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Xiangdong Zhao, Guijie Li, Zhi-Qiang Zhu, Kun Fang, Yuning Yang, Jian Li, and Yuanbin She Org. Process Res. Dev., Just Accepted Manuscript • DOI: 10.1021/acs.oprd.7b00280 • Publication Date (Web): 15 Sep 2017 Downloaded from http://pubs.acs.org on September 15, 2017

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Efficient and Practical Synthesis of Electron Transport Material and Its Key Intermediate

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ABSTRACT: An efficient and practical synthesis of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)triphenylene **4** from two cheap commodity chemicals in five steps with a total yield of 48.6% was developed. And this process had been successfully applied in the synthesis of electron transport material (ETM) **BPyTP-2** in gram scale with a total yield of 47.2%. This practical development of the key intermediate **4** open a door in its further application in the synthesis of other triphenylene-based ETMs and host materials in material field.

Keywords: electron transport material; host material; triphenylene; Scholl oxidation; Suzuki-Miyaura coupling

INTRODUCTION

Since the first practical organic light-emitting diode (OLED) was demonstrated by Tang and VanSlyke in 1987.¹ OLEDs have been attracting more and more attention in both academic and industrial research for their great potential in commercial applications, such as full-color displays and solid-state lighting.²⁻⁵ Both hole transport and electron transport layer (ETL) are critical for most multilayer advanced OLED devices. However, the development of electron transport materials (ETMs) are more important because the electron mobilities are usually one or two orders of magnitude lower than the hole mobilities in OLEDs, which are unfavorable to the charge balance in the emitting layer and the operational lifetime of the devices. In 2012, Adachi and his coworkers developed a series of triphenylene-based ETMs, like **BPyTP-1**⁶, **BPyTP-2**⁶, **2,3'-BPyTP**⁷ and **2,4'-BPyTP**⁷(Figure 1), which could lower driving voltage significantly and also shown great electrochemical stability in green OLEDs, attributing to the high horizontal molecular orientation to substrates⁷. In 2013, triphenylene-based host materials, **BDBF-TP** and **BDBP-TP**, were also developed by Adachi's group, which could lower driving voltages and increase the external quantum efficiency (EQE) compared with that of host materials 4,4'-bis(carbazol-9-yl)-1,1'-biphenyl (CBP) in red phosphorescent OLED.⁸ Recently, it was demonstrated that BPvTP-2 could sever as efficient and stable ETM and widely utilized in platinum(II)-based phosphorescent red⁹ and blue¹⁰ OLEDs and also OLEDs incorporating fluorescence¹¹ or thermally activated delayed fluorescence (TADF) emitters¹². However, the synthetic route of the

ETMs and its key triphenylene-based precursor was rare.



Figure 1. Triphenylene-based electron transport materials and host materials

А for of intermediate four-step strategy the synthesis the kev 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)triphenylene 4 was developed by Adachi's Group in 2012 (Scheme 1).^{6,13} 1,2-Diiodobenzene (\$461/25g, TCI) and 3-(trimethylsilyl)phenylboronic acid (\$257/5g, TCI) were employed as starting materials to afford 1,2-bis(3-(trimethylsilyl)phenyl)benzene 1 through Pd(0)-catalyzed Suzuki-Miyaura coupling reaction. Then bromination, MoCl₅-promoted Scholl oxidation and Pd(II)-catalyzed Miyaura boration were involved via intermediates 2 and 3 to give 4 in a total yield of 17.6%. And a series of ETMs, like BPyTP-2, could be obtained by the Suzuki-Miyaura coulping reaction between 4 and corresponding bromide compounds.^{6,7} The Adachi's synthesis route was relative concise and could be applied in gram-scale synthesis of the ETMs. Nevertheless, both the starting materials were very expensive, and the yields for the bromination and Scholl oxidation were unsatisfied, which resulted in low total yields for both the key intermediate 4 and BPyTP-2 (Scheme 1). In 2008-2012, the synthesis of 2,7-di(trifluoromethylsulfonyloxy)triphenylene (8), which could sever as a potential precursor for the preparation of the key intermediate 4, was independently developed through Suzuki-Miyaura coupling, Scholl oxidation, demethylation and trifluoromethylsulfonylation using

1,2-dibromobenzene and 3-methoxyphenylboronic acid as starting materials by Iida¹⁴, Minakami¹⁵, Kim¹⁶, Brown¹⁷ and their co-workers respectively. However, limitations still remain, like the low yields (45-48%) of Scholl oxidation promoted by FeCl₃ or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in Iida¹⁴, Minakami¹⁵ and Brown's¹⁷ work, or the high reaction temperature (220 °C) of the demethylation in Kim's work¹⁶ (Figure 2). Inspired by Adachi's synthetic strategy and the previous work, herein. we report an improved practical synthetic route for the key intermediate 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)triphenylene 4 and BPyTP-2 starting from inexpensive commodity chemicals 1,2-dibromobenzene (\$260/500g, Energy Chemical) and 3-methoxyphenylboronic acid (\$100/100g, Energy Chemical) with high total yields of 48.6% and 47.2% respectively.

Scheme 1. Adachi's Strategy for the Synthesis of BPyTP-2 and Its Key Intermediate 4





		Iida's work (ref. 14)	Minakami's work (ref. 15)	Kim's work (ref. 16)	Brown's work (ref. 17)	Our work
Step 1	condition yield	6% Pd(PPh ₃) ₄ 6.6 Na ₂ CO ₃ toluene/EtOH/H ₂ O reflux 60%	6% Pd(PPh ₃) ₄ 6.6 Na ₂ CO ₃ toluene/EtOH reflux 79%	$\frac{2\% \text{ Pd}(\text{PPh}_3)_4}{4.0 \text{ Na}_2\text{CO}_3}$ toluene/H ₂ O reflux 70%	0.8% Pd(PPh ₃) ₄ 8.0 Na ₂ CO ₃ toluene/ [/] PrOH reflux 84%	5% Pd(PPh ₃) ₄ 6.0 Na ₂ CO ₃ toluene/EtOH/H ₂ O reflux 96%
Step 2	condition	$\begin{array}{c} 2.5 \ \text{FeCl}_3 \\ \text{H}_2 \text{SO}_4 \ (\text{con.}) \\ \text{CH}_2 \text{Cl}_2 \\ 0^{\circ} \text{C-rt} \end{array}$	2.5 FeCl ₃ H ₂ SO ₄ (con.) CH ₂ Cl ₂ 0°C-rt	>2.0 FeCl ₃ CH ₂ Cl ₂ rt	excess DDQ $1.0 \text{ MeSO}_2\text{H}$ $2.0 \text{ Et}_2\text{O}:\text{BF}_3$ CH_2Cl_2 0°C-rt	(1.0+1.0) MoCl ₅ CH ₂ Cl ₂ rt
	yield	48%	48%	70%	45%	82%
Step 3	condition	2.5 BBr ₃ CH ₂ Cl ₂ 0°C	2.5 BBr ₃ CH ₂ Cl ₂ 0°C	pyridine hydrochloride 220°C	4.7 BBr ₃ CH ₂ Cl ₂ 0°C-rt	HBr/AcOH reflux (purification with column free)
	yield	98%	98%	88%	99%	100%
Step 4	condition	2.5 Tf ₂ O 2.2 pyridine CH ₂ Cl ₂ rt	2.7 Tf ₂ O 2.7 pyridine rt	2.0 Tf ₂ O excess pyridine rt	3.0 Tf ₂ O excess pyridine rt	2.5 Tf ₂ O 8.0 pyridine CH ₂ Cl ₂ , 0°C-rt (purification with column free)
	yield	98%	93%	68%	94%	87%
Total yield		12.4%	35.0%	29.3%	35.2%	68.5%

Figure 2. Comparison of our work with previous work for the preparation of 5-8

RESULTS AND DISCUSSION

One of the key steps was the construction of the triphenylene molecular skeleton through the Scholl oxidation¹⁸, and bromine atom was a weakly deactivating substituent which would result in low conversion. Nevertheless, it was demonstrated that the alkoxyarene substrates for the Scholl oxidation proceeded via arenium cation mechanisms.¹⁸ Therefore, *o*,*p*-directing methoxy group could stabilize the arenium cation and lower the transition-state energy, facilitating the Scholl oxidation. Thus, our synthetic strategy employed 1,2-bis(3-methoxyphenyl)benzene **5** as the substrate for the Scholl oxidation, which could be efficiently synthesized through Suzuki-Miyaura coupling¹⁹ catalyzed by $Pd(PPh_3)_4$ in 96% yield utilizing inexpensive commodity chemicals 1,2-dibromobenzene and 3-methoxyphenylboronic acid as starting materials. Similar reactions for the synthesis of **5** were also reported by previous literatures in 60-80% yield.^{14-17,20,21}

It had been reported that **5** could be oxidized to give 2,7-dimethoxytriphenylene **6** promoted by $FeCl_3^{14-16,22}$ or DDQ¹⁷ in unsatisfied yield. Thus, we next optimized the Scholl oxidation conditions. It was found that one equiv MoCl₅ could not oxidize **5** completely. And adding two equiv MoCl₅ at once or separately in a short time generated unsatisfied yields. However, good yield of 82% could be achieved if the two equiv MoCl₅ were added at intervals of 24 hours. It was noted that insoluble product precipitate of 2,7-dimethoxytriphenylene **6** from solution was observed, which could suppress the oligomerization of product and facilitate the yield enhancement.¹⁴ Recently, this Scholl oxidation intermolecular coupling reaction was improved under acid conditions^{20,21} or utilizing fluoroalkoxy Mo(V) reagent as oxidant²³.

It has been demonstrated that both $BBr_3^{14,15,17,24,25}$ and pyridine hydrochloride¹⁶ could be employed for the demethylation of 6, which suffered from complicated workup or high reaction temperature¹⁶. Thus, demethylation of **6** using concentrated hydrobromic acid²⁶ in acetic acid gave 2,7-dihydroxyltriphenylene **7** in quantitative yield, which further reacted with Tf₂O to afford ditrifluoromethanesulfonate in 87% yield. It was encouraging to find that pure products of both **6** and **7** could be separated easily with column chromatography free. Then, key intermediate **4** could be obtained through the Miyaura boration in a total yield of 48.6% for the five steps, which was much higher than that of the Adachi's synthetic route. Finally, the synthesis of **BPyTP-2** could be completed through Pd(0)-catalyzed Suzuki-Miyaura coupling reaction between **4** and 2-(5-bromopyridin-2-yl)pyridine in gram scale in 47.2% total yield. It was worth mentioning that prolonging reaction time could increase the yield of the last step.

Scheme 2. Improved Strategy for the Synthesis of 4 and BPyTP-2



Importantly, 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)triphenylene **4** was also a key precursor for the synthesis of other ETMs, such as **BPyTP-2**⁶, **2,3'-BPyTP**⁷ and **2,4'-BPyTP**⁷ (Scheme 3), all of which exhibited good device performance. Furthermore, precursor 4 could be also utilized for



CONCLUSION

In summary, an efficient and practical synthetic method of precursor 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)triphenylene **4**, which was a key intermediate for the synthesis of ETMs and host materials, was developed in five steps with a total yield of 48.6%. Moreover,

two cheap commodity chemicals could be employed as the starting materials. Importantly, an improved MoCl₅-promoted Scholl oxidation successfully construct the key triphenylene skeleton in high yield. Furthermore, this process could be successfully applied in the synthesis of ETM **BPyTP-2** in gram scale in a total yield of 47.2%. And it is believed that this practical synthetic route can be also applied in the synthesis of other triphenylene-based ETMs and host materials in the future in material field.

EXPERIMENTAL SECTION

General. All commercial reagents were purchased and used without further purification unless otherwise noted. The CH₂Cl₂ was dried over anhydrous Na₂SO₄ prior to use. Pd(PPh₃)₄ was purchased from Sigma-Aldrich. ¹H spectra were recorded at 400 or 500 MHz, and ¹³C NMR spectra were recorded at 100 or 125 MHz on Varian Liquid-State NMR instruments DMSO-*d*₆ solutions and chemical shifts were referenced to a residual protiated solvent. ¹H NMR spectra were recorded with the residual DMSO-*d*₆ ($\delta = 2.50$ ppm) as the internal reference; and ¹³C NMR spectra were recorded with DMSO-*d*₆ ($\delta = 39.52$ ppm) as the internal reference. The following abbreviations (or combinations thereof) were used to explain ¹H NMR multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, m = multiplet. High Resolution Mass spectra were recorded on LTC FTICR mass spectrometer using DART positive ion mode.

Synthesis of 1,2-bis(3-methoxyphenyl)benzene (5) 3-Methoxyphenylboronic acid (28.80 g, 189.00 mmol, 3.00 equiv) and Na₂CO₃ (40.10 g, 378.00 mmol, 6.00 equiv) were added to a three-necked flask equipped with a magnetic stir bar and a condenser. The flask was then evacuated and backfilled with nitrogen, this evacuation and backfill procedure was repeated twice. Then toluene (150 mL), EtOH (150 mL), H₂O (150 mL), 1,2-dibromobenzene (7.50 mL, 63.00 mmol, 1.00 eq) and Pd(PPh₃)₄ (2.91 g, 2.52 mmol, 0.05 eq) were added under nitrogen. The mixture was then bubbled with nitrogen for 30 min and stirred at refluxed temperature for 2 days until the starting material was consumed completely monitored by TLC. Then the mixture was cooled down to ambient temperature, filtered and washed with plenty of ethyl acetate (100 mL×3). The filtrate was concentrate and the residue was diluted with plenty of ethyl acetate (200 mL), washed with 3M hydrochloric acid and NaHCO₃ solution until there was no bubble to

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generate. The organic layer was separated and dried over anhydrous Na₂SO₄, filtered, concentrated and residue was purified through column chromatography on silica gel using petroleum ether/ethyl acetate (20:1—10:1) as eluent to obtain the desired product as a white solid 12.97 g, and some impure product, which could be further purified by a slurry in hexane/ethyl acetate (10 ml, 5:1) to give another 4.66 g product, thus desired product 5 was obtained in a total of 17.63 g in 96% yield. ¹H NMR (500 MHz, DMSO-*d*₆): δ 3.59 (s, 6H), 6.65 (dd, *J* = 2.5, 1.5 Hz, 2H), 6.70 (ddd, *J* = 7.5, 1.5, 1.0 Hz, 2H), 6.78 (ddd, *J* = 8.0, 2.5, 1.0 Hz, 2H), 7.16 (t, *J* = 8.0 Hz, 2H), 7.40-7.46 (m, 4H). ¹³C NMR (126 MHz, DMSO-*d*₆): δ 54.8, 112.4, 115.0, 121.7, 127.7, 129.0, 130.2, 139.8, 142.4, 158.7. HRMS (TOF MS EI+) for C₂₀H₁₈O₂ [M]⁺: calcd 290.1307, found 290.1303.

Synthesis of 2,7-dimethoxytriphenylene (6) MoCl₅ (7.82 g, 28.60 mmol, 1.00 equiv) was added quickly to a solution of 1,2-bis(3-methoxyphenyl)benzene 5 (8.31 g, 28.60 mmol, 1.00 equiv) in CH₂Cl₂ (500 mL) under nitrogen. The mixture was stirred at room temperature for 24 hours, then the other one equiv MoCl₅ (7.82 g, 28.60 mmol, 1.00 equiv) was added quickly to the mixture again. After being stirred for 24 hours, the mixture was quenched by methanol (100 mL) and stirred for another 1 hour, filtered and washed with CH₂Cl₂ (500 mL). The filtrate was concentrated and residue was purified through column chromatography on silica gel using petroleum ether/ethyl acetate (20:1-10:1-5:1-3:1) as eluent to afford white solid 7.52 g, which was further purified to be slurried in hexane/ethyl acetate (22 mL, 10:1) to afford white solid 6.82 g in 82% yield. ¹H NMR (500 MHz, DMSO-*d*₆): δ 3.99 (s, 6H), 7.28 (dd, *J* = 9.0, 2.5 Hz, 2H), 7.69-7.72 (m, 2H), 8.17 (d, *J* = 2.5 Hz, 2H), 8.59 (d, *J* = 9.5 Hz, 2H), 8.79-8.82 (m, 2H). ¹³C NMR (126 MHz, DMSO-*d*₆): δ 55.4, 105.7, 116.5, 123.3, 123.9, 124.7, 127.5, 129.3, 129.6, 158.1. HRMS (TOF MS EI+) for C₂₀H₁₆O₂ [M]⁺: calcd, 288.1150, found 288.1154.

Synthesis of 2,7-dihydroxytriphenylene (7) A solution of 2,7-dimethoxytriphenylene 6 (4.30 g, 14.90 mmol) in hydrogen bromide acid (30 mL, 48%) and acetic acid (220 mL) refluxed (120 °C) for 2 days under a nitrogen atmosphere. Then the mixture was cooled down to room temperature and the solvent was removed under reduced pressure. The residue was diluted with water (30 mL) and neutralized with a solution of K₂CO₃ until there was no gas to generate. Then the precipitate was filtered

off and washed with water for three times (50 mL×3). The collected solid was dried in under reduced pressure to afford the product as a brown solid in quantitative yield. ¹H NMR (500 MHz, DMSO- d_6): δ 7.14 (dd, J = 9.0, 2.5 Hz, 2H), 7.64-7.67 (m, 2H), 7.97 (d, J = 2.0 Hz, 2H), 8.46 (d, J = 9.0 Hz, 2H), 8.53-8.55 (m, 2H), 9.76 (s, 2H). ¹³C NMR (126 MHz, DMSO- d_6): δ 107.6, 117.2, 122.4, 123.4, 124.4, 127.3, 129.2, 129.3, 156.0. HRMS (DART Positive Ion Mode) for C₁₈H₁₃O₂ [M+H]⁺: calcd 261.0910, found 261.0909 .

Synthesis of triphenylene-2,7-diol bistrifluoromethanesulfonate (8) А solution of 2,7-dihydroxytriphenylene 7 (3.94 g, 14.90 mmol, 1.00 equiv) in CH₂Cl₂ (250 mL) was cooled to 0-5 °C. After adding pyridine (9.60 mL, 119.16 mmol, 8.00 equiv), Tf₂O (6.60 mL, 39.25 mmol, 2.60 equiv) was added dropwise. Then the mixture was stirred at that temperature for 2 hours, quenched by water (25 mL). The mixture was diluted with CH₂Cl₂ until the precipitate was dissolved. The organic layer was separated and dried over anhydrous Na₂SO₄, filtered. The filtrate was concentrated until there was about 40 mL solvent was left, diluted with hexane (200 mL). The precipitate was filtered off and washed with hexane (100 mL), dried. And white solid 6.77 g was obtained in 87% yield. ¹H NMR (500 MHz, DMSO- d_6): δ 7.83-7.86 (m, 4H), 8.90-8.93 (m, 2H), 8.99 (d, J = 2.5 Hz, 2H), 9.03 (d, J = 9.5 Hz, 2H). ¹³C NMR (126 MHz, DMSO- d_6): δ 116.70, 118.35 (q, J = 320 Hz), 120.7, 124.4, 127.3, 128.1, 128.6, 129.1, 131.5, 149.2. HRMS (DART Positive Ion Mode) for $C_{20}H_{10}F_6O_6S_2$ [M]⁺: calcd for 523.9818, found 523.9814.

Synthesis of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)triphenylene (4) Triphenylene-2,7-diol bistrifluoromethanesulfonate 8 (9.00 g, 17.16 mmol, 1.00 equiv), bis(pinacolato)diboron (17.43 g, 68.65 mmol, 4.00 equiv), KOAc (10.10 g, 102.96 mmol, 6.00 equiv) and Pd(dppf)Cl₂ (0.84 g, 1.03 mmol, 0.06 equiv) were added to a three-necked flask equipped with a magnetic stir bar and a condenser. The flask was then evacuated and backfilled with nitrogen, this evacuation and backfill procedure was repeated twice. Then dioxane (136 mL) was added under nitrogen. The mixture was then bubbled with nitrogen for 20 minutes and stirred at 80 °C for 2 days. Then the mixture was cooled down to ambient temperature. The solvent was removed and the residue was purified through column chromatography on silica gel using petroleum ether/ethyl acetate (60:1-40:1) as eluent to obtain the desired product containing some bis(pinacolato)diboron, The obtained solid was further purified by a slurry in hexane/ethyl acetate (20:1) at room temperature for 4-6 hours to give pure white solid 5.86 g in 71% yield. ¹H NMR (500 MHz, DMSO-*d*₆): δ 1.39 (s, 24H), 7.75-7.78 (m, 2H), 7.98 (dd, *J* = 8.0, 1.0 Hz, 2H), 8.76-8.79 (m, 2H), 8.84 (d, *J* = 8.0 Hz, 2H), 9.03 (s, 2H). ¹³C NMR (126 MHz, DMSO-*d*₆): δ 24.7, 84.0, 123.33, 123.4, 128.0, 128.8, 128.9, 129.7, 131.1, 132.8. HRMS (DART Positive Ion Mode) for C₃₀H₃₄¹⁰B₂O₄ [M]⁺: calcd 478.2710, found 478.2710.

Synthesis of 2,7-bis(6-(pyridin-2-yl)pyridin-3-yl)triphenylene (BPyTP-2)

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)triphenylene **4** (5.16 g, 10.80 mmol, 1.00 equiv), 2-(5-bromopyridin-2-yl)pyridine (5.60 g, 23.76 mmol, 2.20 equiv, synthesized according reported literature²⁷) and Pd(PPh₃)₄ (0.62 g, 0.54 mmol, 0.05 equiv) were added to a three-necked flask equipped with a magnetic stir bar and a condenser. The flask was then evacuated and backfilled with nitrogen, this evacuation and backfill procedure was repeated twice. Then toluene (90 mL), EtOH (22 mL) and a solution of K₂CO₃ (4.50 g in 18 mL H₂O, 32.40 mmol, 3.00 equiv) were added under nitrogen through syringe. The mixture was then bubbled with nitrogen for 20 minutes and stirred at refluxed temperature for 2.5 days. Then the mixture was cooled down to ambient temperature. The precipitate was filtered off and washed with water (100 mL), acetone (100 mL), ethyl acetate (100 mL), ether (150 mL) and then dried under reduced pressure to afford a slight yellow solid 5.67 g in 97% yield. ¹H NMR (500 MHz, DMSO-*d*₆): δ 7.51 (ddd, *J* = 7.5, 4.5, 1.0 Hz, 2H), 7.80-7.82 (m, 2H), 8.01 (td, *J* = 8.0, 1.5 Hz, 2H), 8.21-8.23 (m, 2H), 8.51 (d, *J* = 8.0 Hz, 2H), 8.57 (d, *J* = 8.0 Hz, 2H), 8.62 (dd, *J* = 8.0, 2.0 Hz, 2H), 8.75-8.76 (m, 2H), 9.04 (d, *J* = 9.0 Hz, 2H), 9.15 (dd, *J* = 6.5, 3.5 Hz, 2H), 9.25 (s, 2H), 9.37 (d, *J* = 1.5 Hz, 2H). MS(+ESI) for C₃₈H₂₄N₄ [M]⁺ : calcd 536.2, found 536.2.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: xxx xxx.

NMR and MS data of compounds 4-8 and 2,2'-BPyTP (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the National Natural Science Foundation of China (Grant No. 21602198, 21776259 and 21476270), "Qianjiang Talents Plan" (Grant No. QJD1602017), National Science Foundation of United State (CHE-0748867) and Department of Energy (Contract No. EE0007090) for partial support of this work.

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