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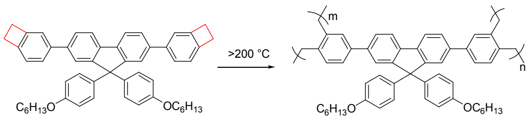
Benzocyclobutene resin with fluorene backbone: a novel thermosetting material with high thermostability and low dielectric constant

A new benzocyclobutene monomer with fluorene backbone was synthesized, which showed low melting point and good solubility and can be thermally converted to a cross-linked network with low dielectric constant and high thermostability, suggesting that the new monomer had potential applications in electrical and microelectronic industry.

Yuanqiang Wang, Jing Sun, Kaikai Jin, Jiajia Wang, Chao Yuan, Jiawei Tong, Shen Diao, Fengkai He, and Qiang Fang*

ToC figure



Polymer showed:

Dielectric constant < 2.75 (0.15-30 MHz)

5% weight loss temperatureat 437 °C in N_2

a char yield of 47.6% at 1000 °C in N_2

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PAPER

Benzocyclobutene resin with fluorene backbone: a novel thermosetting material with high thermostability and low dielectric constant

Yuanqiang Wang,[a§] Jing Sun,[a§] Kaikai Jin,[a] Jiajia Wang,[a] Chao Yuan,[a] Jiawei Tong,[a] Shen Diao,*[ab] Fengkai He,[a] and Qiang Fang*[a]

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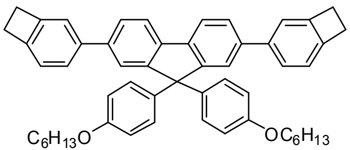
A fluorene-based monomer(**FB**) with thermally cross-linkable benzocyclobutene groups is reported here. This monomer showed good solubility in the common organic solvents and had low melting point (128 °C). When being treated at high temperature (> 200 °C), the monomer converted to a cross-linked network structure (**PFB**).TGA data exhibited that **PFB** had high thermostability with the 5% weight loss temperature of 437 °C and 372 °C in N_2 and air, respectively. Moreover, **PFB** showed a char yield of 47.6% at 1000 °C in N_2. In regard to the electrical properties, **PFB** indicated an average of dielectric constants of about 2.7 ranging from 0.15 MHz to 30 MHz. All these results suggest that **FB** could be used as the varnish for insulating enameled wire in electrical industry, and as encapsulation resins in microelectronic industry.

1. Introduction

Fluorene-based π-conjugated polymers and small molecules have been received much attention in the past decades because of their excellent optical properties and potential applications in the fields of information and biology.[1-7] Among these polymers and small molecules, the 9,9-dialkylfluorene derivatives have been well investigated due to that their properties can be conveniently controlled by converting the substituent groups at the 9th position of the fluorene molecules.[8-12] Therefore, there have been a lot of reports regarding to the polymers or small molecules containing a 9,9-dialkyl-2,7-fluorene unit. These fluorene-containing derivetives have been utilized in organic light emiting diodes (OLEDs) and bioscience fields.[13-20]

In comparison with the above mentioned π-conjugated fluorene-based derivatives, however, the insulating fluorene-based derivatives have attracted less attention. It is noted that fluorene is derived from coal tar and its large output should be consumed. Accordingly, developing the new application of fluorene is very necessary.

Recently, we have paid much attention to develop the new materials with high thermostability and low dielectric constants, which could be used in microelectronic industry.[21-24] On the basis of high thermostability and large free volume of fluorene moiety, the introduction of fluorene groups into the backbone of the organic materials may endow the materials with good heat resistance and high insulating capacity. On the other hand, benzocyclobutene-based derivatives have recognized as high performance materials.[25-27] Thus, the combination of fluorene and benzocyclobutene in a molecule could obtain a new high performance material. This inspired us to design and synthesize a molecule with a fluorene backbone and cross-linkable benzocyclobutene groups. The chemical structure of the new molecule (**FB**) is shown in Scheme 1. This compound showed good solubility in common organic solvents and low melting point (128 °C). When treated at high temperature (> 200 °C), **FB** converted to a cross-linked network structure (**PFB**), which exhibited high thermostability and low dielectric constant. This is a new example of low-*k* benzocyclobutene (BCB) resin with fluorene backbone.[28] Here, we report the details.



FB

Scheme 1. Chemical structure of new monomer in this work**.**

2. Experimental

2.1 Materials

All starting chemicals were purchased from Aldrich and used as received. Benzocyclobutene-4-boronic acid was purchased from Chemtarget Technologies Co., Ltd, China, and purified by column chromatography on SiO_2 using a mixture of ethyl acetate and *n*-hexane (40:1, v/v) as the eluent. The obtained compound showed a purity of 98.7% (HPLC). Dimethylsulfone (DMSO) was dried over CaH_2 and distilled under reduced pressure before use.

2.2 Measurement

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 spectrometer. FT-IR spectra were run on a Nicolet spectrometer with KBr pellets. Differential scanning calorimetry (DSC) was determined with TA Instrument DSC (Q200) at a heating rate of 10 K/min under nitrogen flow with a rate of 50 mL/min. The DSC measurement was performed for 3 times for each sample. For each test, the Tzero aluminum pans were used and the filled amount of the sample was 4-7 mg. Thermogravimetric analysis (TGA) was performed on a TG209F1 apparatus at a heating rate of 10 K/min in a nitrogen atmosphere or air with a flow rate of 30 mL/min. The TGA measurement was performed for 3 times for each sample. For each experiment, platinum boats were used, and grinded powder-like samples with a filled amount of near 10 mg were employed.

The dielectric constant (k) of the cured samples was measured ranging from 0.15 MHz to 30 MHz on cured cylindric samples (average diameters were 10 mm and thicknesses were 2-3 mm, respectively) at room temperature using a 4294A Precision Impedance Analyzer (Agilent). Before each measurement the samples were thoroughly dried under vacuum.

2.3 Synthesis

Synthesis of 2,7-dibromo-9,9-bis(4-hydroxyphenyl)fluorene (1).[29] A solution of 2,7-dibromofluoren-9-one (14.0 g, 41.0 mmol), phenol (23.8 g, 246 mmol), and methansulfonic acid (50 mL) was stirred at room temperature for overnight. Then the mixture was poured into water, and the obtained solid was filtered and washed with water. The crude **1** thus prepared. To purify **1**, a solution of crude **1** in ethyl acetate was added drop wise to *n*-hexane to obtain a precipitate. The precipitate was filtrated and dried under reduced pressure to give pure **1** as a white powder with a yield of 90%. ^{1}H NMR (400 MHz, acetone-d_6, ppm) δ 8.33 (s, 2H), 7.85 (d, 2H), 7.56 (d, 4H), 7.02 (d, 4H), 6.76 (d, 4H). ^{13}C NMR (100 MHz, acetone-d_6, ppm) δ 156.53, 154.34, 137.99, 135.36, 130.68, 129.05, 128.98, 122.21, 121.29, 115.24, 64.46. EI-MS(m/z): $M^+ = 508$ (100%).

Synthesis of 2,7-dibromo-9,9-bis(4-hexyloxyphenyl)fluorene (2).[29] A mixture of **1** (10.16 g, 20.0 mmol), K_2CO_3 (6.22 g, 45.0 mmol), and DMSO (50 mL) was stirred at 75 °C for 0.5 h under argon atmosphere. To the obtained solution was added 1-bromohexane (6.00 g, 36.3 mmol) through syringe. The mixture was stirred at 75 °C for overnight. After being cooled to room temperature, the solution was diluted by ethyl acetate (100 mL). The separated organic phase was washed with water (3×60 mL) and dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was obtained, which was purified by a flash column chromatography on SiO_2 using a mixture of petroleum ether and CH_2Cl_2 as the eluent (10:1 v/v). Pure **2** was obtained as a colorless oil with a yield of 83.7%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.56 (d, 2H), 7.45 (d, 4H), 7.04 (d, 4H), 6.76 (d, 4H), 3.90 (s, 4H), 1.73 (d, 4H), 1.37 (d, 12H), 0.91 (d, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 158.28 , 153.81, 137.88, 136.28, 130.76, 129.32, 129.03, 121.86, 121.55, 114.39, 67.95, 64.44, 31.62, 29.28, 25.78, 22.66, 14.11. EI-MS (m/z): $M^+ = 676.1$ (100%).

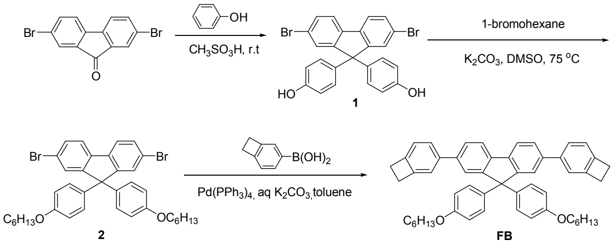
Synthesis of 2,7-dibenzocyclobutene-9,9-bis(4-hexyloxyphenyl)fluorene (FB). To a mixture of **2** (0.68 g, 1 mmol), benzocyclobutene-4-boronic acid (0.44 g, 3 mmol), tetrakis-(triphenylphosphine)palladium ($Pd(PPh_3)_4$) (0.0058 g, 0.05 mmol) and toluene (10 mL) was added aq K_2CO_3 solution (5 mL, 2 M) under argon. The mixture was heated to 75 °C and maintained at the temperature for 12 h. After being cooled to room temperature, the mixture was diluted with ethyl acetate (30 mL), and filtered. The separated organic phase was washed with water (3 × 60 mL), and dried over anhydrous Na_2SO_4, filtered, and concentrated. The obtained residue was purified by flash column chromatography on SiO_2 using a mixture solvent of petroleum ether and CH_2Cl_2 as the eluent (20:1 v/v) to give **FB** as a white solid with a yield of 85% and with a purity of 99.3% (HPLC). ^{1}H NMR (400 MHz, acetone-d_6, ppm) δ 7.94 (d, 2H), 7.62 (d, 4H), 7.42 (d, 2H), 7.27 (s, 2H), 7.21 (d, 4H), 7.09 (d, 2H), 6.81 (d, 4H), 3.91 (t, 4H), 3.17 (s, 8H), 1.75-1.63 (m, 4H), 1.45-1.27 (m, 12H), 0.87 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 157.88, 152.74, 146.22, 144.88, 141.75, 140.58, 138.58, 137.97, 129.26, 126.64, 126.16, 125.04, 122.73, 121.59, 120.30, 114.13, 67.90, 64.36, 31.61, 29.49, 29.43, 29.29, 25.77, 22.64, 14.08. EI-MS (m/z) : $M^+ = 722.4$ (100%).

2.4 Sample preparation

FB (5.0 g) was placed in a flat-bottomed glass tube with a diameter of 10 mm and a highness of 85 mm under argon atmosphere. The tube was heated to 130 °C and kept at the temperature for 30 min so that a transparent melting liquid was obtained. The temperature was then elevated and kept at 150 °C for 1 h, 170 °C for 1 h, 210 °C for 5 h, 240 °C for 5 h, and 280 °C for 5 h respectively. Thus, a completely cured sample was obtained.

3. Results and discussion

3.1 Synthesis and characterization



Scheme 2. Synthetic route of **FB**.

The procedure for the synthesis of **FB** is shown in Scheme 2. As shown in Scheme 2, the monomer **FB** was prepared in a yield of 85% by using the standard Suzuki coupling reaction between 2,7-dibromo-9,9-bis(4-hexyloxyphenyl)fluorene (**2**) and benzocyclobutene-4-boronic acid. The obtained monomer showed a purity of 99.3% (HPLC), implying that it can meet the requirement of the polymerization.

The chemical structure of **FB** was characterized by its ^{1}H and ^{13}C NMR spectra (Fig. 1 and Fig. 2). As can be seen from Fig. 1, the peaks at 6.81-7.94 ppm are attributed to the protons at the aromatic ring. The peak at 3.17 ppm is attributed to the hydrogen of $-CH_2$ group at cyclobutene. The peaks at 3.91, 1.63-1.75, 1.27-1.45, and 0.87 ppm derive from the protons of alkyl chains ($-C_6H_{13}$). Moreover, as can be seen from ^{13}C NMR spectrum (Fig. 2), the peaks of the carbon atoms in the aromatic ring appear at 157.88, 152.74, 146.22, 144.88, 141.75, 140.58, 138.58, 137.97, 129.26, 126.64, 126.16, 125.04, 122.73, 121.59, 120.30, 114.13 ppm. The peaks of the carbon atoms of cyclobutene locate at 29.49 and 29.43 ppm, respectively. For the peak appearing at 67.90 ppm is ascribed to the carbon atom at 9th position of the fluorene. The peaks at 29.43-29.29 ppm are attributed to the carbon atoms of cyclobutene. The signals of the carbon atoms in the alkyl chain ($-C_6H_{13}$) appear at 64.36, 31.61, 29.49, 25.77, 22.64, 14.08 ppm. Thus, all data are consistent with the proposed, exhibiting that the chemical structure of **FB** has been confirmed.

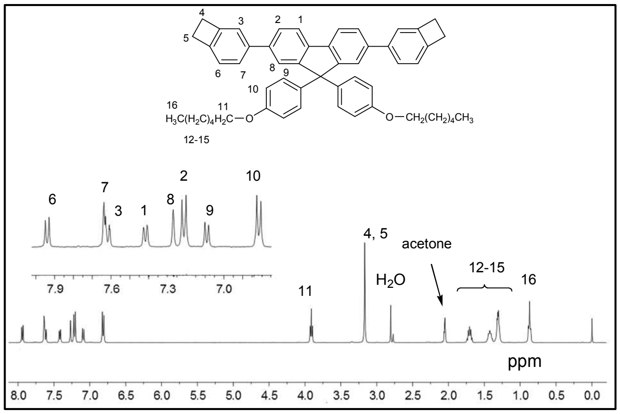


Fig. 1 ^1H NMR spectrum of **FB** (400 MHz, acetone-d_6).

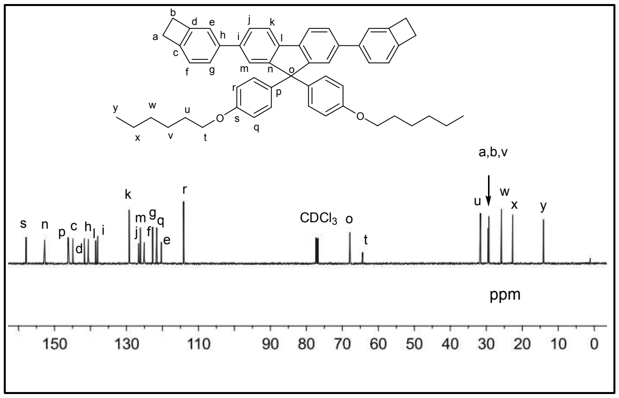


Fig. 2 ^{13}CNMR spectrum of **FB** (100 MHz, $CDCl_3$).

The solubility of **FB** was aslso investigated. As depicted in Table 1, **FB** showed good solubility in common organic solvents.

Table 1. Solubility of **FB** in organic solvents.*

toluene	DMF	DMSO	CH_2Cl_2	acetone	ethyl acetate	ethanol	CH_3CN	cyclohexanone
+	♀	♀	+	♀	♀	♀	♀	+

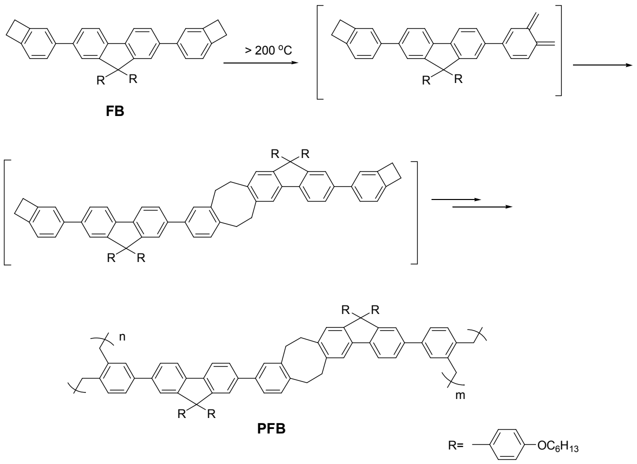
* **FB** (20 mg) in organic solvent (1 g).

\+ Soluble at room temperature.

♀ Soluble at heating

3.2 Curing behavior

Upon heating, the four-membered-ring on bezocyclobutene opens to produce a highly reactive *o*-quinodimethane intermediate.[22,25-27,30-32] This active intermediate has a tendency to form a product with eight-membered-ring via self-coupling or produce a copolymer through Diels-Alder reaction.[22,25-27,30-32] To well understand the thermally cross-linking (or curing) of **FB**, Scheme 3 describes the polymerization reaction.



Scheme 3. Thermal polymerization reaction of **FB**.

The curing behavior of **FB** was characterized by DSC, and the results are shown in Fig. 3. As depicted in Fig. 3, the endothermic peak indicating the melting point of **FB** is observed at 128 °C. The curing onset temperature of **FB** is at about 204 °C and the curing peak temperature locates at 260 °C. The curing of **FB** is attributed to the ring opening and polymerization of benzocyclobutene groups in **FB**, similar to the curing behaviors of the benzocyclobutene containing compounds.[22,25-27,30,31]

DSC trace of cured **FB** (called as **PFB**) showed a smooth line (Fig.3, red line), suggesting that **FB** has completely cured under the curing conditions, shown in the experimental section. Moreover, there is no evidence of a glass transition in a range of temperatures from 50 to 350 °C, indicating that **PFB** has high thermostability.

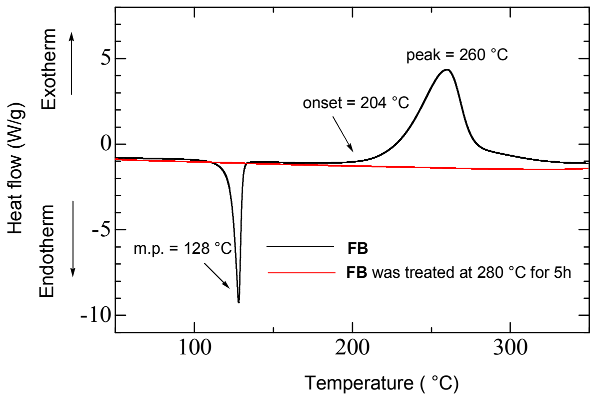


Fig. 3 DSC traces of **FB** and **PFB** at a heating rate of 10 K/ min.

The curing degree of **FB** was also monitored by DSC. When **FB** was heated at 204 °C for 1 h and 3 h, respectively, an obvious exothermal peak was observed, indicating that **FB** was partly cured at the onset temperature. Further elevating the temperature to the curing peak temperature (260 °C, see Fig. 3) resulted in weakening of the exothermal peak. After **FB** was heated to 280 °C and kept at the temperature for 5 h, the DSC trace exhibited that **FB** was fully cured (Fig. 3, red line).

The curing reaction of **FB** was also detected by FT-IR spectroscopy. Fig. 4 shows FT-IR spectra for **FB** and **PFB**. The absorption peaks at 922 and 877 cm^{-1} belonging the in-plane ring stretching vibration of C-H in the four-membered ring of benzocyclobutene group disappear after the curing reaction, suggesting that **FB** has been fully converted to **PFB**.[22,32]

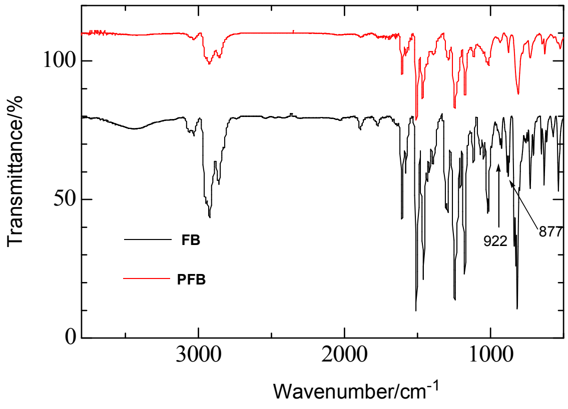


Fig. 4 FT-IR spectra of **FB** and **PFB**.

3.3 Thermostability

The thermostability of **PFB** was evaluated by thermogravimetry (TGA). The results are shown in Fig. 5. As depicted in Fig. 5, **PFB** shows 5% weight loss temperature (T_5) in N_2 and air at 437 °C and 372 °C, respectively. Such results imply that **PFB** has high thermostability. Furthermore, **PFB** shows a residual weight (R) of 47.6% at 1000 °C in N_2. This high thermostability is attributed to the rigid biphenyl structure of fluorene backbone.

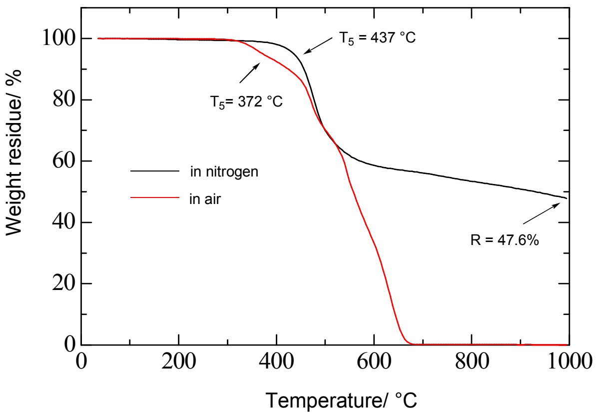


Fig. 5 TGA curves of **PFB**, measured in N_2 and air with a heating rate of 10 K/min. T_5 is the temperatures when weight loss is 5%. R is residual weight of the sample at 1000 °C in N_2.

3.4 Dielectric properties

Fig.6 shows the dielectric constant (*k*) of **PFB** depending on the frequencies. As can be seen from Fig. 6, **PFB** shows an average dielectric constant (*k*) of about 2.70 in a range of frequencies from 0.15 MHz to 30 MHz. Such a result is attributed to the large free volume of bulky fluorene. It is noted that the *k* value of **PFB** is also comparable to the values of organic low-*k* materials such as polyimides (3.1-3.4),[33,34] SiLK resins (2.65)[35] and polycyanate esters (2.61-3.12)[36]. The average dissipation factors of **PFB** was also measured, which was about 0.028 ranging the frequencies from 0.15 MHz to 30 MHz.

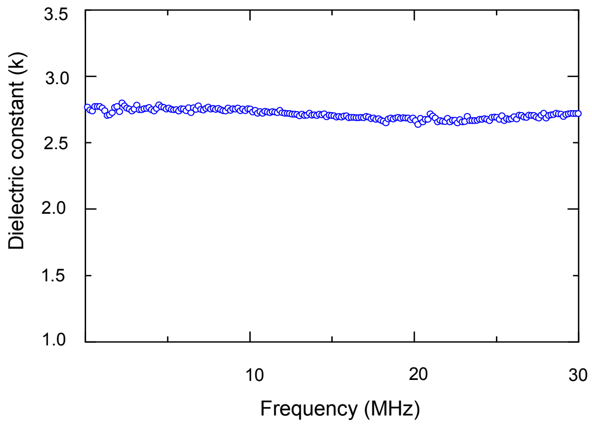


Fig. 6 Dielectric constant (*k*) of **PFB** at different frequencies.

4. Conclusions

A new monomer (**FB**) consisting of fluorene and benzocyclobutene units was successfully synthesized. After being heated at a high temperature (> 200 °C), **FB** converted to a cross-linked network structure (**PFB),** which showed an average dielectric constant (*k*) of about 2.70 in the range of frequencies from 0.15 MHz to 30 MHz. Such a low *k* value was comparable to the commercially polymeric low-*k* materials such as polyimides (PIs), SiLK resins, polycyanate esters and most of benzocyclobutane-containing polymers. **PFB** also showed high thermostability with a 5% weight loss temperature (T_5) of 437 °C and 372 °C in N_2 and air, respectively. Moreover, **PFB** had a residual weight (R) of 47.6% at 1000 °C under N_2. All these results suggest that **FB** could be used as the varnish for insulating enameled wire in electrical industry, and as encapsulation resins in microelectronic industry.

Acknowledgements

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Notes and references

[a] *Laboratory of Synthetic and Self-Assembly Chemistry for Organic Functional Molecules, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, PR China. E-mail: qiangfang@mail.sioc.ac.cn; Fax & Tel: (+86) 21-54925337*

[b] *School of Chemistry and Chemical Engineering, Yantai University, Yantai, 264005, PR China. E-mail: diaoshen315@163.com*

[§] *These authors contributed equally.*

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