

Exploring Chiral and Achiral Properties of Novel Multilayer 3D Polymers: Synthesis and Characterization

Sai Zhang,^{1*} Qingzheng Xu,² Xiuyuan Qin,³ Yutin Wang,¹ Jialing Mao,⁴ Yue Zhang,^{1,4} Guigen Li^{5*}

¹ School of Pharmacy, Continuous Flow Engineering Laboratory of National Petroleum and Chemical Industry, Changzhou University, Changzhou, Jiangsu Province, 213164, China. Email: zhangsai@cczu.edu.cn, zyjs@cczu.edu.cn. Tel: +86-519-86334598.

² School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu Province, 210093, China

³ School of Life and Science, Nanjing Normal University, Nanjing, Jiangsu Province, 210046, China

⁴ School of Environmental Science and Engineering, Continuous Flow Engineering Laboratory of National Petroleum and Chemical Industry, Changzhou University, Changzhou, Jiangsu Province, 213164, China.

⁵ Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas, 79415, USA, E-mail: Guigen.li@ttu.edu

*Corresponding Author

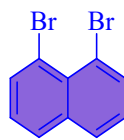
Section S1. General Information

All processes were magnetically stirred in oven-dried glassware with anhydrous solvents under Ar. Syringes, stainless steel or polyethylene cannulas, rubber septa, or a weak Ar counter-flow adding solvents, liquids, and solutions. Ice/water (0 °C) or dry ice/acetone (-78 °C) cooling baths were created in Dewar vessels. High-temperature processes used heated oil baths. Rotavapors at 40-65 °C eliminated solvents. All yields are separate chromatographic and NMR yields.

Without additional purification, all commercially accessible compounds were utilized as received. Without further purification, solvents such CH₃OH, toluene, EA, ether, DCM, dioxane, and acetone were employed. An Innovation Technology solvent system delivers THF and DCM.

On 400 MHz and 500 MHz instruments with TMS as an internal standard, the ¹H and ¹³C NMR spectra were captured. The residual solvent signal (= 7.26 for CDCl₃) was utilized to reference the ¹H NMR spectra. The signal of the solvents was employed in the ¹³C NMR spectra (= 7.16 for CDCl₃ and). Chemical shifts (δ) with regard to TMS were reported in ppm. Chemical shift, multiplicity (singlet, doublet, triplet, multiplet), coupling constant (J, Hz), and integration are used to describe the data. The TOSOH EcoSEC HLC-8420 GPC, which has a dual-flow refractive index detector, was used to collect GPC data. Along with the RI detector, a UV detector is also provided for usage with UV visible polymers. The range of the installed columns is 500-107 Da. Samples were conducted at a flow rate of 0.7 mL/min for 25 minutes. Our investigations used polystyrene (PS) standards for calibration.

Section 2. Synthetic Procedure



1

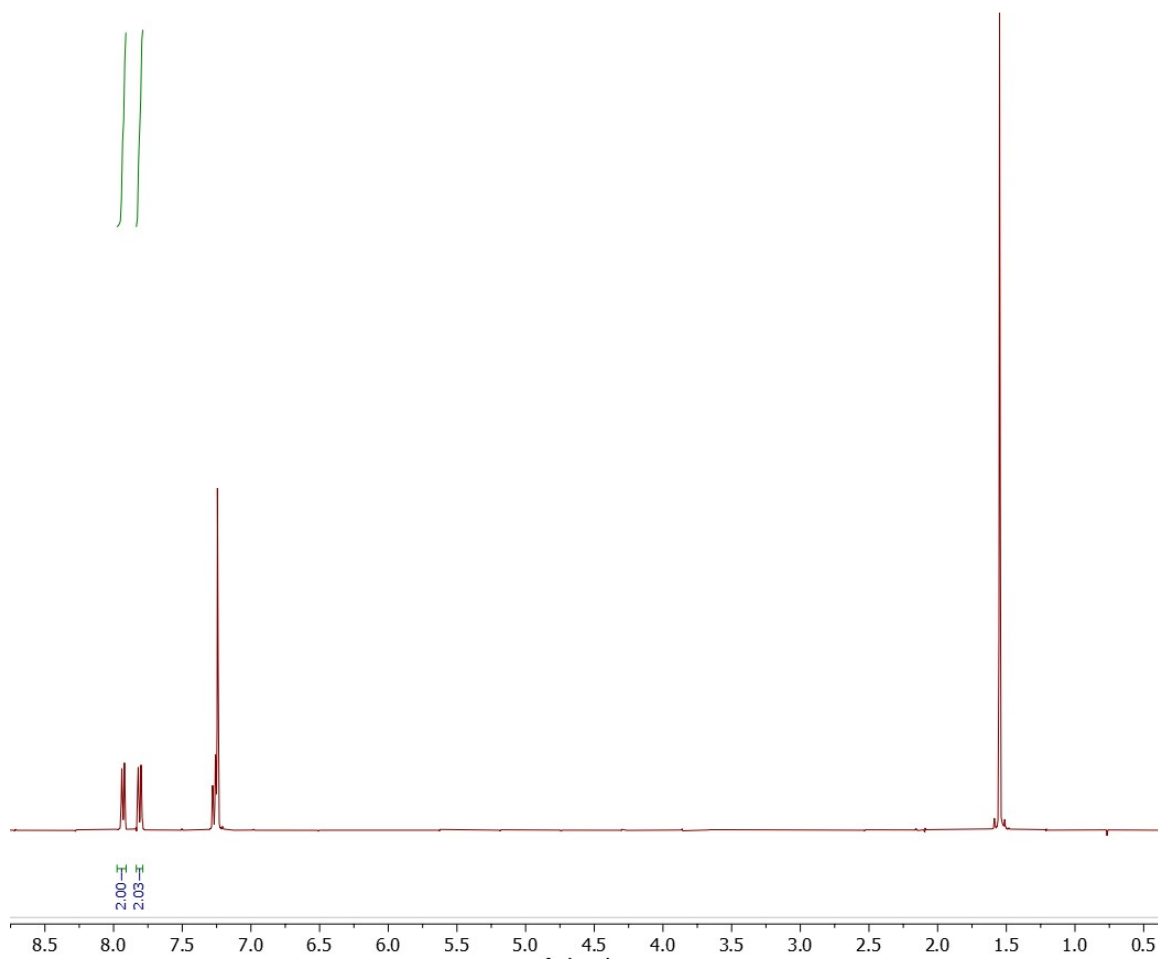


Figure S1. ¹H NMR of **1**

The synthetic procedure was reported by former work.¹ m/z, 285.2 [M+H]⁺.

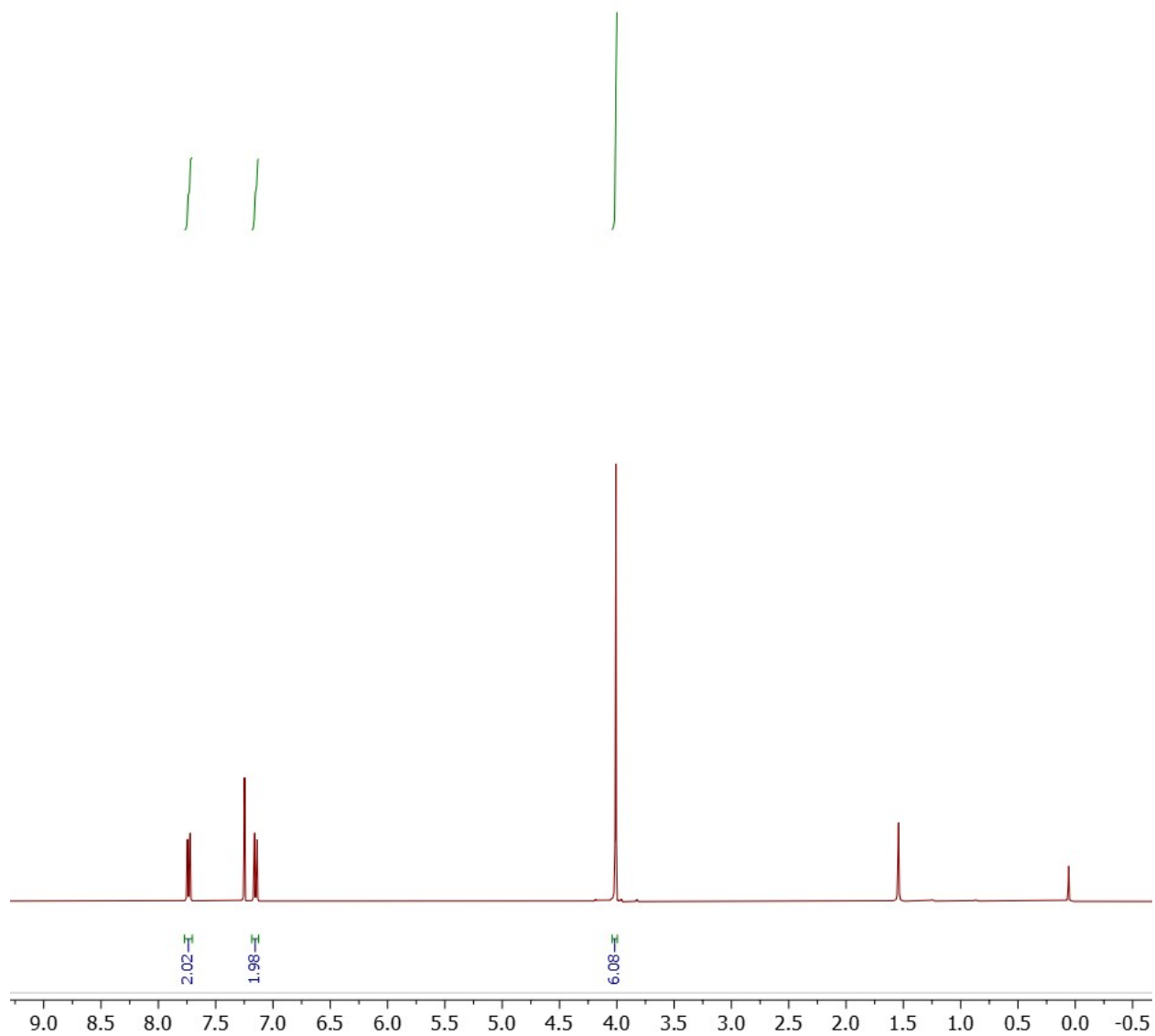
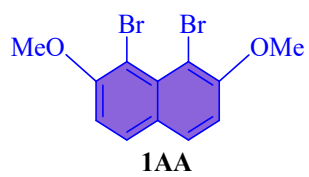


Figure S2. ¹H NMR of **1AA**

The synthetic procedure was reported by former work.¹ MS(ESI): m/z, 345.6 [M+H]⁺

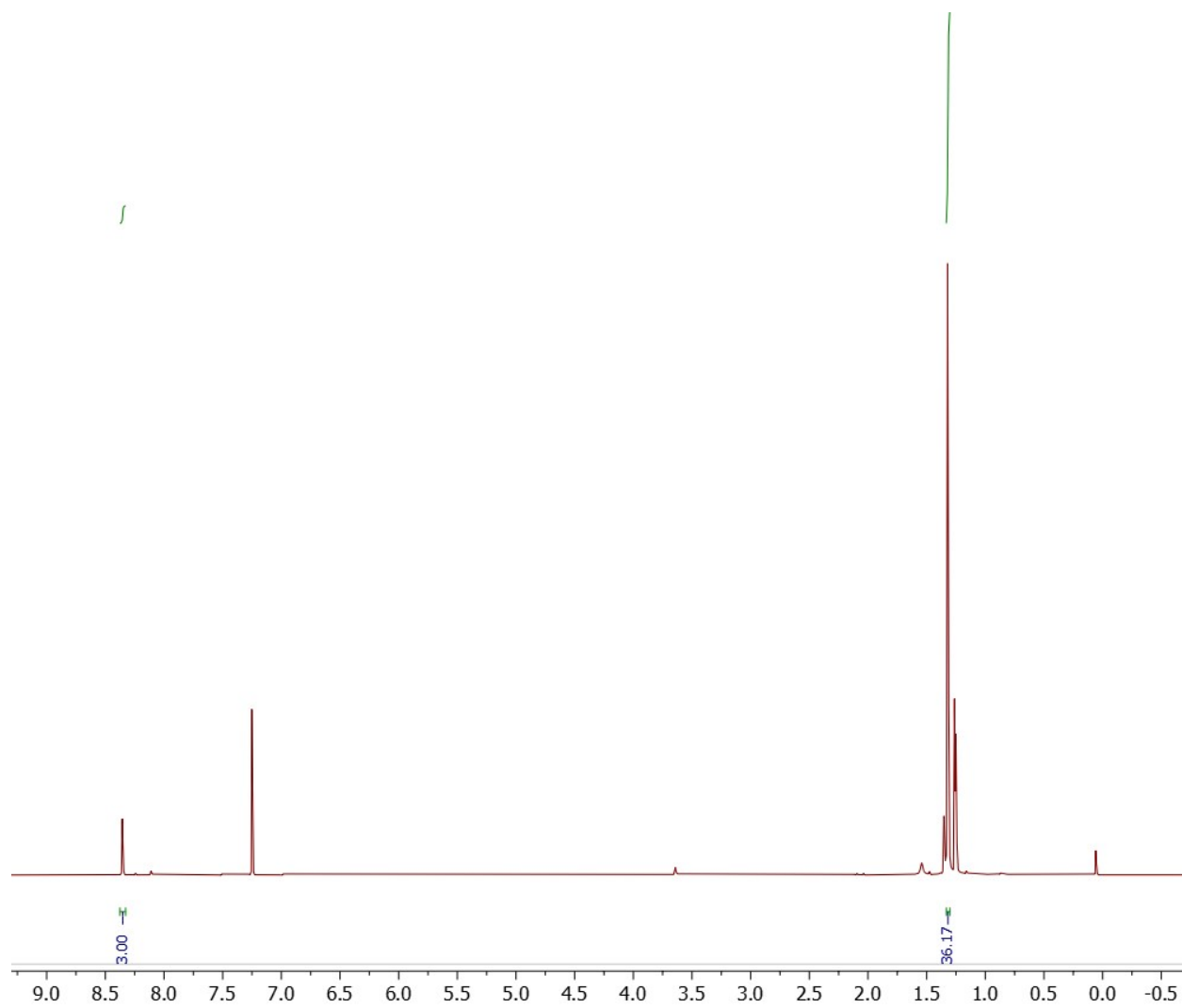
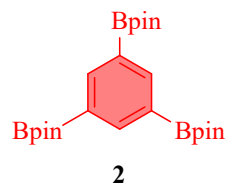
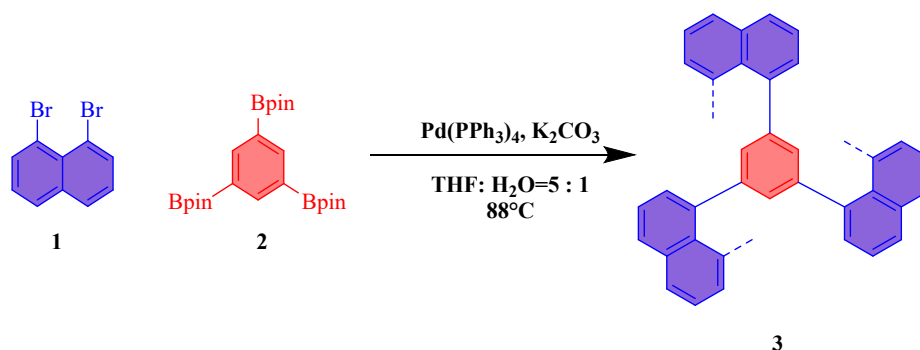


Figure S3. ¹H NMR of **2**

The synthetic procedure was reported by former work.² MS(ESI): m/z, 457.3111 [M + H]⁺.

General Procedure for polymer 3,4,5,6



A 50 mL oven-dried round-bottom flask was filled with 1,3-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (60.0 mg, 0.132mmol, 1 equiv), 1,8-dibromonaphthalene (56.4 mg, 0.197 mmol, 1.5 equiv), Pd(PPh₃)₄ (7.59 mg, 0.007 mmol, 5% equiv), The round-bottom flask was filled with 2 mL H₂O and 10 mL THF. Argon was added after the round bottom flask had been vacuum-degassed. Then, for more than 96 hours, it was heated at 88°C. To reach room temperature, the mixture was chilled. In a single pot, the resultant mixture was then added to MeOH/HCl. The components that had precipitated were collected by filtration through a Buchner funnel and repeatedly rinsed with methanol and water. The solid was further dried to produce earthy yellow solid (62.7mg, 54% yield, M_n=9867, M_w=10168, PDI=1.030). ¹H NMR (400 MHz, CHLOROFORM-D) δ 8.01 – 6.04 (Ar-H).

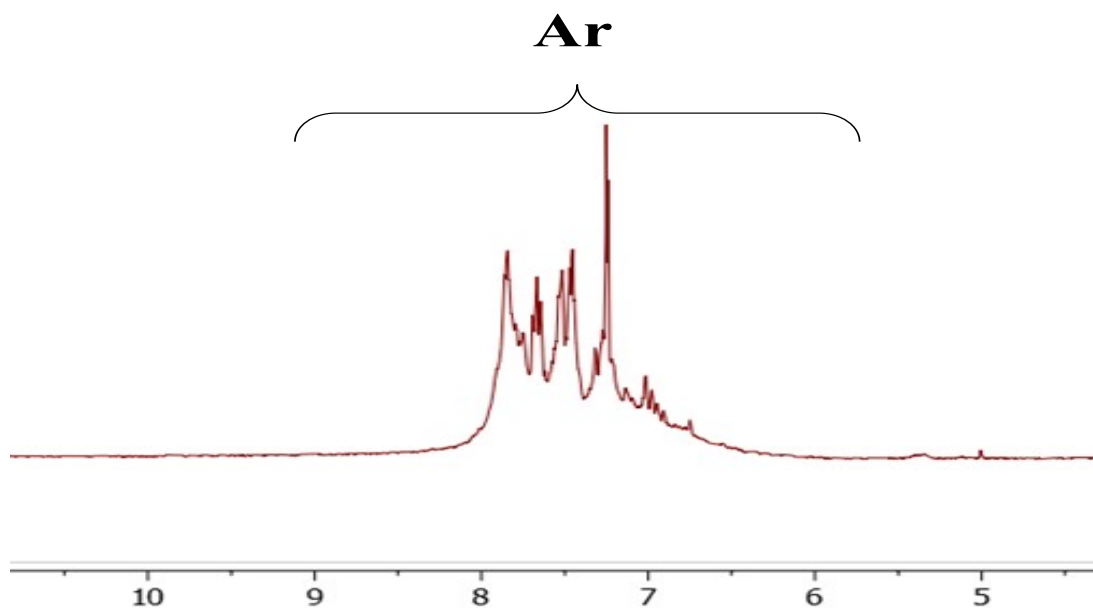


Figure S4. NMR of Polymer 3

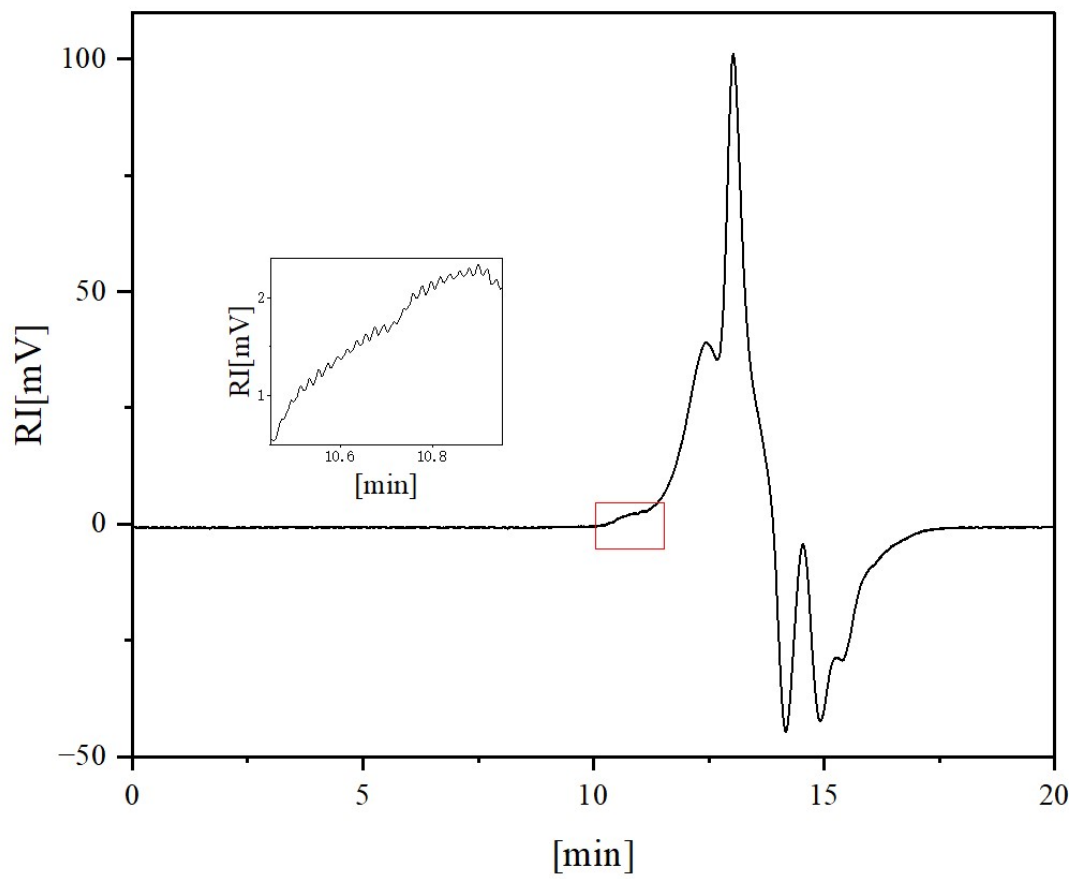
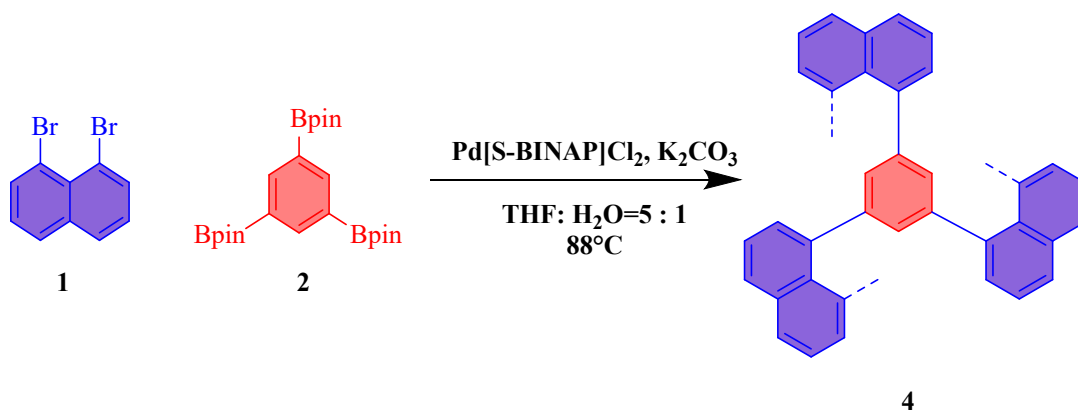


Figure S5. GPC of Polymer 3



A 50 mL oven-dried round-bottom flask was filled with 1,3-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (60.0 mg, 0.132mmol, 1 equiv), 1,8-dibromonaphthalene (56.4 mg, 0.197 mmol, 1.5 equiv), Pd(S-BINAP)Cl₂ (5.3 mg, 0.006 mmol, 5% equiv). The round-bottom flask was filled with 2 mL H₂O and 10 mL THF. Argon was added after the round bottom flask had been vacuum-degassed. Then, for more than 96 hours, it was heated at 88°C. To reach room temperature, the mixture was chilled. In a single pot, the resultant mixture was then added to MeOH/HCl. The components that had precipitated were collected by filtration through a Buchner funnel and repeatedly rinsed with methanol and water. The solid was further dried to produce earthy yellow solid (41mg, 35% yield, $[\alpha]_D^{RT} = -4$ (c=0.1, THF, $M_n=7325$, $M_w=7781$, PDI=1.062). ¹H NMR (400 MHz, CHLOROFORM-D) δ 8.39 – 5.73 (Ar-H).

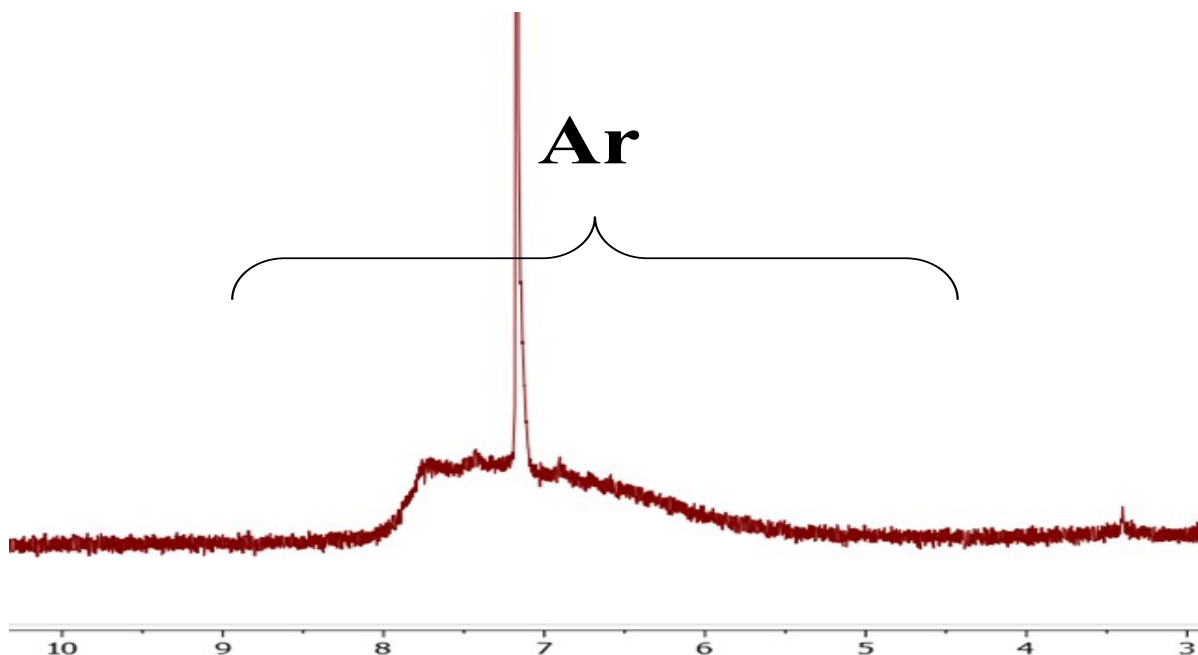


Figure S6. NMR of polymer 4

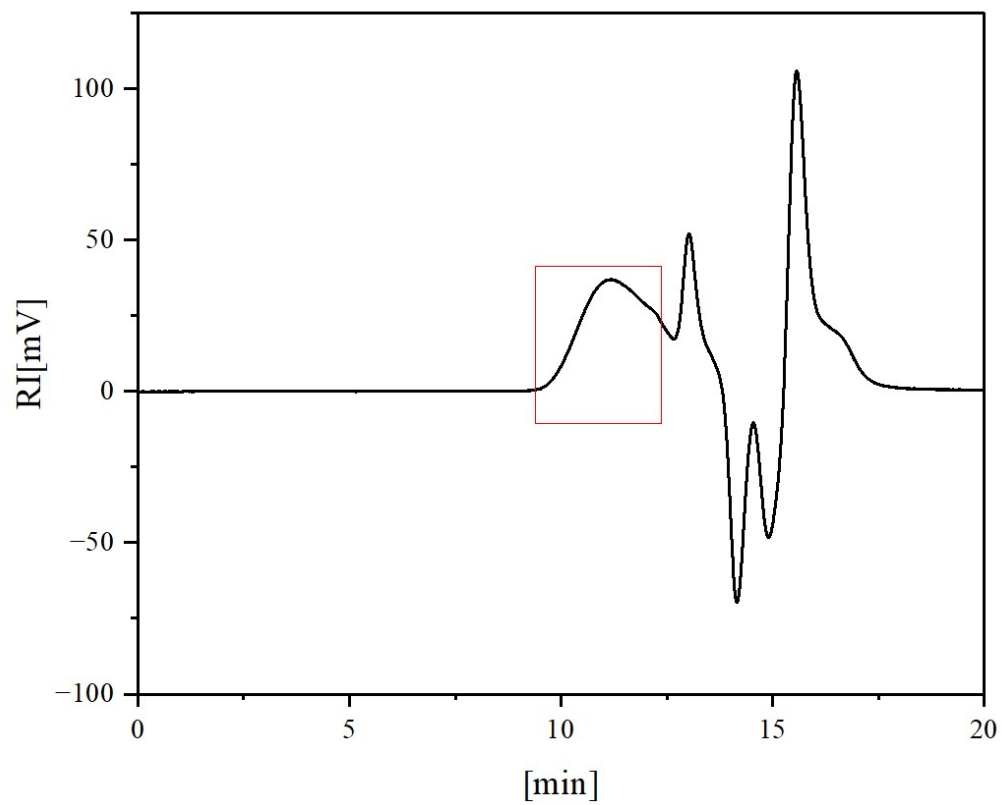
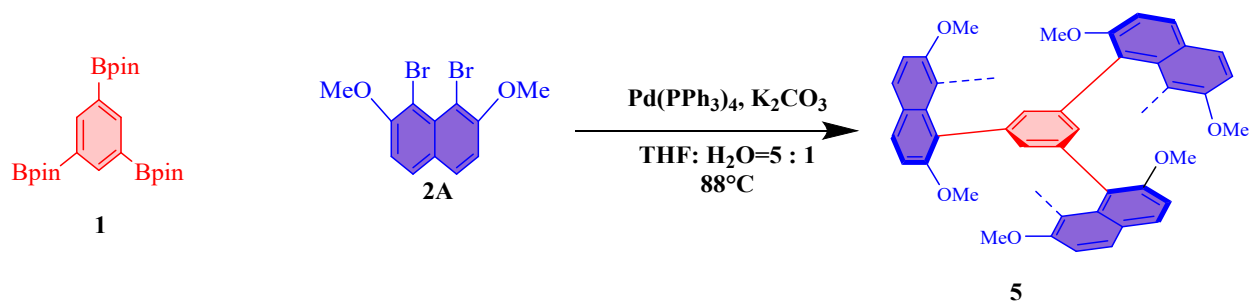


Figure S7. GPC of Polymer 4



A 50 mL oven-dried round-bottom flask was filled with 1,3-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (60.0 mg, 0.132mmol, 1 equiv), 1,8-dibromo-2,7-dimethoxynaphthalene (68.2 mg, 0.196 mmol, 1.5 equiv), Pd(PPh₃)₄ (7.59 mg, 0.007 mmol, 5% equiv), The round-bottom flask was filled with 2 mL H₂O and 10 mL THF. Argon was added after the round bottom flask had been vacuum-degassed. Then, for more than 96 hours, it was heated at 88°C. To reach room temperature, the mixture was chilled. In a single pot, the resultant mixture was then added to MeOH/HCl. The precipitated components were collected by filtration through a Buchner funnel and repeatedly rinsed with methanol and water. The solid was further dried to produce earthy yellow solid (44.6mg, 35% yield, M_n=5520, M_w=8183, PDI=1.030). ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.75 – 6.88 (Ar-H), 3.97–3.57(OMe-H).

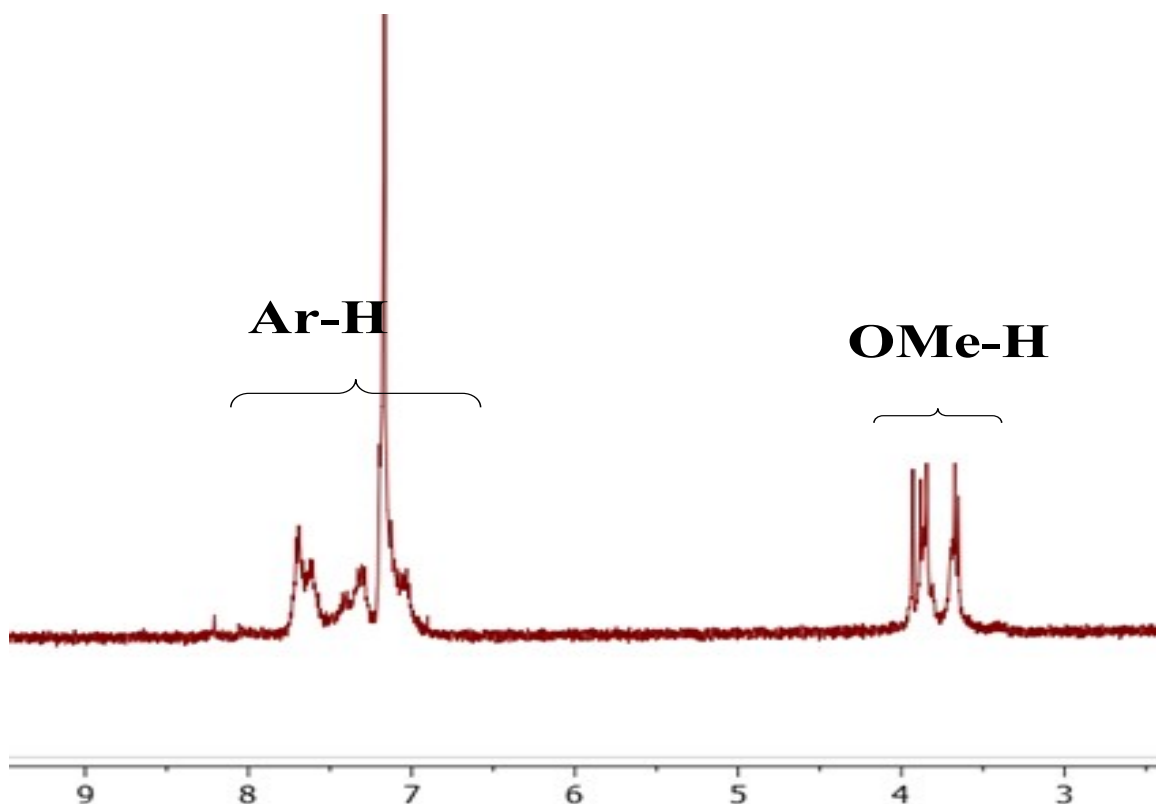


Figure S8. NMR of Polymer 5

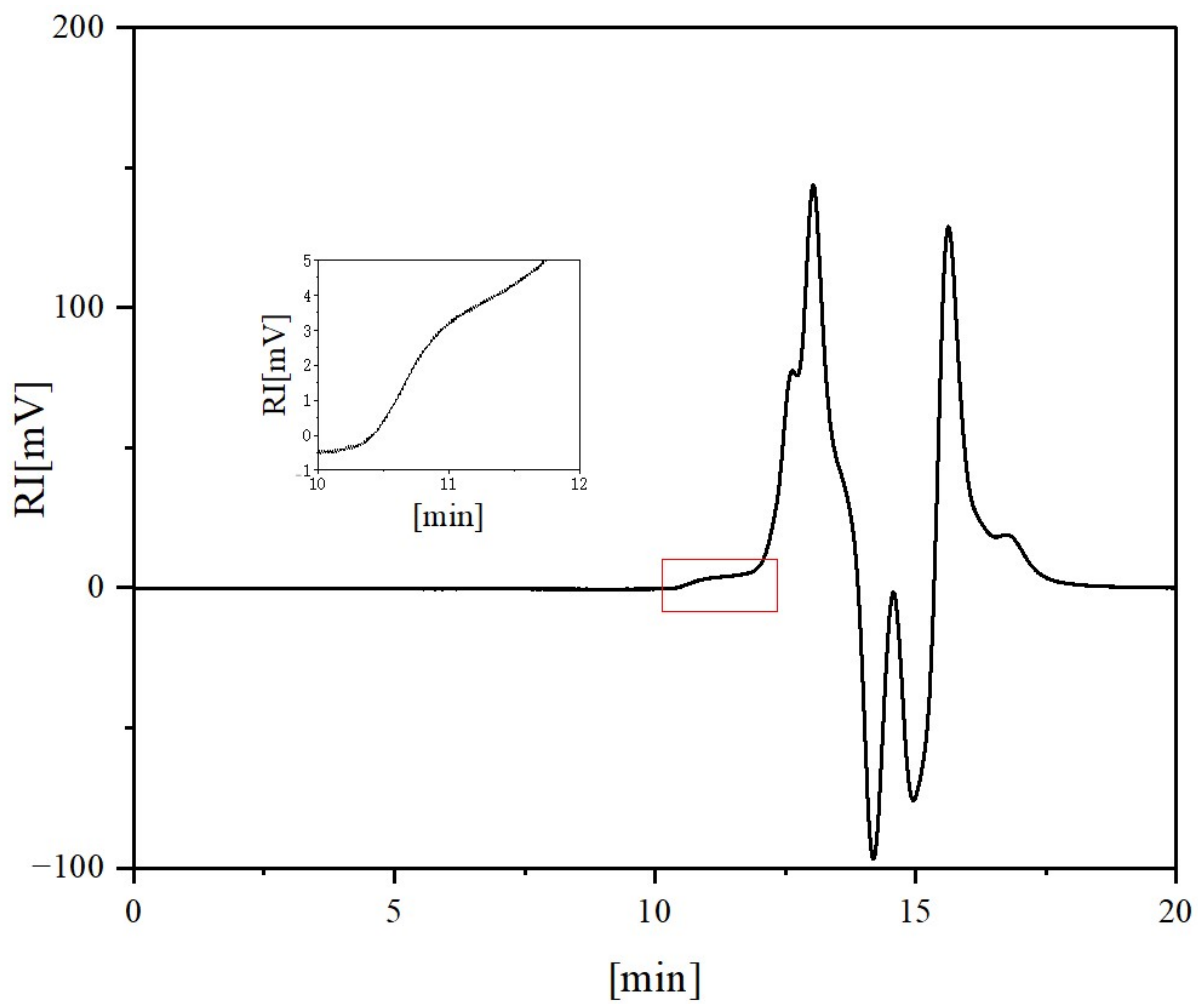
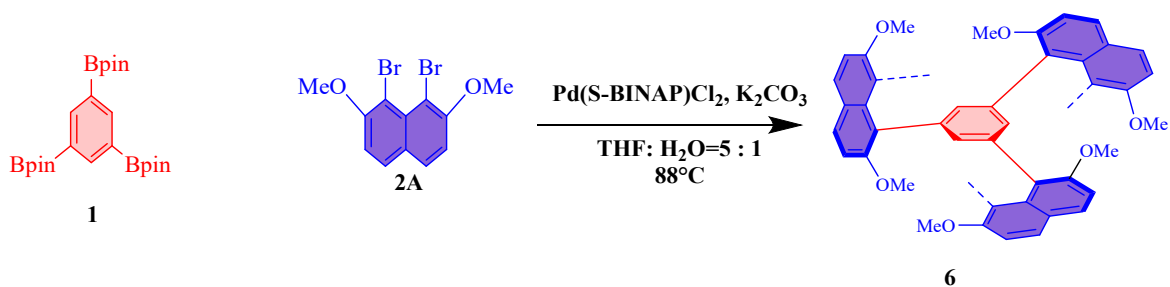


Figure S9. GPC of Polymer 5



A 50 mL oven-dried round-bottom flask was filled with 1,3-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (60.0 mg, 0.132mmol, 1 equiv), 1,8-dibromo-2,7-dimethoxynaphthalene (68.2 mg, 0.196 mmol, 1.5 equiv), Pd(PPh₃)₄ (7.59 mg, 0.007 mmol, 5% equiv), The round-bottom flask was filled with 2 mL H₂O and 10 mL THF. Argon was added after the round bottom flask had been vacuum-degassed. Then, for more than 96 hours, it was heated at 88°C. To reach room temperature, the mixture was chilled. In a single pot, the resultant mixture was then added to MeOH/HCl. The precipitated components were collected by filtration through a Buchner funnel and repeatedly rinsed with methanol and water. The solid was further dried to produce earthy yellow solid (44.6mg, 35% yield, M_n=4153, M_w=5235, PDI=1.261). ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.75 – 6.88 (Ar-H), 3.97–3.57(OMe-H).

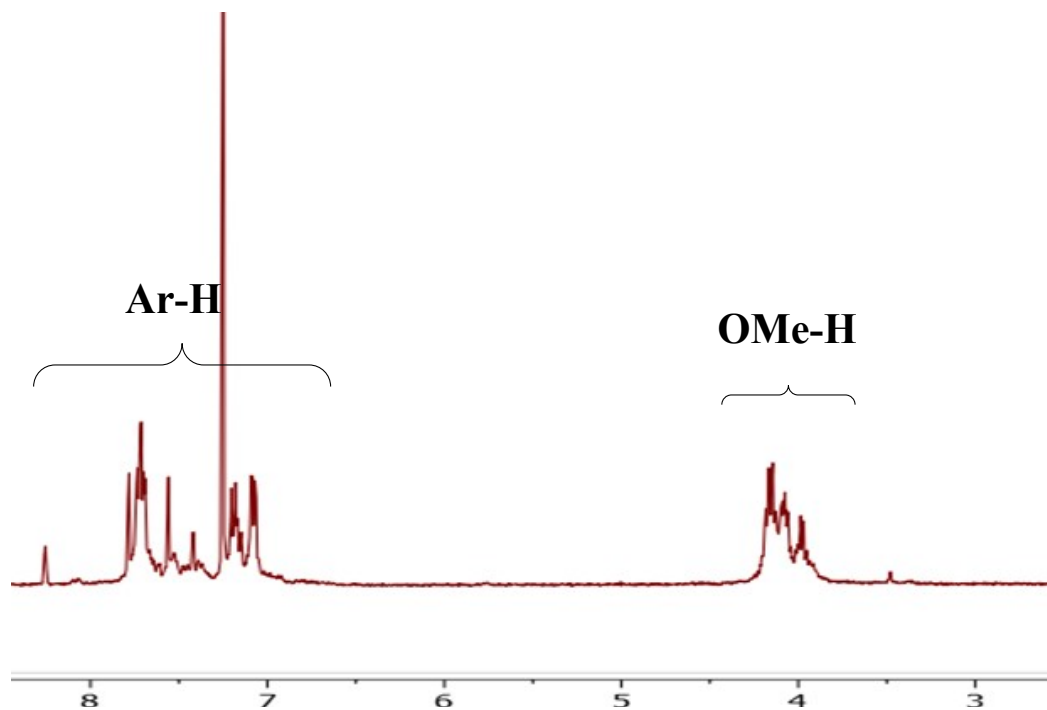


Figure S10. NMR of Polymer 6

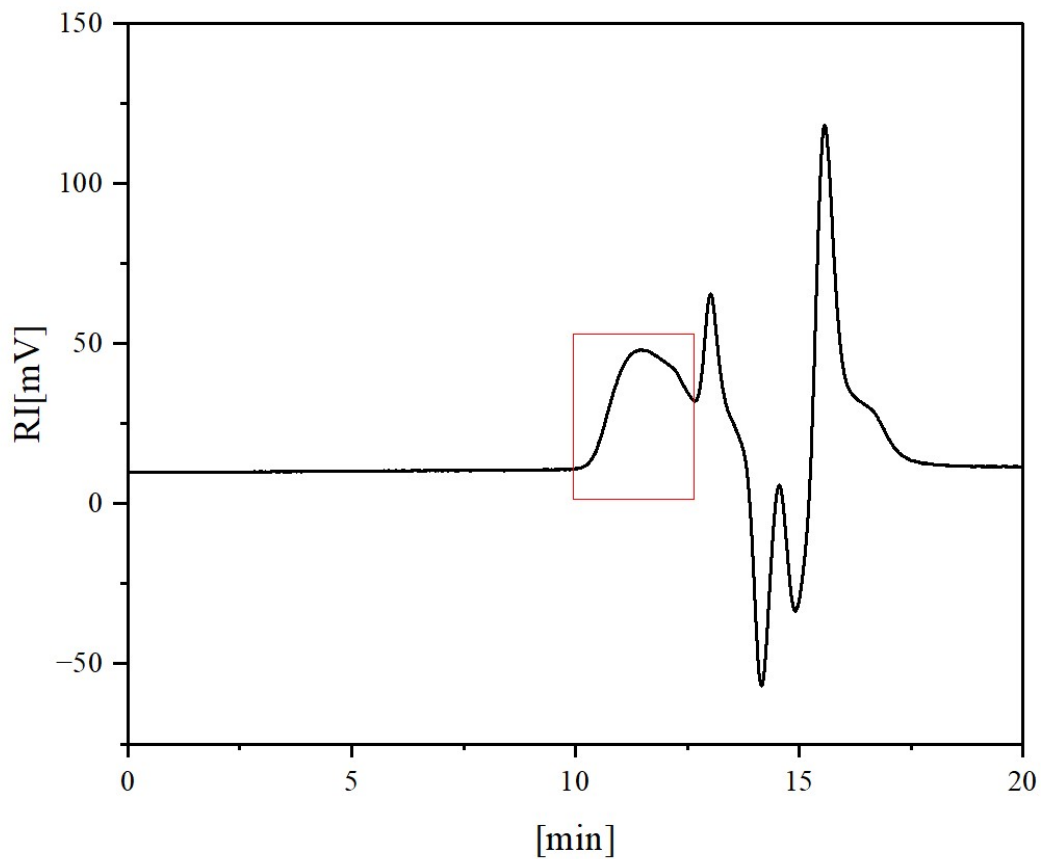


Figure S11. NMR of Polymer 6

Reference

1. G. Wu, Y. Liu, Z. Yang, L. Ma, Y. Tang, X. Zhao, H. Rouh, Q. Zheng, P. Zhou, J.-Y. Wang, F. Siddique, S. Zhang, S. Jin, D. Unruh, A. J. A. Aquino, H. Lischka, K. M. Hutchins and G. Li, *Research (Wash. D.C.)*, 2021, **2021**, 3565791.
2. N. M. Padial, C. Chinchilla-Garzón, N. Almora-Barrios, J. Castells-Gil, J. González-Platas, S. Tatay and C. Martí-Gastaldo, *J. Am. Chem. Soc.*, 2023, **145**, 21397–21407.