compounds. The fluorescence quantum yields of **C12F**, **C12Cl**, and **C12Br** in THF were determined as 51%, 33%, and 28%, respectively. In solid state, the fluorescence quantum yields of **C12F**, **C12Cl**, and **C12Br** were changed from 54%, 39%, and 35% before grinding to 44%, 30%, and 31% after grinding, and to 53%, 37%, and 35% after annealing, respectively. This result indicated the synthesized compounds showed high fluorescence both in solution and solid state, although slight decrease of fluorescence was observed after grinding in solid state.

It has been proposed that change of aggregated phase by external mechanical forces usually led to mechanofluorochromic nature [31]. Thus, SWAXS measurements were employed to determine the micro-structures of these compounds in original, ground, and annealed states (Fig. 4). The sharp scattering peaks was observed for the original sample of **C12F**, indicating crystalline structures with high order (Fig. 4a). After the original **C12F** were ground by external mechanical forces, change from crystalline structure to low crystalline structure or amorphous state occurred, which was evidenced by the attenuation and disappearance of the original sharp peaks. Interestingly, the annealed sample of **C12F** from the ground one led to the recovery of the crystalline phase, which was accompanied with the appearance of sharp

peaks that was consistent with the original samples. The above result indicated that the mechanofluorochromic behaviour of **C12F** was derived from aggregated state transition from ordered to low ordered molecular aggregation. However, all of the original, ground, and annealed states of the compounds of **C12Cl** and **C12Br** showed low ordered state in their molecular aggregated phase, which could be observed in Fig. 4b and 4c. Thus, no obvious change of aggregated phase happened in these different states, leading to no apparent mechanofluorochromic behaviour.

<Fig. 4>

To further discuss the change of the aggregation state in the mechanofluorochromic process, differential scanning calorimetry (DSC) of the solid-state before and after grinding have been measured and provided in Fig. 5. The first heating and second heating process of the synthesized compounds were determined. In the case of **C12F**, the first heating curve of the original sample and ground sample exhibited little difference. However, the second heating curves of these two samples showed obvious difference, as a cold crystallization peak located at 75 °C and a melting peak at 86 °C appeared in the original sample, while the ground sample had no temperature transition in the heating process. In the contrast, **C12Cl** and **C12Br** showed no obvious difference either in original state or in ground state for the two heating processes. The above result demonstrated **C12F** had better crystallinity than the other two compounds, which was beneficial for the production of obvious mechanofluorochromic feature.

<Fig. 5>

To deeply understand the mechanofluorochromism of the as-prepared compounds in molecular level, we conducted quantum mechanical computations *via* Gaussian 03 software to gain the optimized geometry of the compounds in their lowest energy spatial conformations (Fig. 6). The highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of these compounds were also obtained according to the density functional method at the B3LYP/6-31 G level after structural optimization [32]. From the optimized geometry of the compounds, conspicuous difference of **C12F** comparing to **C12Cl** and **C12Br** in the conformation of alkyl chain could be observed, which suggested much straighter alkyl group existed in **C12F**. The HOMOs of these compounds exhibited dispersed electron cloud distributions located at the phenothiazinyl phenylacrylonitrile group of the molecules, whereas the electron clouds of the LUMOs showed migration of electron clouds to the halogen end group. It is noteworthy that the migration trend of the electron clouds from HOMO to LUMO is in this order: **C12F** > **C12Cl** $\approx$ **C12Br**. The calculated frontier orbital energy levels of **C12F**, **C12Cl**, and **C12Br** were showed in Table 1. The calculated HOMO–LUMO gaps for **C12F**, **C12Cl**, and **C12Br** were 3.13, 3.11 and 3.12 eV, respectively. Meanwhile, the energy gaps calculated from UV-vis absorption spectra for **C12F**, **C12Cl**, and **C12Br** were 2.61, 2.51, and 2.48 eV, respectively. These results were consistent with the above migration trend of electron clouds of three compounds. Time-dependent density functional theory (TD-DFT) were carried out to compare the results of electronic structure calculations with experimental data. Oscillator strength and dipole moment of the compounds were listed in Table 1. **C12F** had larger oscillator strength and dipole moment than that of **C12Cl**, which was consistent with the energy gap values. However, **C12Br** showed the largest

oscillator strength and dipole moment, which was inconsistent with trend of electron clouds migration and energy gap values. In addition, the synthesized compounds all adopted twisted spatial conformations in the optimized geometry. The dihedral angles of the phenothiazinyl group and the adjacent phenyl group were calculated as 54° for all of three compounds. The results from quantum mechanical computations demonstrated the significant difference in the conformation of alkyl chain, migration of electron clouds, energy gap between **C12F** and the other two derivatives, which was beneficial for the generation of obvious mechanofluorochromic feature for **C12F**.

<Fig. 6>

<Table 1>

Furthermore, the time-resolved emission-decay behaviours of **C12F**, **C12Cl**, and **C12Br** in original, ground, and annealed states were investigated. The lifetime data were illustrated in Table 2. Two relaxation pathways of the fluorescence decays were found for these three compounds, implying that the time-resolved FL spectra of the compound containing independent emissions from different π -conjugation extent evidenced by the two detected lifetimes. The weighted mean lifetimes $\langle\tau\rangle$ of the original, ground, and annealed states of these samples were determined. The ground state of **C12F** showed significant decrease of $\langle\tau\rangle$ as compared to its original and annealed states. However, different states of **C12Cl** and **C12Br** exhibited almost the same $\langle\tau\rangle$. According to this result, the difference of time-resolved emission-decay behaviour might be the reason inducing different mechanofluorochromism of the compounds.

<Table 2>

4. Conclusions

In summary, we have reported three new alkyl phenothiazinyl phenylacrylonitrile derivatives (**C12F**, **C12Cl**, and **C12Br**) with different halogen end groups. These compounds showed apparent and similar TICT and AIE features. The mechanofluorochromic feature of the compounds were significantly affected by halogen group, as the fluorine-substituted compound exhibited obvious mechanofluorochromic performance, while the chlorine- and bromine-substituted compounds showed almost no mechanofluorochromism. Such differences of mechanofluorochromic property were investigated by SWAXS, quantum mechanical computations, and time-resolved emission-decay behaviours studies. The results revealed that the mechanofluorochromism of **C12F** might be derived from the following reasons: crystalline-amorphous phase transformation between the original and ground state, **easy crystallinity of the compound**, straight conformation of alkyl chain, large migration of electron clouds from HOMO to LUMO, **higher energy gap**, and significant decrease of $\langle\tau\rangle$. The study of halogen effect on mechanofluorochromic properties in this work would provide a new path to adjust the fluorescent feature of mechanofluorochromic materials.

Acknowledgements

This research was supported by the Guizhou Province Science and Technology Planning Project ([2015]2068), the National Science Foundation of China (Nos. 21134004, 21474057 and 51503046), the National 973 Project (No. 2011CB935700), and the Research Project for High-level Talents of Guizhou Institute of Technology (XJGC201503).

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Figure Captions

Scheme 1 Synthetic routes of **C12F**, **C12Cl**, and **C12Br**.

Fig. 1 PL spectra of **C12F**, **C12Cl**, and **C12Br** in THF/water mixed solvents (10 μ M) with different water fractions. The insets depict changes in PL peak intensity and emission images of the compounds in different water fraction mixtures under 365 nm UV illumination.

Fig. 2 UV-vis absorption spectra of **C12F**, **C12Cl**, and **C12Br** in THF/water mixed solvents (10 μ M) with different water fractions.

Fig. 3 Normalized solid-state PL spectra of (a) **C12F**, (b) **C12Cl**, and (c) **C12Br** in original (-o), ground (-g), and annealed (-a) states. (d) Repeated fluorescence switch of **C12F**, **C12Cl**, and **C12Br** by grinding and annealing cycles.

Fig. 4 SWAXS patterns of (a) **C12F**, (b) **C12Cl**, and (c) **C12Br** in original (-o), ground (-g), and annealed (-a) states.

Fig. 5 DSC curves of (a) **C12F**, (b) **C12Cl**, and (c) **C12Br** in original (-o) and ground (-g) states.

Fig. 6 Optimized geometry and calculated spatial electron distributions of HOMOs and LUMOs of **C12F**, **C12Cl**, and **C12Br**.

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Table 1 Electronic spectral data of **C12F**, **C12Cl**, and **C12Br** calculated with TDDFT at the B3LYP/6-31 G level.

Compound	f^a	μ (debye) ^b	HOMO (eV)	LUMO (eV)	E_1 (eV) ^c	E_2 (eV) ^d
C12F	0.2527	7.65	-5.39	-2.26	3.13	2.61
C12Cl	0.2397	7.59	-5.42	-2.31	3.11	2.51
C12Br	0.2551	7.69	-5.42	-2.30	3.12	2.48

^a Oscillator strength. ^b Dipole moment. ^c Energy gap calculated from quantum chemical analysis. ^d Energy gap calculated from UV-vis absorption spectra

Table 2 Solid-state fluorescence lifetime data of **C12F**, **C12Cl**, and **C12Br** in original, ground, and annealed states.

Sample		τ_1 (ns) ^a	A_1 ^b	τ_2 (ns) ^a	A_2 ^b	$\langle\tau\rangle$ (ns) ^c
C12F	Original	4.95	0.01	14.46	0.99	14.38
	Ground	7.45	0.35	12.19	0.66	10.56
	Annealed	6.96	0.08	13.09	0.92	12.60
C12Cl	Original	4.83	0.18	11.54	0.82	10.33
	Ground	8.64	0.37	10.23	0.63	9.64
	Annealed	6.84	0.27	12.32	0.73	10.84
C12Br	Original	5.04	0.75	10.99	0.25	6.53
	Ground	4.48	0.86	16.12	0.14	6.11
	Annealed	4.83	0.82	12.52	0.18	6.21

^a Fluorescence lifetime. ^b Fractional contribution. ^c Weighted mean lifetime