# Tetrahedron 70 (2014) 924-929



Contents lists available at ScienceDirect

# Tetrahedron

journal homepage: www.elsevier.com/locate/tet

# Influence of alkyl length on properties of piezofluorochromic aggregation induced emission compounds derived from 9,10-bis[(*N*-alkylphenothiazin-3-yl)vinyl]anthracene





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# ARTICLE INFO

Article history: Received 17 October 2013 Received in revised form 27 November 2013 Accepted 5 December 2013 Available online 13 December 2013

### Keywords:

Aggregation induced emission Reversible piezofluorochromic property Alkyl-length dependent Crystalline—amorphous phase transformation Divinylanthracene derivative Stimuli-responsive luminescent material

# ABSTRACT

Three 9,10-bis[(*N*-alkylphenothiazin-3-yl)vinyl]anthracene derivatives with different propyl, hexyl, and dodecyl side chains (**AnPh<sub>3</sub>**, **AnPh<sub>6</sub>**, and **AnPh<sub>12</sub>**) were synthesized and confirmed by standard spectroscopic methods. All of the compounds exhibited obvious aggregation induced emission (AIE) and piezofluorochromic (PFC) properties. The PFC behaviors were investigated and showed that proportional alkyl-length dependent relationship existed not only in the ground states of the compounds, but also in the melted states compared with the fumed states of the compounds. The PFC mechanism was explored and ascribed to the crystalline—amorphous phase transformation. More importantly, these derivatives showed reversible significant PFC properties and reproducibility in various states including fumed, ground, annealed, and melted states, making them promising stimuli-responsive and smart luminescent materials for pressure-sensors, information-recording, and light-emitting device applications.

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# 1. Introduction

Piezofluorochromic (PFC) materials have attracted great interest in sensors, security inks, and memory chips applications due to their advanced luminescent properties that change in response to external force stimuli with superior high efficiency and reproducibility.<sup>1,2</sup> Molecular assembly structure change is one major PFC way and believed easier to realize the dynamic control of the fluorescent process than that of chemical structure change.<sup>1</sup> The first example appeared in 2002, Weder and collaborators reported on cyano-substituted diphenylethene derivatives as the first two PFC materials.<sup>3</sup> However, rare organic PFC materials had been reported until 2010 due to the notorious problem of aggregationcaused quenching (ACQ) effect exist in solid state of organic compounds, and eventually cause the lack of property–structure relationship established for these kinds of materials.<sup>4–8</sup> Aggregationinduced emission (AIE) materials with advanced anti-ACQ performance have been developed involving various architectural frameworks, such as siloles,<sup>9</sup> tetraphenylethene,<sup>10–14</sup> triphenylethene,<sup>15–20</sup> distyrylanthracene,<sup>21–23</sup> cyano-substituted diarylethene derivatives<sup>24–30</sup> conjugated molecules, and utilized for chemosensor, and bioimaging applications.

In 2010, our group incorporated AIE feature into the PFC material, and thus obtained a piezofluorochromic AIE (PAIE) compound derived from tetraphenylethylene and divinylanthracene.<sup>31</sup> Since then, a number of new PAIE materials had been synthesized in our lab, and a common structure—property relationship had been established for helping identifying and synthesizing more novel PFC materials.<sup>32–37</sup> Hereafter, a series of novel organic PAIE compounds were synthesized and greatly broadened the field of PFC materials.<sup>38–54</sup> In view of this situation, the very critical thing is to explore in-depth the structure—property relationship of PFC materials and clearly understand the piezofluorochromism.

It is well known that alkyl chain length has a significant impact on the PFC property. In the previous work, six multifunctional organic PFC materials derived from 9,10-distyrylanthracene with various alkyl endgroups have been reported in our group,

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exhibiting obvious proportional relationship of chain lengthdependent PFC behavior.<sup>37</sup> A similar research was investigated about the alkyl chain length effect of 9,10-bis(p-alkoxystyryl)anthracenes by Yang' group.<sup>55</sup> Very recently, they have also explore the length-dependent PFC behavior of 9.10-bis[(9.9dialkylfluorene-2-yl)vinyl]anthracene and 9,10-bis[(N-alkylcarbazol-3-vl)vinvl]-anthracene derivatives, which interestingly showed apparent different chain length-dependent properties. Among the former derivatives, proportional relationship of chain lengthdependent PFC behavior was observed, whereas the latter ones exhibited inverse relationship of alkyl chain length effect, however, the morphology of solid state before and after grinding didn't show conspicuous divergence.<sup>39,40</sup>

In this contribution, we have designed and facilely synthesized a series of 9,10-bis[(*N*-alkylphenothiazin-3-yl)vinyl]anthracene derivatives with various length of alkyl chains (propyl, hexyl, and dodecyl) (**AnPh<sub>3</sub>**, **AnPh<sub>6</sub>**, and **AnPh<sub>12</sub>**, Scheme 1), which showed obvious AIE feature and PFC behavior. Then quantum mechanical computations were conducted to reveal the origin of the AIE effect. Solid fluorescence spectra and UV–vis spectra were studied to explore their PFC properties. Furthermore, the piezofluorochromism was investigated by differential scanning calorimetry (DSC), small and wide-angle X-ray scattering (SWAXS), and time-resolved emission-decay behaviors. The results demonstrate that synthesized compounds are not only reversible PFC materials but also display proportional relationship of chain length-dependent behavior.



Scheme 1. Schematic showing the chemical structures of AnPh<sub>3</sub>, AnPh<sub>6</sub>, and AnPh<sub>12</sub>.

# 2. Results and discussion

The fluorogens **AnPh<sub>3</sub>**, **AnPh<sub>6</sub>**, and **AnPh<sub>12</sub>** were prepared by the Wittig–Horner reaction with extremely high yields of 94–98% following the synthetic route shown in Scheme S1. Theirs structures were characterized and confirmed by standard spectroscopic methods. To gain the lowest energy spatial conformations of the compounds, we conducted quantum mechanical computations via Gaussian 03 software. The highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of **AnPh<sub>3</sub>**, **AnPh<sub>6</sub>**, and **AnPh<sub>12</sub>** were obtained (Fig. 1) according to the density functional method at the B3LYP/6-31 G level after the structural optimization.<sup>56</sup>

The HOMOs of these compounds exhibited dispersed electron cloud distributions located at phenothiazine and anthracene groups on the molecules, whereas the electron clouds of the LUMOs showed migration from both sides of the phenothiazine groups to the anthracene core groups. It is noteworthy that all of the compounds adopted twisted spatial conformations from the optimized structure. The dihedral angles of the anthracene groups and the adjacent phenothiazine groups were calculated as  $64^{\circ}$  for all these compounds. From these twisted conformations, we can speculate the AIE properties of these three compounds according to the restricted intramolecular rotation mechanism of AIE materials proposed by Tang et al.<sup>57</sup>

To determine whether the compounds are AIE-active, the photoluminescence (PL) emission spectra of their diluted mixtures were investigated using THF–water mixtures with different water fractions. As shown in Fig. 2A, when the water fraction is lower than



Fig. 1. Calculated spatial electron distributions of HOMOs and LUMOs of  $AnPh_3$ ,  $AnPh_6$ , and  $AnPh_{12}$ .



**Fig. 2.** PL spectra of (A) **AnPh<sub>3</sub>**, (B) **AnPh<sub>6</sub>**, and (C) **AnPh<sub>12</sub>** in THF–water mixtures with different water fractions. The insets depict the changes in PL peak intensities under different water fractions.

50%, the PL intensity of **AnPh**<sub>3</sub> is indeed very weak. However, when the water fraction reaches 60%, a significant increase of PL intensity is observed from 9.0 to 940 a.u., which showed approximately 104 times higher than that in the pure THF, demonstrating the extraordinary AIE feature of **AnPh**<sub>3</sub>. Similar phenomena can be observed in the other two compounds (Fig. 2B and C). It is worth mentioning that the PL intensities exhibit a zig-zag pattern as the water fractions increase. This may be due to the affect of different types of nanoparticle suspensions including crystal or amorphous morphology existed in the solution.<sup>36</sup>

The twisted conformations bring about AIE features to the compounds, meanwhile, may generate PFC properties for them. Therefore, the compound **AnPh**<sub>3</sub> was ground in a mortar with a pestle directly, the fluorescent color of the compound changed from yellow to orange immediately (Fig. 3A), which revealed conspicuous PFC behavior. After the ground **AnPh**<sub>3</sub> was conducted with annealing or fuming treatment, the fluorescent color returned to its original appearance, demonstrating good reversibility in the fluorescent emission. The ground, fumed or annealed sample were further carried out for melting treatment. An interesting phenomenon could be observed that the fluorescent color changed to orange-red with even longer wavelength emission. More importantly, the melted sample could recover its very original state just via recrystallized procedure. Similar diverse phenomena appeared in the other two synthesized compounds (Fig. 3B and C).



**Fig. 3.** Fluorescent images of (A) **AnPh<sub>3</sub>**, (B) **AnPh<sub>6</sub>**, and (C) **AnPh<sub>12</sub>** with different treatments (ground, fumed, annealed, melted, and recrystallized) when taken at room temperature under 365 nm UV light.

To quantitatively measure the fluorescent wavelength changes of the three compounds among the different states, solid-state fluorescent spectra were carried out. As shown in Fig. 4A, the fluorescent emission wavelength of the fumed AnPh<sub>3</sub> sample located at 566 nm. When ground, the wavelength red-shifted to 599 nm with a 33 nm wavelength shift. While the fumed or ground sample was heated to obtain a melted state sample, the emission even red-shifted to a longer emission wavelength at 620 nm, which exhibited a 54 nm red-shift compared with the fumed one. The resulted ground sample can easily return to the original state with short-wavelength by fuming with an organic vapor like dichloromethane or via annealing on a hot plate at 150 °C for 5 min (Fig. 4B), demonstrating excellent reversibility of the obtained PFC material. The fluorescent wavelength of the fumed **AnPh<sub>6</sub>** sample was 563 nm (Fig. S1A), while its ground sample red-shifted to 603 nm with a 40 nm wavelength shift. The melted state of AnPh<sub>6</sub> derived from its fumed or ground state showed a 619 nm for the emission



**Fig. 4.** (A) Normalized solid-state fluorescent spectra of **AnPh**<sub>3</sub> in fumed, ground, and melted states; (B) Normalized solid-state fluorescent spectra of **AnPh**<sub>3</sub> in ground and annealed states; (C) Normalized solid-state UV–vis spectra of **AnPh**<sub>3</sub> in fumed, ground, annealed, and melted states.

wavelength, which emerged a 56 nm red-shift than that of the fumed **AnPh<sub>6</sub>**. Compared with the previous two compounds, the fluorescent wavelength of the fumed **AnPh<sub>12</sub>** sample exhibited a shorter emission wavelength at 551 nm (Fig. S2A), when ground in a mortar, the resulting wavelength moved to 596 nm with a red-shift of 45 nm. The emission of the melted sample of **AnPh<sub>12</sub>** reached 629 nm with a 78 nm red-shift compared with its fumed state. The above result indicated that the longer the alkyl chain length is, the more obvious red-shift not only the ground sample but also the melted sample is. The solid-state UV–vis spectra also revealed the changes in fumed, ground, annealed, and melted states (Fig. 4C, Figs. S1C and S2C). The annealed sample showed similar absorption as the fumed one. When the samples were ground, the absorption areas ranging from 500 nm to 700 nm

significantly increased. Whereas the samples were in melted states, the absorption at 500–700 nm further dramatically increased, even more obviously than that of the ground ones. These results demonstrate that these compounds are not only PFC materials but also piezochromic materials (color change under external force) as well. As shown in Fig. S3, the melted samples can easily recover to the original state by recrystallization. These reversible color change features make them promising candidates for optical recording and temperature- or pressure-sensing systems.

To determine the mechanism of the PFC compounds, SWAXS measurements and DSC experiments were conducted (Fig. 5, Figs. S4 and S5). SWAXS measurements were employed to elucidate the micro-structures of the compounds in fumed, ground, annealed, and melted states. The sharp scattering peaks were observed for the fumed samples, indicating an ordered crystalline structure. After grinding, a transition from crystalline structure to amorphous phase occurred with the above sharp peaks attenuated or even disappeared. When annealed, the ground samples led to the recovery of the crystalline structure by accompanying the appearance of sharp peaks that coincided with the original sample. Melting treatments of the ground, fumed or annealed sample were further carried out for the SWAXS measurements, the result showed that complete transition to amorphous phase occurred with the diffraction peaks disappeared. The results indicate that the reversible transition between the ordered and disordered molecular aggregations is crucial for the PFC features. Reproducible heating DSC result showed that the ground state of AnPh<sub>3</sub> had an endothermic peak located at 135 °C before the melting point with enthalpy value 3.7 kI mol<sup>-1</sup>, whereas no endothermic peak appeared around this temperature for the fumed state. Meanwhile,



**Fig. 5.** (A) SWAXS patterns of **AnPh**<sub>3</sub> in fumed, ground, annealed, and melted states; (B) DSC curves of **AnPh**<sub>3</sub> in fumed and ground states.

it should be mentioned that the up and down peaks around 260 °C could be observed, which represented the melt-crystallization transformation process. The ground samples of **AnPh<sub>6</sub>** and **AnPh<sub>12</sub>** also emerged endothermic peaks located at 136 °C and 132 °C with enthalpy values 6.6 kJ mol<sup>-1</sup> and 1.7 kJ mol<sup>-1</sup>, respectively. The trace of endothermic peaks around the same temperature range still could not be found in the fumed samples. The DSC results indicated that the ground samples showed significant changes of the morphologies with respect to the fumed states.

The time-resolved emission-decay behaviors of **AnPh<sub>3</sub>**, **AnPh<sub>6</sub>**, and **AnPh<sub>12</sub>** in fumed, ground, annealed, and melted states were investigated to obtain further information of the PFC materials. The time-resolved fluorescence curves and the lifetime data are illustrated in Fig 6 and Table 1, respectively. Two relaxation pathways were found in the fluorescence decays, indicating that the timeresolved PL spectra of the compound included independent emissions from the segments with different  $\pi$ -conjugation extent



**Fig. 6.** Time-resolved emission-decay curves of (A) **AnPh**<sub>3</sub>, (B) **AnPh**<sub>6</sub>, and (C) **AnPh**<sub>12</sub> in fumed, ground, annealed, and melted states.

#### Table 1

Solid-state fluorescence lifetime data of AnPh<sub>3</sub>, AnPh<sub>6</sub>, and AnPh<sub>12</sub> in fumed, ground, annealed, and melted states

Sample	State	$\tau_1 (ns)^a$	$A_1^{\mathbf{b}}$	$\tau_2(ns)^a$	$A_2^{\mathbf{b}}$	$<\tau>(ns)^{c}$
AnPh <sub>3</sub>	Fumed	1.32	0.40	3.20	0.60	2.45
	Ground	1.20	0.41	3.17	0.59	2.36
	Annealed	1.43	0.52	3.43	0.48	2.39
	Melted	0.71	0.39	2.23	0.61	1.64
AnPh <sub>6</sub>	Fumed	1.38	0.46	3.50	0.54	2.52
	Ground	1.25	0.38	3.44	0.62	2.61
	Annealed	1.34	0.41	3.27	0.59	2.48
	Melted	0.97	0.25	2.84	0.75	2.37
AnPh <sub>12</sub>	Fumed	1.57	0.52	3.57	0.48	2.53
	Ground	1.68	0.42	3.80	0.58	2.91
	Annealed	1.82	0.53	3.62	0.47	2.67
	Melted	0.99	0.17	5.06	0.83	4.37

<sup>a</sup> Fluorescence lifetime.

Fractional contribution. <sup>c</sup> Weighted mean lifetime.

according to the detected multiple lifetimes. The weighted mean lifetimes  $<\tau>$  of the fumed, annealed, and ground samples didn't exhibit obvious differences, although the fluorescent emission wavelength of them showed significant divergences. Interestingly, the  $<\tau>$  of melted sample emerged stupendous discrepancy compared with the other states. While the melted **AnPh<sub>3</sub>** showed the shortest  $\langle \tau \rangle$  among the various states, and the melted **AnPh<sub>6</sub>** sample showed similar  $\langle \tau \rangle$  with its other states, whereas the melted **AnPh<sub>12</sub>** compound exhibited the longest  $<\tau>$  than that of the other three states. The reason of these divergences is still not clear, but the changes of the conjugation extent in the solid-state aggregates may be the major cause for the PFC mechanism. From the HOMOs and LUMOs of three derivatives via quantum mechanical computations, the conjugation extent didn't seem any difference in the molecules with various alkyl chain lengths. The various alkyl chain lengths mainly affect the crystalline structure and melting point, which can be observed from the SWAXS patterns and DSC curves of these compounds. This result indicated that the aggregation state of the derivatives could be altered with different alkyl chain lengths, thus affecting the macroscopic properties including fluorescent spectra and fluorescence decay times.

# 3. Conclusions

In summary, we have reported new alkyl length-dependent solid-state PFC characteristics of AIE-active 9,10-bis[(N-alkylphenothiazin-3-yl)vinyl]anthracene derivatives with different propyl, hexyl, and dodecyl side chains (AnPh<sub>3</sub>, AnPh<sub>6</sub>, and AnPh<sub>12</sub>). The PFC behaviors were investigated and found that red-shifted extent of the ground samples would increased as the length of alkyl chain increased. The melted samples of the synthesized derivatives also exhibited proportional alkyl length-dependent features with respect to their fumed states. The derivatives showed reversible significant PFC properties and reproducibility in various states including fumed, ground, annealed, and melted states. These excellent properties make the compounds promising stimuli-responsive and smart luminescent materials for pressure-sensors, information-recording, and light-emitting device applications. The alkyl length-dependent relationship established in this contribution should be helpful in guiding researchers to synthesize PFC materials and in-depth understand the PFC mechanism.

#### 4. Experimental procedure

# 4.1. General

4.1.1. Materials and characterization. 9,10-Bis(chloromethyl)anthracene, phenothiazine, 1-bromopropane, 1-bromohexane, and 1bromododecane purchased from Alfa Aesar were 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. Ultrapure water was used in the experiments.

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured on a IEOL 400 MHz spectrometer [CDCl<sub>3</sub> as solvent and tetramethylsilane (TMS) as the internal standard]. HRMS was obtained on Shimadzu LCMS-IT-TOF high resolution mass spectrometry. Fluorescence spectra and lifetime were measured on FLS 920 lifetime and steady state spectrometer. Solid state UV-vis spectra were recorded on a Hitachi U4100 UV-vis-NIR spectrophotometer. Differential scanning calorimetry (DSC) curves were performed on TA Instruments DSC Q2000 at a heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub> atmosphere. 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 form from 0.06 to 29 nm<sup>-1</sup>.

The THF-water mixtures 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 prepared by grinding using a mortar and pestle. The fumed samples were prepared by treating the ground samples with CH<sub>2</sub>Cl<sub>2</sub> vapors for 5 min. The annealing experiments were done on a hot-stage with an automatic temperature control system for 5 min with the annealing temperatures at 150 °C. The recrystallized samples were obtained via recrystallized treatment with THF/EtOH mixed solvents.

4.1.2. Synthesis of AnPh<sub>3</sub>, AnPh<sub>6</sub>, and AnPh<sub>12</sub>. Synthetic route of the compounds AnPh<sub>3</sub>, AnPh<sub>6</sub>, and AnPh<sub>12</sub> was showed in Scheme S1. The intermediate 1 was synthesized according to the literature.<sup>37</sup> The phenothiazine-3-carbaldehyde intermediates (**2**) with different alkyl chain length (R=n-C<sub>3</sub>H<sub>7</sub>, n-C<sub>6</sub>H<sub>13</sub>, n-C<sub>12</sub>H<sub>25</sub>) were synthesized according to the literature.<sup>35,58,5</sup>

Synthesis of 9,10-bis[(N-propylphenothiazin-3-yl)vinyl]anthracene (**AnPh<sub>3</sub>**). Tetraethyl anthracene-9,10-diylbis(methylene) diphosphonate (1) (0.24 g, 0.50 mmol) and 10-propyl-10H-phenothiazine-3-carbaldehyde (2) (0.32 g, 1.2 mmol) were dissolved in THF (20 mL), and then t-BuOK (0.3 g) was added under N<sub>2</sub> gas. The solution was stirred at room temperature overnight. After removing the solvent under reduced pressure, the residue was recrystallized with THF/EtOH to give AnPh<sub>3</sub> (0.16 g, 97% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 1.05 (t, 6H, J=7.2 Hz), 1.83–1.93 (m, 4H), 3.87 (t, 4H, J=7.2 Hz), 6.77 (s, 1H), 6.82 (s, 1H), 6.85–6.98 (m, 6H), 7.11–7.21 (m, 4H), 7.34–7.53 (m, 8H), 7.74 (s, 1H), 7.79 (s, 1H), 8.35 (q, 4H, J=3.2 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 145.08, 145.06, 132.73, 131.98, 129.70, 126.55, 125.51, 125.25, 115.54, 115.51, 49.41, 20.27, 11.42. HRMS calcd for C<sub>48</sub>H<sub>40</sub>N<sub>2</sub>S<sub>2</sub>, [M+H]<sup>+</sup>: 709.2706, found 709.2712.

The syntheses of 9,10-bis[(N-hexylphenothiazin-3-yl)vinyl]anthracene (**AnPh**<sub>6</sub>) and 9,10-bis[(*N*-dodecylphenothiazin-3-yl)vinyl] anthracene (AnPh<sub>12</sub>) were similar to that of AnPh<sub>3</sub>.

**AnPh<sub>6</sub>** (94% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 0.90 (t, 6H, J=3.2 Hz), 1.28–1.52 (m, 12H), 1.85 (quint, 4H, J=6.8 Hz), 3.90 (t, 4H, J=7.6 Hz), 6.78 (s, 1H), 6.82 (s, 1H), 6.85–6.97 (m, 6H), 7.12–7.20 (m, 4H), 7.37-7.51 (m, 8H), 7.75 (s, 1H), 7.79 (s, 1H), 8.36 (q, 4H, I=3.2 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 145.09, 145.06, 132.73, 131.95, 129.70, 126.56, 125.25, 124.43, 115.48, 115.46, 47.70, 31.58, 27.00, 26.76, 22.71, 14.10. HRMS calcd for C54H52N2S2, [M+H]<sup>+</sup>: 793.3645, found 793.3636.

**AnPh<sub>12</sub>** (98% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 0.88 (t, 6H, J=3.2 Hz), 1.23–1.38 (m, 32H), 1.46 (quint, 4H, J=3.2 Hz), 1.85 (quint, 4H, J=7.2 Hz), 3.89 (t, 4H, J=7.2 Hz), 6.78 (s, 1H), 6.82 (s, 1H), 6.86-6.97 (m, 6H), 7.13-7.20 (m, 4H), 7.37-7.53 (m, 8H), 7.75 (s, 1H), 7.79 (s, 1H), 8.36 (q, 4H, J=3.2 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 145.08, 145.06, 132.73, 131.95, 129.70, 125.43, 125.25, 124.43, 115.48, 115.46, 47.69, 32.00, 29.72, 29.66, 29.63, 29.43, 29.36, 27.05, 27.01, 22.77, 14.20. HRMS calcd for  $C_{66}H_{76}N_2S_2$ ,  $[M+Na]^+$ : 983.5342, found 983.5392.

# Acknowledgements

This research was supported by the National Science Foundation of China (Nos. 21134004, 21201108), and the National 973 Project (No. 2011CB935700), China Postdoctoral Science Foundation (2013T60100, 2012M520243).

# Supplementary data

Detailed information about synthetic route, normalized fluorescent spectra, UV–vis spectra, SWAXS patterns, and DSC curves of **AnPh<sub>6</sub>** and **AnPh<sub>12</sub>** in different states were provided. Supplementary data related to this article can be found at http://dx.doi.org/ 10.1016/j.tet.2013.12.015.

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