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RESEARCH ARTICLE

Synthesis and optical properties of soluble low bandgap poly (pyrrole methine) with alkoxyl substituent

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Abstract A soluble low bandgap poly (pyrrole methine) with alkoxyl substituent, poly {(3-hexanoyl)pyrrole-[2,5-diyl(*p*-tetradecyloxybenzylidene)]} (PHPDTBE), was synthesized and characterized by ^{1}H nuclear magnetic resonance (^{1}H-NMR), Fourier transform-infrared (FT-IR), elemental analysis (EA) and gel permeation chromatography (GPC). PHPDTBE was readily soluble in weak polar organic solvents. The absorption peaks of PHPDTBE solution and film were located at around 458 and 484 nm, respectively. The optical bandgaps of PHPDTBE film for indirect allowed and direct allowed transitions were measured to be 1.66 and 2.35 eV, respectively. PHPDTBE film had few defects in the energy band and the Urbach energy of PHPDTBE film was calculated to be about 0.19 eV. The resonant third-order nonlinear optical susceptibilities of PHPDTBE solution and film measured by degenerate four-wave mixing (DFWM) technique at 532 nm were all in the order of 10^{-8} esu, which was about 1~3 orders of magnitude larger than that of the other ordinary π-conjugation polymers.

Keywords poly (pyrrole methine), low bandgap, Urbach energy, third-order nonlinear optical property

1 Introduction

The nonlinear optical (NLO) π-conjugated polymers have attracted a lot of interests since Sauteret et al. first reported that polydiacetylene crystal with *p*-toluene sulfonic acid substituent (PDA-PTS) showed large third-order NLO susceptibility ($\chi^{(3)}$) in 1976 [1]. The NLO π-conjugated polymers could be applied widely in photoelectric modulator, optical switching, optical storage and other all-optical devices because of their advantages such as large NLO susceptibility, ease of processing and convenience of molecular design [2–4].

According to theoretical analysis, the π-conjugated polymers with long effective conjugation length and low bandgap were the most likely candidates for NLO materials. Poly (pyrrolyl methine) was one of the typical NLO π-conjugated polymers with low bandgap and high delocalization degree of π electron [5,6]. Unfortunately, the unsubstituted poly (pyrrolyl methine) was difficult to dissolve in common solvents, which limited its practical application seriously. In our previous work [7], poly (pyrrolyl methine) grafted butyryl and *p*-hydroxyphenyl groups (PBPDHBE) was synthesized and the results showed that PBPDHBE possessed low optical bandgap and large third-order NLO susceptibility, but only dissolved in strong polar solvents such as *N*-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO) and N,N-Dimethylformamide (DMF), which made it difficult to obtain high-quality thin film for its practical application. In this paper, a soluble low bandgap poly(pyrrole methine) with alkoxyl substituent, poly{(3-hexanoyl)pyrrole-[2,5-diyl(*p*-tetradecyloxybenzylidene)]} (PHPDTBE) was synthesized by the reaction of 1-bromotetradecane with hydroxyl group at the benzene in order to graft the long-chain flexible tetradecyloxy group onto the backbone chain of poly(pyrrolyl methine) and further improve its solubility. Moreover, the molecular structure, solubility, UV-Visible absorption, optical bandgap, Urbach energy and third-order NLO properties of PHPDTBE were also discussed preliminarily.

2 Experiments

2.1 Reagents

Pyrrole was freshly distilled and stored under the aerated nitrogen condition in a refrigerator (0°C) until required. Terahydrofuran (THF) was distilled over sodium metal and stored in the dark prior to use. Tosyl chloride had been

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recrystallized from petroleum ether and stored in the dark before it was used. Dichloromethane (CH_2Cl_2) was distilled over anhydrous magnesium sulfate and stored in the dark prior to use. Other reagents were used as supplied.

2.2 Measurements

^{1}H nuclear magnetic resonance (^{1}H-NMR) spectrum was obtained with a Bruker Advance III 400 NMR spectrometer, deuteriochloroform ($CDCl_3$) was used as a solvent and tetramethylsilane (TMS) as an internal standard. The Fourier transform-infrared (FT-IR) spectrum was measured with potassium bromide (KBr) pellet by a Perkin-Elmer Lambda 900 FT-IR spectrometer. Elemental analysis was performed on a Vario EL III analyzer. The molecular weight and its distribution were determined by gel permeation chromatography (GPC) using a Waters 1515 with THF as an eluent and polystyrene (PS) as a standard. UV-Visible absorption spectrum was recorded on a Hitachi U-2001 UV-Visible spectrometer.

2.3 Synthesis

The synthetic route to PHPDTBE and its intermediates was given in Fig. 1. 0.1 mol *p*-hydroxybenzaldehyde was added to a solution of 0.11 mol sodium ethoxide in 100 mL ethanol at refluxing temperature under nitrogen. After refluxing 30 min, 0.12 mol 1-bromotetradecane in 45 mL ethanol was added in the reaction mixture. After continuous stirring for 24 h at refluxing temperature in nitrogen atmosphere, the reaction mixture was poured into water. The organic precipitate was filtered and recrystallized from ethanol to give the desired product *p*-tetradecoxybenzaldehyde (TB).

0.18 mol potassium metal was added to a solution of 0.02 mol pyrrole in 60 mL THF at room temperature under nitrogen. After refluxing 2 h, the reaction mixture was cooled at room temperature and 0.16 mol tosyl chloride in 120 mL THF was added. After 24 h at room temperature under stirring in nitrogen atmosphere, the solution was poured into water. The organic precipitate was filtered and recrystallized from methanol to give the desired product 1-tosylpyrrole (TP).

0.055 mol hexanoyl chloride was added at 0°C to a solution of 0.06 mol aluminum chloride in 250 mL CH_2Cl_2 under nitrogen. After stirring for 30 min, 0.05 mol TP in 50 mL CH_2Cl_2 was added slowly. After continuous stirring for 1.5 h at room temperature, the reaction mixture was

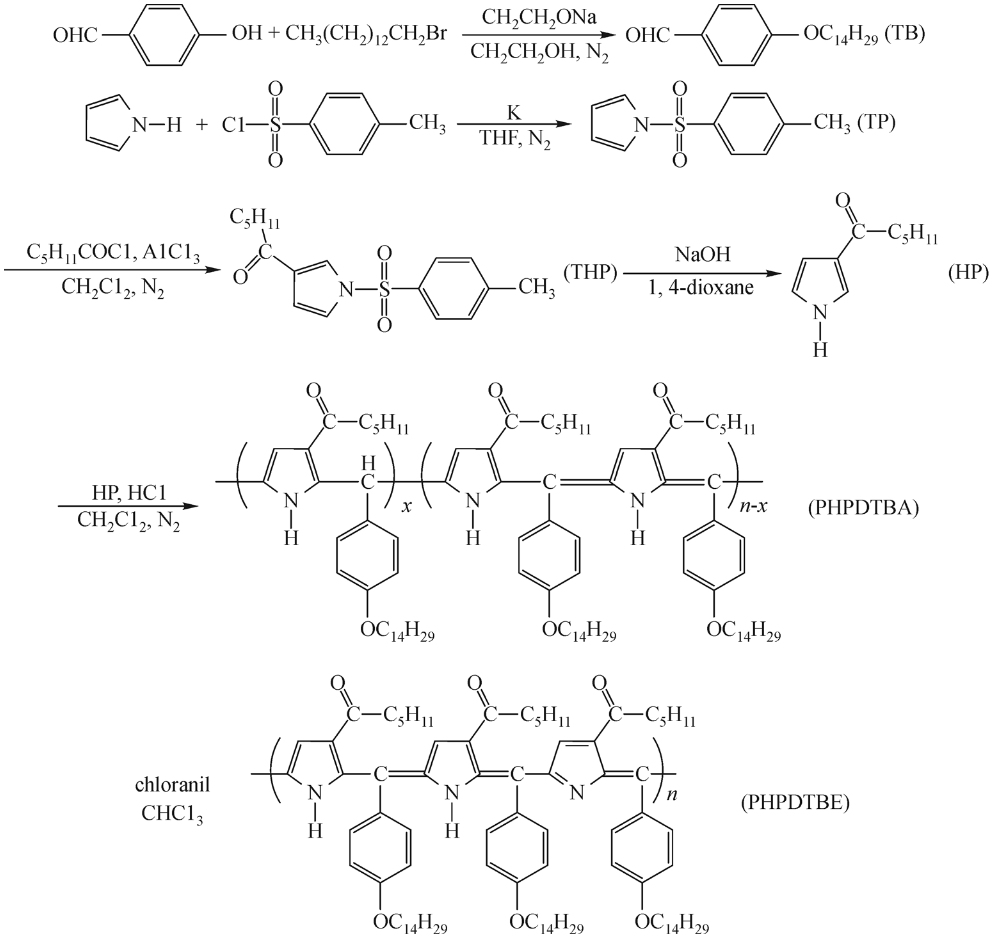

Fig. 1 Synthetic route to PHPDTBE and its intermediates

poured into cold water and extracted with CH_2Cl_2. The organic phase was washed with cold water until the pH reached 7, and then the organic phase was dried over anhydrous magnesium sulfate. After evaporation of the solvent, the remained was recrystallized from petroleum ether to give the desired product 1-tosyl-3-hexanoylpyrrole (THP).

Twenty mmol THP in 80 mL dioxane was added to a solution of 0.16 mol sodium hydroxide (NaOH) in 80 mL deionized water. After continuous stirring at 60°C for 12 h, the organic phase was separated and then the aqueous phase was extracted with ethyl acetate. The combined organic phase was dried over anhydrous magnesium sulfate. After evaporation of the solvent, the remained was recrystallized from hexane to give desired product 3-hexanoylpyrrole (HP).

Under stirring and nitrogen, the hydrochloric acid (HCl) was added to a solution of 16 mmol TB in 40 mL CH_2Cl_2 until the pH reached 1, and then 16 mmol HP in 40 mL CH_2Cl_2 was added in 30 min. Continued to stir for 10 h at room temperature, the solvent was evaporated. The remainder was immersed in 2 mol/L ammonia water for 6 h, and then was washed with the deionized water until the pH of water phase reached 7. The product poly {(3-hexanoyl)pyrrole-[2,5-diyl(*p*-tetradecyloxybenzylidane)]} (PHPDTBA) was obtained after the solid product was washed with ethanol until the transparent ethanol filtrate was observed. 3 mmol chloranil was added to a solution of 1.0 g PHPDTBA in 30 mL trichloromethane ($CHCl_3$). After continuous stirring for 8 h, $CHCl_3$ was evaporated and the product PHPDTBE was obtained after the remainder was washed with ether until the ether filtrate was transparent. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.43 (s, 1H, N-H), 7.60~7.08 (m, 5H, 1py-H and 4Ar-H), 4.04 (t, 2H, $ArOCH_2$), 2.83 (t, 2H, $COCH_2$), 1.85 (m, 2H, $ArOCH_2$-CH_2-), 1.60 (m, 2H, $COCH_2$-CH_2-), 1.28 (s, 26H, $C_{11}H_{22}$ and C_2H_4), 0.88 (s, 6H, $2CH_3$); IR (KBr, cm^{-1}): ν = 3453.84, 2923.65, 2852.55, 1643.14, 1599.02, 1503.33, 1466.54; Anal. calcd for $C_{87}H_{125}N_3O_6$: C 80.23, H 9.85, N 3.02; found: C 81.54, H 9.79, N 3.12. GPC (THF, $g \cdot mol^{-1}$): Mn = 5673, Mw = 6481; PDI: 1.14.

3 Results and discussion

3.1 Solubility

A certain amount of PHPDTBE powder was added to 10 mL organic solvent. After stirring at room temperature for 24 h, the insoluble substance was separated by centrifugation. The solubility of PHPDTBE listed in Table 1 was calculated after the insoluble substance was filtered, dried and weighted. The results showed that PHPDTBE was readily soluble in weak polar organic solvents such as benzene, CH_2Cl_2, THF and $CHCl_3$, and the solubility improved with the increase of the polarity of solvents. In addition, PHPDTBE was nearly insoluble in strong polar organic solvents such as DMF and DMSO. It was due to that the polarity of poly (pyrrolyl methine) decreased with the grafting of weak polar flexible groups including hexanoyl and tetradecyloxy groups onto the backbone chain of poly (pyrrolyl methine).

3.2 Light absorption spectral studies

The UV-Visible absorption spectra of PHPDTBA and PHPDTBE in CH_2Cl_2 solutions as well as PHPDTBE film were shown in Fig. 2. The absorption maximum of PHPDTBA in CH_2Cl_2 solution was located at 352 nm assigned to the π-π* transition of π-conjugated electron resulting from the partly π-conjugated structure in PHPDTBA. Compared with PHPDTBA, PHPDTBE had a significant optical absorption located at 458 nm ascribed to the π-π* transition of π-conjugated electron, which confirmed that the completed π-conjugated backbone chain formed in PHPDTBE. In addition, the UV-Visible absorption relative to π-π* transition of PHPDTBE film showed a red shift to 484 nm, which indicated that the changes of aggregation state and molecular configuration of PHPDTBE from in solution form to in film form [8].

3.3 Optical constants

The optical constants of PHPDTBE such as optical bandgap (E_g) and Urbach energy (E_u) were obtained by UV-Visible absorption spectra in this paper. According to the Tauc formula, the relationship between the E_g value and photon energy ($h\nu$) was as follows [9,10].

$$(\alpha h\nu)^n \propto C(h\nu - E_g), \tag{1}$$

where α was the absorption coefficient, $h\nu$ was the energy of incident photons, and n was the power, which characterized the electronic transition, whether it was direct or indirect during the absorption process in the K-space. Specially, n was 2, 2/3, 1/2 and 1/3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions, respectively. The factor C depended on the transition probability and could be assumed to be constant within the optical frequency range. As shown in Fig. 3, the bandgaps of PHPDTBE for indirect allowed and

Table 1 Solubility of PHPDTBE in various solvents

solvent (polarity)	benzene (3.0)	CH_2Cl_2 (3.4)	THF (4.2)	$CHCl_3$ (4.4)	DMF (6.4)	DMSO (7.2)
solubility/($g \cdot mL^{-1}$)	0.48	0.54	0.61	0.70	insoluble	insoluble

Note: the figures in bracket stand for the polarity of solvents

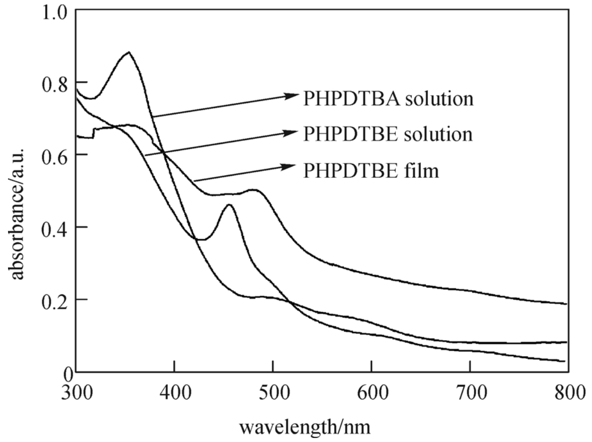

Fig. 2 UV-Visible absorption spectra of PHPDTBA solution, PHPDTBE solution and PHPDTBE film

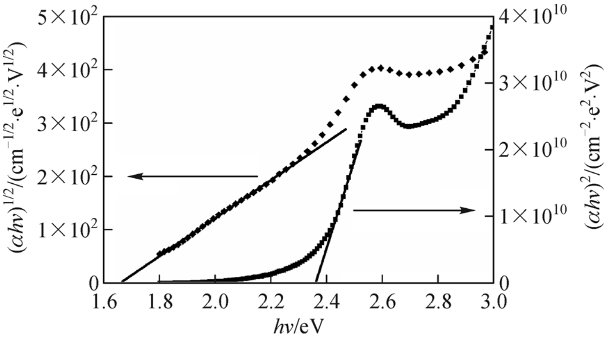

Fig. 3 Optical bandgap of PHPDTBE

direct allowed transitions were 1.66 and 2.35 eV, respectively. The low E_g value of PHPDTBE could be contributed to the formation of large π-conjugated backbone chain, and the withdrawing electron group such as hexanoyl group and donating electron group such as *p*-tetradecyloxyphenyl group on the backbone chain of PHPDTBE, that the former could lower the lowest unoccupied molecular orbital (LUMO) energy and the later could raise the highest occupied molecular orbital (HOMO) energy, resulting in the decrease of transition energy of π-conjugated electron between valence band and conduction band.

The absorption coefficient near the band edge for PHPDTBE film showed an exponential dependence on the photon energy ($h\nu$), which followed the Urbach formula [11],

$$\alpha(\nu) = \alpha_0 \exp(h\nu/E_u), \tag{2}$$

where α_0 was a constant, ν was the frequency of radiation, and E_u was Urbach energy, which was a parameter indicative of mechanism of optical transition. The E_u value could be calculated from the reciprocal of the slope of the straight line in the linear region of a plot of natural logarithm of the absorption coefficient with the photon energy shown in Fig. 4. It was found that the E_u value for PHPDTBE film was calculated to be about 0.19 eV, which suggested that PHPDTBE film had few defects in the energy band [12].

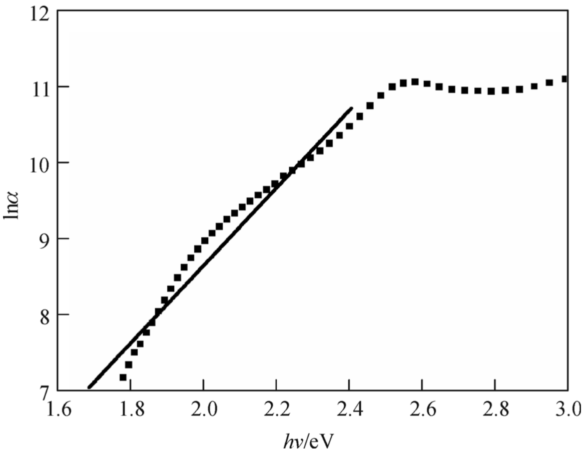

Fig. 4 Urbach energy of PHPDTBE

3.4 Optical nonlinearity

The third-order NLO properties of PHPDTBE in CH_2Cl_2 solution and in film state were measured by the DFWM technique and a schematic representation for experimental setup was shown in Fig. 5. The second harmonic monochromatic light (532 nm) from a *Q*-switched Nd: YAG laser frequency-doubled at a repetition rate of 10 Hz with a pulse width of 35 ps was used as the pump source. DFWM measurement was performed at room temperature in a phase conjugate (PC) geometry, where the two strong counter propagating pump beams (I_f, I_b) and a weak probe beam (I_p) with the same wavelength interacted in a NLO medium while satisfying the temporal and spatial coherence. When phase matching condition was fulfilled, a new PC beam (I_s) could generate along the counter propagating direction with respect to I_p. The output I_s was measured by an RjP-765a Si probe. The experimental setup for the DFWM technique was calibrated by measuring the $\chi^{(3)}$ value of carbon disulfide (CS_2) of 0.68×10^{-12} esu, which was in agreement with that reported elsewhere [13,14].

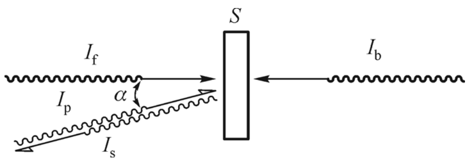

Fig. 5 Schematic representation for experimental setup for the DFWM technique, where I_f, I_b, I_p and I_s were forward pump beam intensity, backward pump beam intensity, probe beam intensity and signal beam intensity, individually; *S* was the sample; *α* was the intersection angle of forward pump beam and probe beam, which was about 5°

The UV-Visible absorption spectra of PHPDTBE solution and film showed obvious optical absorption at the wavelength of 532 nm, thus the resonant third-order optical nonlinearity of PHPDTBE was measured in this paper. Being similar to those reported elsewhere, the resonant $\chi^{(3)}$ value of PHPDTBE could be obtained by comparing the measured signal for PHPDTBE with that for the reference (CS_2) under the same experimental condition (Eq. (3)) [15,16]. The nonlinear refractive index (n_2) and the second-order hyperpolarisability (γ_S) were calculated by using Eqs. (4) and (5) [17,18].

$$\chi_S^{(3)} = \left(\frac{I_S}{I_R}\right)^{1/2}\left(\frac{n_S}{n_R}\right)^2 \frac{a_S L_S \exp(a_S L_S/2)}{1-\exp(-a_S L_S)}\chi_R^{(3)}, \tag{3}$$

$$n_2 = \frac{12\pi\chi_S^{(3)}(\mathrm{esu})}{n_S^2}, \tag{4}$$

$$\gamma_s = \frac{\chi_S^{(3)}}{Nf^4}. \tag{5}$$

Here, the subscripts 'S' and 'R' referred to PHPDTBE and CS_2, respectively. I was the intensity of the signal beam, L was the sample path length and the thickness of the PHPDTBE film that was prepared on quartz glass plate by spin coating from the PHPDTBE solution at room temperature was about 340 μm, n was the linear refractive index, α was the linear absorption coefficient and the α values of the PHPDTBE solution and the PHPDTBE film at 532 nm were 6.26×10^3 and $1.45 \times 10^4\ \mathrm{cm}^{-1}$, respectively, N was the number density of the PHPDTBE in CH_2Cl_2 solution (in cm^3) and the concentration of the PHPDTBE solution was 4.38×10^{-4} mol/L, and f was the Lorentz local field factor given by

$$f = \frac{n_S^2+2}{3}. \tag{6}$$

The obtained values of $\chi^{(3)}$, n_2 and γ_s were outlined in Table 2.

Table 2 Third-order NLO properties of PHPDTBE solution and film studied at 532 nm

sample	$\chi^{(3)}$/ (10^{-8}esu)	n_2/ (10^{-7}esu)	γ_s/(10^{-26}esu)
PHPDTBE solution	2.05	3.63	2.16
PHPDTBE film	3.49	4.72	–

It was found that the resonant $\chi^{(3)}$ values of PHPDTBE solution and film were all in the order of 10^{-8} esu, which were about 1~3 orders of magnitude larger than that of the other ordinary π-conjugation polymers, such as polydiacetylene (in 10^{-10} esu) [19], polyacetylene (in 10^{-10} esu) [20], polythiophene (in 10^{-9} esu) [21], polyaniline (in 10^{-10}~10^{-11} esu) [22] and poly(*p*-phenylenevinylene) (in 10^{-9}~10^{-11} esu) [23]. According to the theoretical model presented by Sauterret, the low bandgap made remarkable contributions to the large $\chi^{(3)}$ value of π-conjugated polymer [1]. Therefore, it was reasonable that PHPDTBE synthesized in this paper with low E_g value exhibited large $\chi^{(3)}$ value. In addition, the electron acceptor such as hexanoyl group and electron donor such as *p*-tetradecyloxyphenyl group on the backbone chain of PHPDTBE had also contributions to the large $\chi^{(3)}$ value.

4 Conclusions

In summary, a soluble low bandgap poly(pyrrole methine) with alkoxyl substituent, poly{(3-hexanoyl)pyrrole-[2,5-diyl(*p*-tetradecyloxybenzylidene)]} (PHPDTBE), was synthesized and characterized successfully in this paper. PHPDTBE was readily soluble in the weak polar solvents and the solubility improved with the increase of the polarity of solvents. The optical absorption of PHPDTBE solution and film was broad and the absorption peaks were located at around 458 and 484 nm, respectively. PHPDTBE had a low optical bandgap (E_g) and the E_g values of PHPDTBE film for indirect allowed and direct allowed transitions were measured to be 1.66 and 2.35 eV, respectively. PHPDTBE film had few defects in the energy band and the Urbach energy (E_u) value was calculated to be about 0.19 eV. PHPDTBE exhibited preeminent NLO properties and the resonant $\chi^{(3)}$ values of PHPDTBE solution and film measured by DFWM technique at 532 nm were all in the order of 10^{-8} esu, which was about 1~3 orders of magnitude larger than that of the other ordinary π-conjugation polymers, because of its low E_g value and the substituent groups including hexanoyl group and *p*-tetradecyloxyphenyl group on the backbone chain of PHPDTBE.

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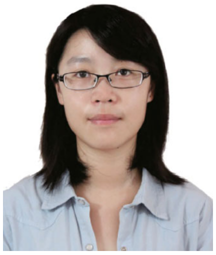

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