

Synthesis of metalloporphyrin-based conjugated microporous polymer spheres directed by bipyridine-type ligands

Guipeng Ji, Zhenzhen Yang, Yanfei Zhao, Hongye Zhang, Bo Yu, Jilei Xu, Huanjun Xu, Zhimin Liu*

Beijing National Laboratory for Molecular Sciences, Key Laboratory of Colloid, Interface and Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
E-mail: liuzm@iccas.ac.cn

Contents

1. General experimental methods.....	S2
2. Synthesis of Zn-CMPs ⁵	S7
3. Table S1 Zn+TB-CMP particles obtained under different conditions.	S8
4. Table S2 Contrast tests for possible mechanism ^a	S8
5. Table S3 Elemental analysis.....	S9
6. ¹³ C NMR analysis.....	S9
Figure S1	S9
7. SEM images of Zn+TB-CMPs obtained under different conditions.....	S10
Figure S3	S10
Figure S4	S10
Figure S5	S11
8. N ₂ sorption isotherms	S11
Figure S6	S11
Figure S7	S12
9. Fourier transform infrared (FT-IR) spectra.	S12
Figure S8	S12
10. Time-dependent TEM images of the bulky Zn+TB-CMP.....	S13
Figure S9	S13
11. ¹ H NMR spectra of the time-dependent reaction solution	S13
Figure S10	S13
12. Reference.....	S14

1. General experimental methods.

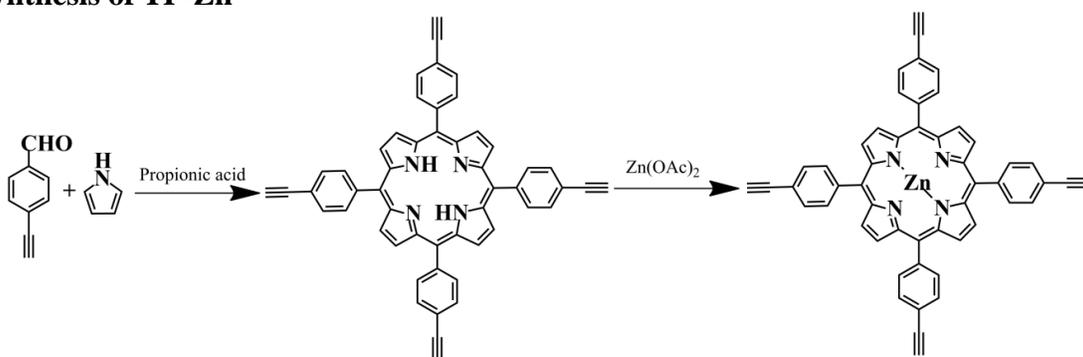
Materials

All reagents and solvents were purchased from Beijing Chemical Company and were used without further purification, unless indicated otherwise. [5,10,15,20-tetrakis(4-ethynylphenyl)porphyrin]zinc(II) (TP-Zn),¹ 2,8-dibromo-6H,12H-5,11-methanodibenzo[b,f]diacine (TB),² 1,4-bis(pyridin-4-ylethynyl)benzene (BPEB) were prepared following procedures reported in the literature with some modifications.

Instrumentation

Liquid ¹H NMR spectra were recorded in CDCl₃ or DMSO using internal reference (the residue proton peaks of CHCl₃ at 7.26 ppm and DMSO at 2.5 ppm) on Bruker 400 spectrometer. Liquid ¹³C NMR was recorded at 100.6 MHz in CDCl₃ using residual CHCl₃ as internal reference (the residue proton peaks of CHCl₃ at 77.02 ppm and DMSO at 40.03 ppm). Solid-state NMR experiments were performed on a Bruker WB Avance II 400 MHz spectrometer. The ¹³C CP/MAS NMR spectra were recorded with a 4-mm double-resonance MAS probe and with a sample spinning rate of 12.0 kHz; a contact time of 2 ms (ramp 100) and pulse delay of 3 s were applied. FT-IR spectra of the samples were collected on a TENSOR 27 FTIR at a resolution of 2 cm⁻¹. Matrix Assisted Laser Desorption/ Ionization-Time of Flight Mass (MALDI-TOF MS) spectra were performed on a Bruker Autoflex III spectrometer using tetrahydrofuran as a matrix. Electron Impact Mass (EI MS) Spectra were performed on DFS Mass Spectrometer. The elemental analysis of the polymer was determined using a Flash EA1112 analyzer. The nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020M system. The samples were treated at 120°C for 12 h before the measurements. Surface areas were calculated from the adsorption data using Langmuir and Brunauer-Emmett-Teller (BET) methods. The pore-size-distribution curves were obtained from the adsorption branches using non-local density functional theory (NLDFT) methods. Field emission scanning electron microscopy (SEM) observations were performed on a Hitachi S-4800 microscope operated at an accelerating voltage of 10.0 kV. Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-1011 and JEM-2010. Transmission electron microscope operated at 200 kV. The hydrodynamic diameter of the CMPs was achieved using a Zetasizer Nano at 25 °C. The thermal properties of the materials were evaluated using a thermogravimetric analysis (TGA) instrument (STA PT1600 Linseis) over the temperature range of 25°C to 800°C under air atmosphere with a heating rate of 10°C/min.

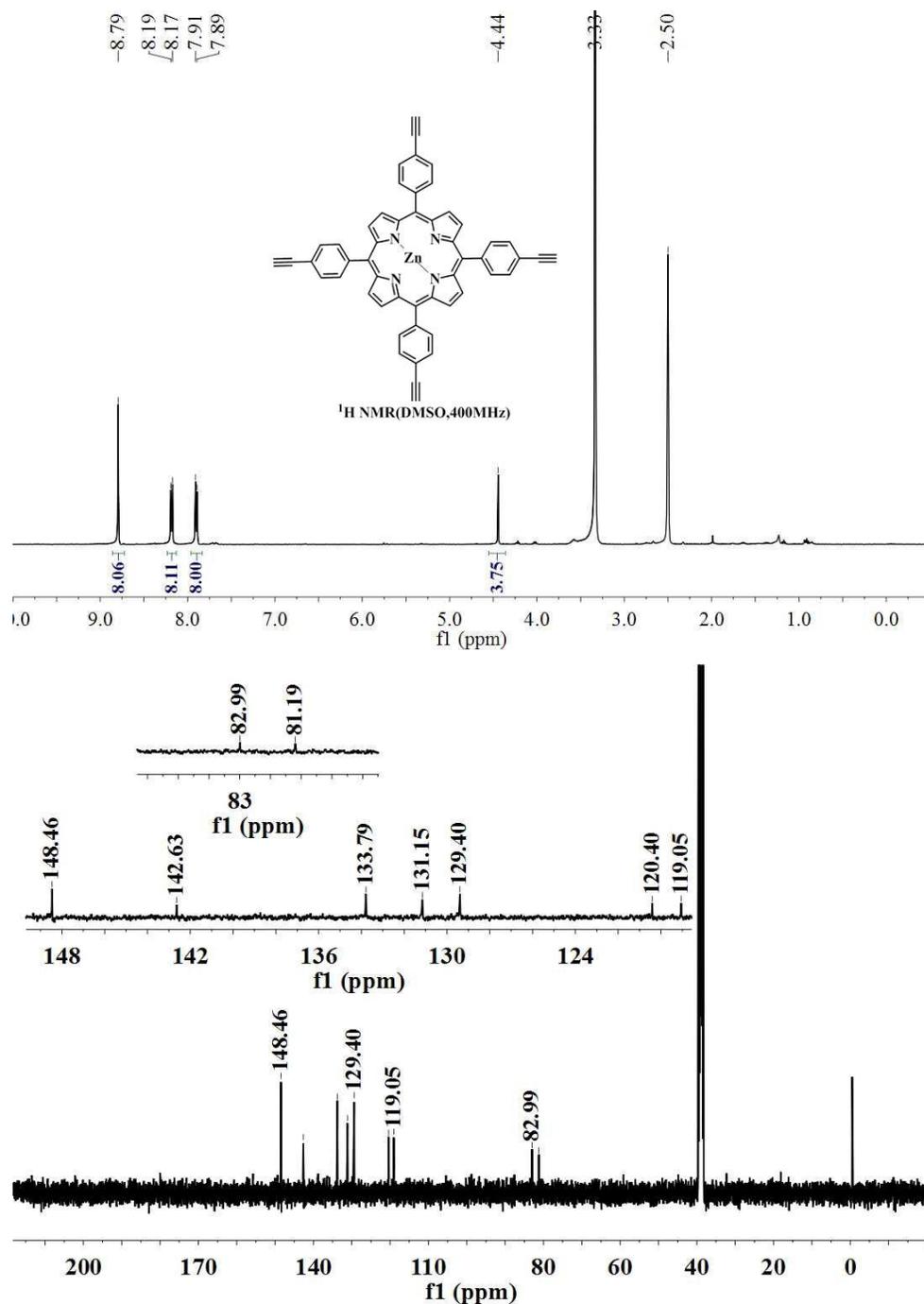
(1) Synthesis of TP-Zn^{1,3}



4-Alkynebenzaldehyde (5.21 g, 40 mmol) was dissolved in a mixture of nitrobenzene (80 mL) and propionic acid (150 mL). After heated to 120°C, the mixture was charged with fresh pyrrole (3.2 mL, 46 mmol), and it turned dark black immediately. After stirred at 120°C for 2 h, it was cooled to room temperature. Left to stand overnight, the mixture was filtered to get dark brown crystals. Washed with methanol until the filtrate was colorless, the crystals were purified by column chromatography (CH₂Cl₂). The solvent was removed in vacuo to get the product 1.2 g as a brown solid. (17% yield)

For the synthesis of TP-Zn, 5,10,15,20-tetrakis(4-ethynylphenyl)porphyrin (1.2g, 1.7mmol) was dissolved in 400mL of the mixture CHCl₃/CH₃OH (3:1), and then Zn(OAc)₂ (3g, 16mmol) was added. The solution was stirred violently at room temperature for 36h. After the solvent was removed by reduced pressure distillation, the product was extracted with CHCl₃/H₂O, and was then purified by column chromatography (CH₂Cl₂/EtOAc= 4:1), getting 1g of brown product (85% yield).

¹H NMR (DMSO, 400 MHz) data: δ 4.46 (CCH, s, 4H), 7.90 (m-ArH, d, 8H), 8.21 (o-ArH, d, 8H), 8.81 (b-H, s, 8H); ¹³C NMR (DMSO, 100.6 MHz) δ 81.19, 82.99, 119.05, 120.4, 129.4, 131.15, 133.79, 142.63, 148.46; MALDI-TOF calculated for [M]: C₅₂H₂₈N₄Zn (774.19), found [M] (772, 773, 774, 775, 776).

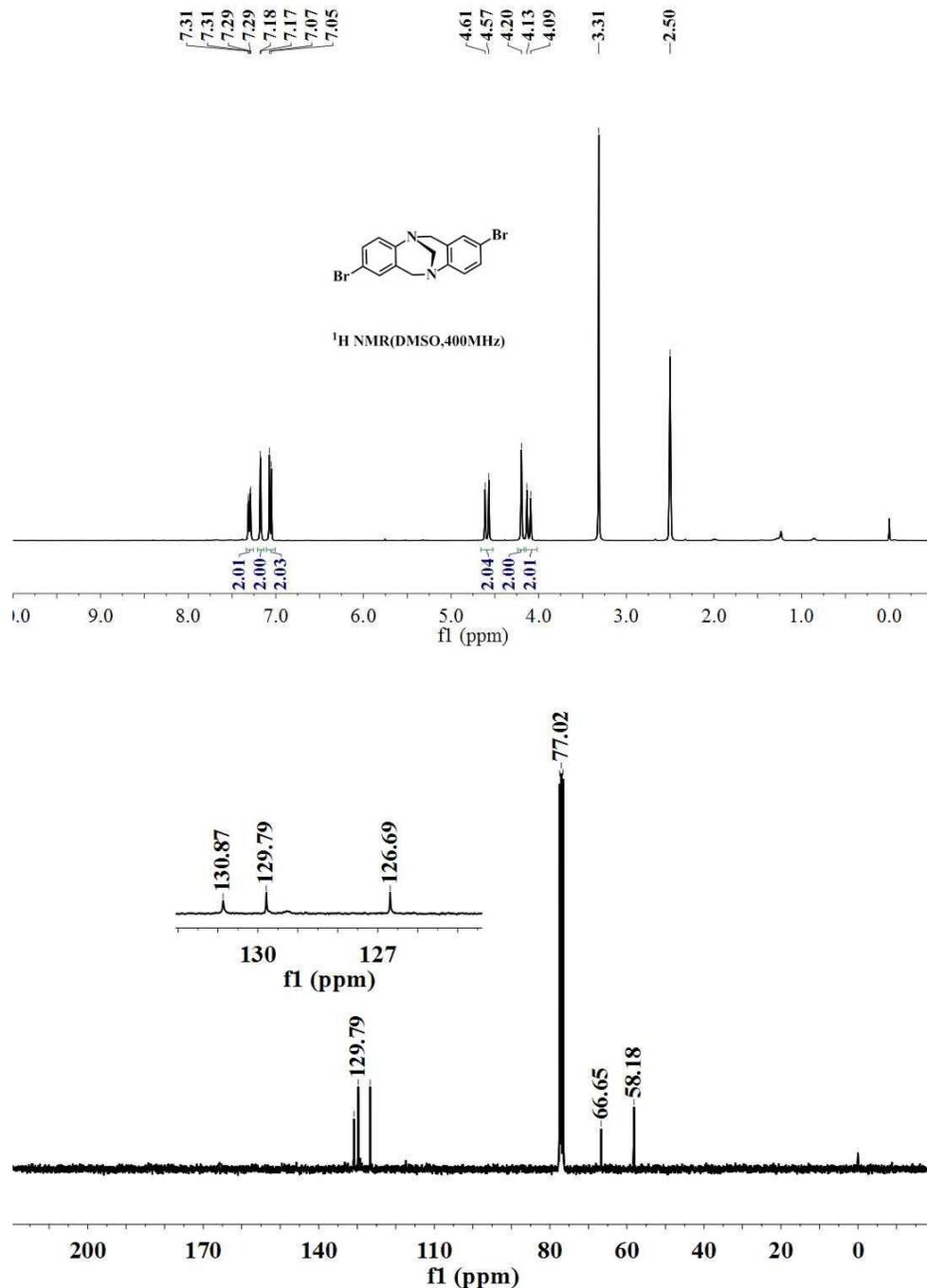


(2) Synthesis of TB²

To a stirred mixture of aniline (1.725 g, 10 mmol) and paraformaldehyde (0.63 g, 21 mmol) was added trifluoroacetic acid (TFA) (20 mL) dropwise and stirring was continued for 82 h at 0°C. After TFA was removed by vacuum distillation, water (5 mL) was added, followed by addition of a saturated aqueous solution of NH₃ (10 mL). The aqueous layer was extracted with dichloromethane. The combined organic layers were dried with MgSO₄, filtered, concentrated by

vacuum distillation and purified by column chromatography (Petroleum ether/CH₂Cl₂=1:1) to get light yellow product. (45% yield).

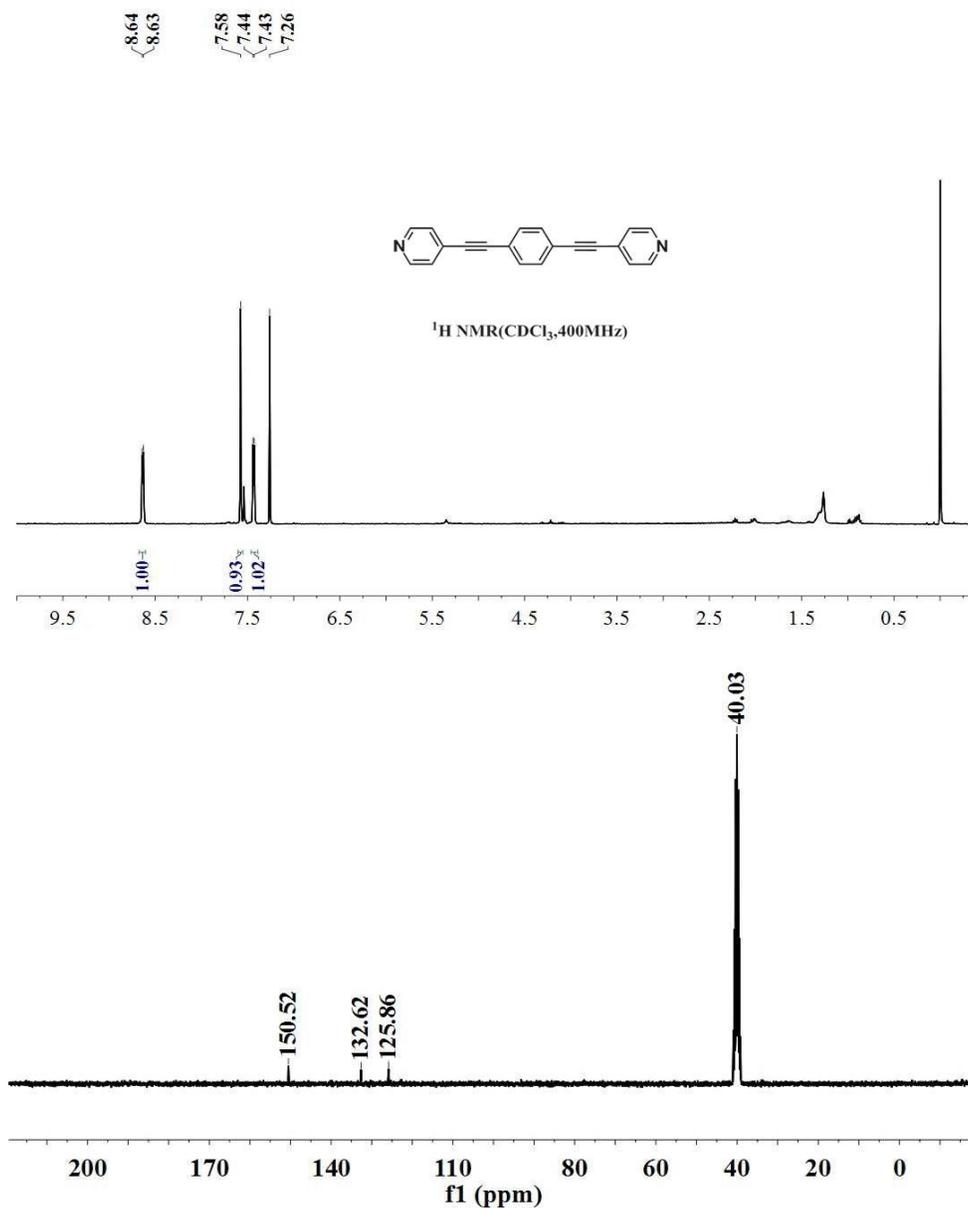
¹H-NMR (DMSO, 400 MHz) data: 4.10 (d, 2H, H-6endo and H-12endo), 4.20 (s, 2H, H-13), 4.60 (d, 2H, H-6exo and H-12exo), 7.06 (d, 2H, H-4 and H-10), 7.18 (d, 2H, J = 1.5 Hz, H-1 and H-7), 7.30 (dd, 2H, H-3 and H-9); ¹³C NMR (CDCl₃, 100.6 MHz) δ 58.18, 66.65, 126.69, 129.79, 130.87; EI-MS calculated for [M]: C₂₀H₁₂N₂ (380.08), found [M] (377, 378, 379, 380, 381, 382), [M-Br] (297, 298, 299, 300, 301, 302), [M-Br₂] (218, 219, 220).



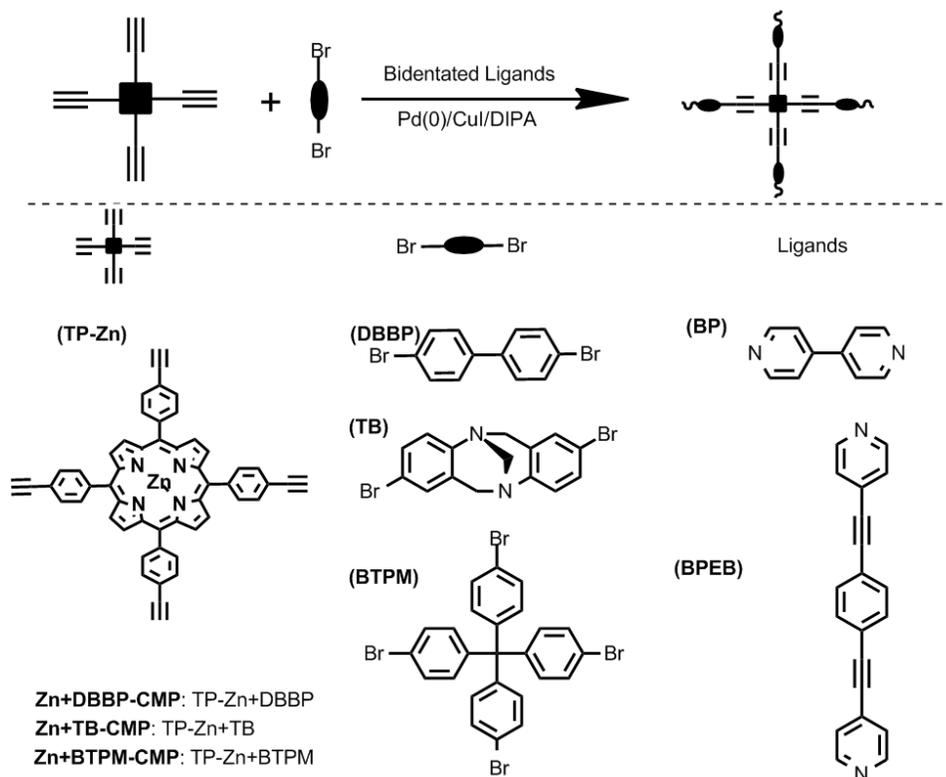
(3) Synthesis of BPEB⁴

1,4-Diethynylbenzene (126 mg, 1 mmol), 4-Iodopyridine (416 mg, 2 mmol), diisopropylamine (20 mL), Pd(PPh₃)₄ (115 mg, 0.1 mmol), and CuI (19 mg, 0.1 mmol) was dissolved in 120 mL of the mixture of CHCl₃/THF (2:1). After degassed 3 times by Freeze-Pump-Thaw, The solution was stirred vigorously for 36 h at room temperature. The solvent was removed by reduced pressure distillation, and the product was purified by column chromatography (CH₂Cl₂), getting pale pink powders, which had blue fluorescent in CH₂Cl₂ solution (25% yield).

¹H-NMR (CDCl₃, 400 MHz) data: 7.43 (β-Py-H, d, 4H), 7.58 (Ben-H, s, 4H), 8.63 (α-Py-H, d, 4H); 8.16 (o-Ar-H, d, 3J = 8.40 Hz, 8H); 8.84 (b-H, s, 8H); ¹³C NMR (DMSO, 100.6 MHz) δ 125.86, 132.62, 150.52; EI-MS calculated for [M]: C₂₀H₁₂N₂ (280.32), found [M] (278, 279, 280, 281, 282), [M-N₂] (251, 252, 253, 254), [M-C₅H₅N] (199, 200, 201)



2. Synthesis of Zn-CMPs ⁵



TP-Zn (100 mg, 0.13 mmol) and brominated monomer (0.26 mmol) were dissolved in CHCl_3 (60 mL) containing ligand (e.g., BP or BPEB, 0.06mmol), diisopropylamine (10 mL) and stirred at room temperature for 12 h. Then, the solution was degassed 3 times by Freeze-Pump-Thaw, after which $\text{Pd}(\text{PPh}_3)_4$ (22 mg, 0.02 mmol), and CuI (5 mg, 0.025 mmol) was added. Then, the solution was stirred for desired time at desired temperature under nitrogen or air atmosphere. During the reaction process, the solution turned cloudy obviously. After filtration and washing with THF and CHCl_3 for three times, dark green or brown solid was obtained, which was further treated by Soxhlet extraction using THF and CHCl_3 , and dried under vacuum at 120°C overnight. Dark green or brown solid was collected. TP-Zn was completely converted confirmed by the colorless of the reaction solution.

3. Table S1 Zn+TB-CMP particles obtained under different conditions.

Entry	Ligand ^a	Gas	T/t	Solvent	Yield% ^b	Morphology	Size ^c
1	No	N ₂	25°C /12 h	THF	70	Figure S2a	-
2	No	N ₂	25°C /12 h	CHCl ₃	68	Figure S2a	-
3	No	N ₂	25°C /12 h	THF/CHCl ₃ (1:1)	65	Figure S2a	-
4	BP(1:2)	N ₂	25°C /12 h	THF	69	Figure S2b	-
5 ^d	BP(1:2)	N ₂	25°C /12 h	Toluene	72	Figure S2c	-
6	BP(1:2)	N ₂	25°C /12 h	CHCl ₃	67	Figure S4b	350
7 ^e	BP(1:2)	N ₂	25°C /12 h	CHCl ₃	66	Figure S2a	-
8	BP(1:2)	N ₂	50°C /12 h	CHCl ₃	71	Figure S2b	-
9	BP(1:1)	N ₂	25°C /12 h	CHCl ₃	67	Figure S4b	340
10	BP(2:1)	N ₂	25°C /12 h	CHCl ₃	69	Figure S2b	-
11	Pyridine(1:1)	N ₂	25°C /12 h	CHCl ₃	67	Figure s2a	-
12	BPEB(1:2)	N ₂	25°C /12 h	CHCl ₃	69	Figure S4b	360
13 ^f	BP(1:2)	N ₂	25°C /12 h	CHCl ₃	65	Figure S4c	350
14	BP(1:2)	N ₂	25°C /96 h	CHCl ₃	73	Figure S4b	370
15	BP(1:2)	N ₂	0°C /48 h	CHCl ₃	69	Figure S4a	400
16	BP(1:2)	air	0°C /48 h	CHCl ₃	66	Figure S3a	360
17	BP(1:2)	air	20°C /12 h	CHCl ₃	61	Figure S3b	560
18	BP(1:2)	air	25°C /12 h	CHCl ₃	61	Figure S3c	740
19 ^g	BP(1:2)	N ₂	25°C /24 h	Toluene	74	Figure S2c	-
20 ^h	BP(1:2)	N ₂	25°C /12 h	CHCl ₃	71	Figure S5a	320
21 ⁱ	BP(1:2)	N ₂	25°C /12 h	CHCl ₃	72	Figure S5a	380

^a Numbers in the bracket was the molar ratio of ligand and TP-Zn. ^b The yield was calculated based on the amount of added substances. ^c Got by the DLS method (nm). ^d Diisopropylamine (20 mL) was added. ^e Bipyridine was added after the reaction reacted for 12 h. ^f TP-Zn (200 mg) was added(2 fold concentration). ^g the system was reacted at 100°C for another 12 h. ^h Zn+DBBP-CMP spheres were synthesized. ⁱ Zn+BTPM-CMP spheres were synthesized.

Table S2 Contrast tests for possible mechanism^a

Entry	R-≡	R'-Br	gas	T/t	phenomenon	Yield% ^b
1	1,3,5-triethynyl benzene	TB-Br	N ₂	25°C /12 h	bulk bodies	65%
2	TP-Zn	-----	N ₂	25°C /12 h	no precipitate	-
3	TP-Zn	-----	Air	0°C /12 h	little precipitate	-
4	TP-Zn	-----	Air	25°C /12 h	much precipitate	93%

^a CHCl₃ was used as solvent for these contrast tests with bipyridine inside. ^b The yield was calculated based on the amount of added substances.

5. Table S3 Elemental analysis.

Entry	C%	H%	N%	Zn%	Total%	Br% ^a	Br% ^b	Efficiency% ^c
Zn-DBBP-CMPs	73.94	4.84	5.94	5.30	90.02	9.98	22.92	56.45
Zn-TB-CMPs	74.78	5.15	6.52	5.03	91.48	8.52	20.89	59.22
Zn-BTPM-CMPs	76.36	4.38	6.31	4.96	92.01	7.99	22.73	64.85

^a Br contents of CMPs (the CMPs were composed of C, H, N, Zn, Br). ^b Br contents of substance (TP-Zn and R-Br). ^c the reaction efficiencies was obtained by $1-(\text{Br}\%^{\text{a}}/\text{Br}\%^{\text{b}})$.

6. ¹³C NMR analysis

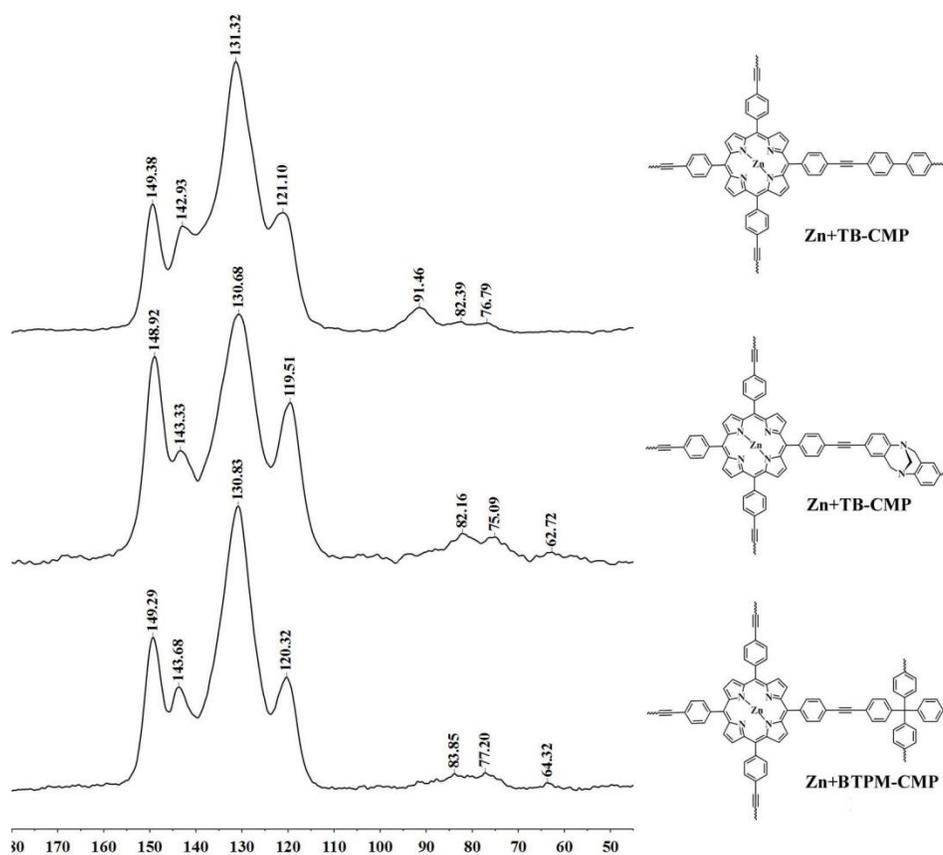


Figure S1 Solid-state ¹³C-CP/MAS NMR spectra for the CMP spheres

7. SEM images of Zn+TB-CMPs obtained under different conditions

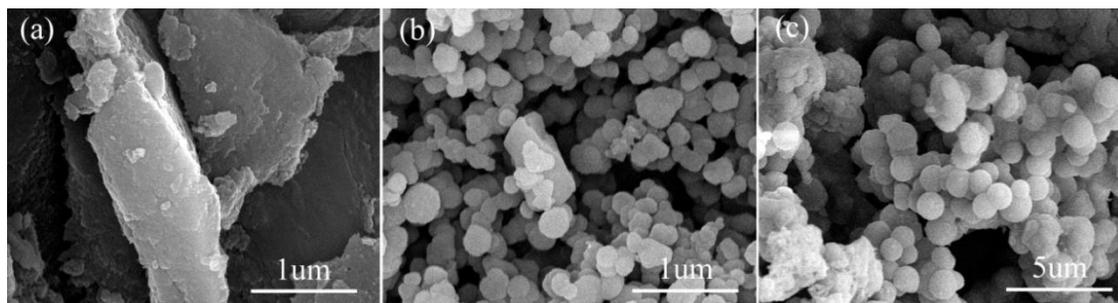


Figure S2 SEM images of the Zn+TB-CMPs obtained in different solvents: (a) THF/CHCl₃ without ligand or with pyridine, (b) the mixture of THF and CHCl₃ in the presence of bipyridine, (c) toluene in the presence of bipyridine.

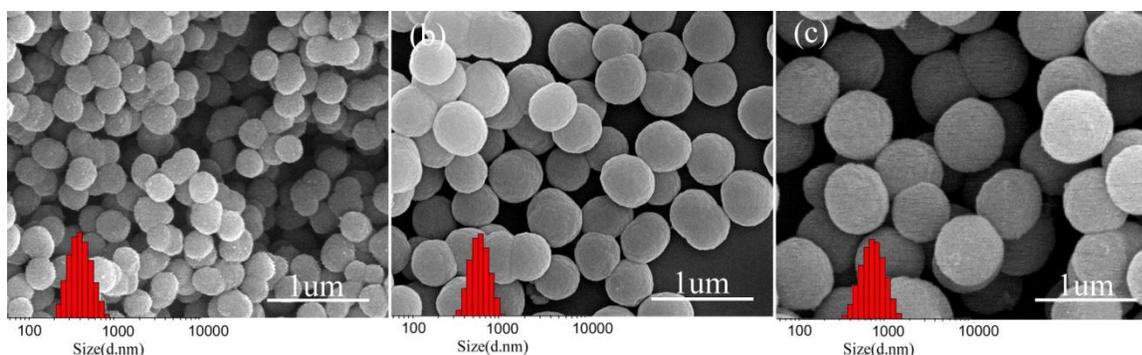


Figure S3 SEM images of the Zn+TB-CMPs obtained under air atmosphere in CHCl₃ with bipyridine: (a) 0°C, (b) 20°C, (c) 25°C.

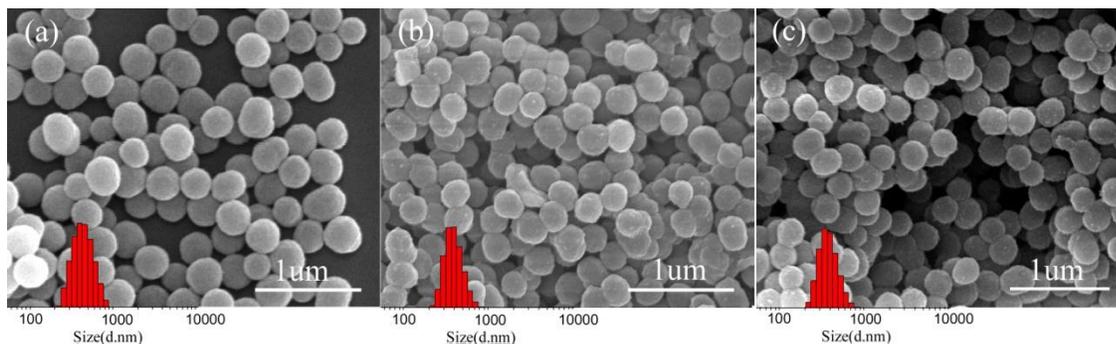


Figure S4 SEM images of the Zn+TB-CMPs obtained under N₂ atmosphere with bipyridine in CHCl₃ at different temperature and concentration: (a) 0°C, (b) 25°C, (c) 25°C, obtained in the solution with 2-fold TP-Zn and TB concentrations.

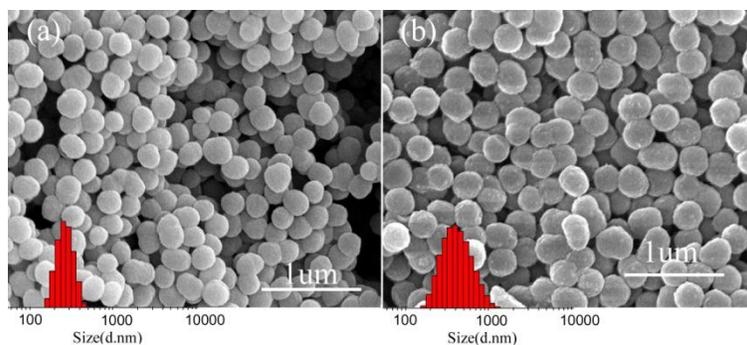


Figure S5 SEM images of the **Zn-CMP** spheres obtained via the coupling of porphyrin and other monomers in CHCl_3 with bipyridine: (a) **Zn+DBBP-CMP** spheres obtained at 25°C . (b) **Zn+BTPM-CMP** spheres obtained at 25°C .

8. N_2 sorption isotherms

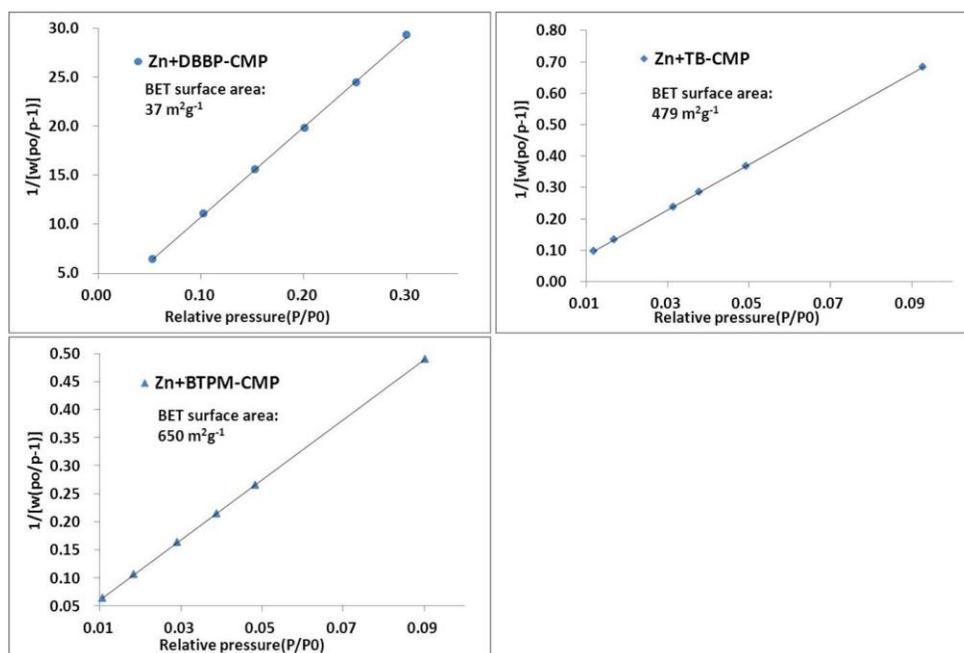


Figure S6 BET plot from N_2 isotherms at 77 K of the **CMP** spheres.

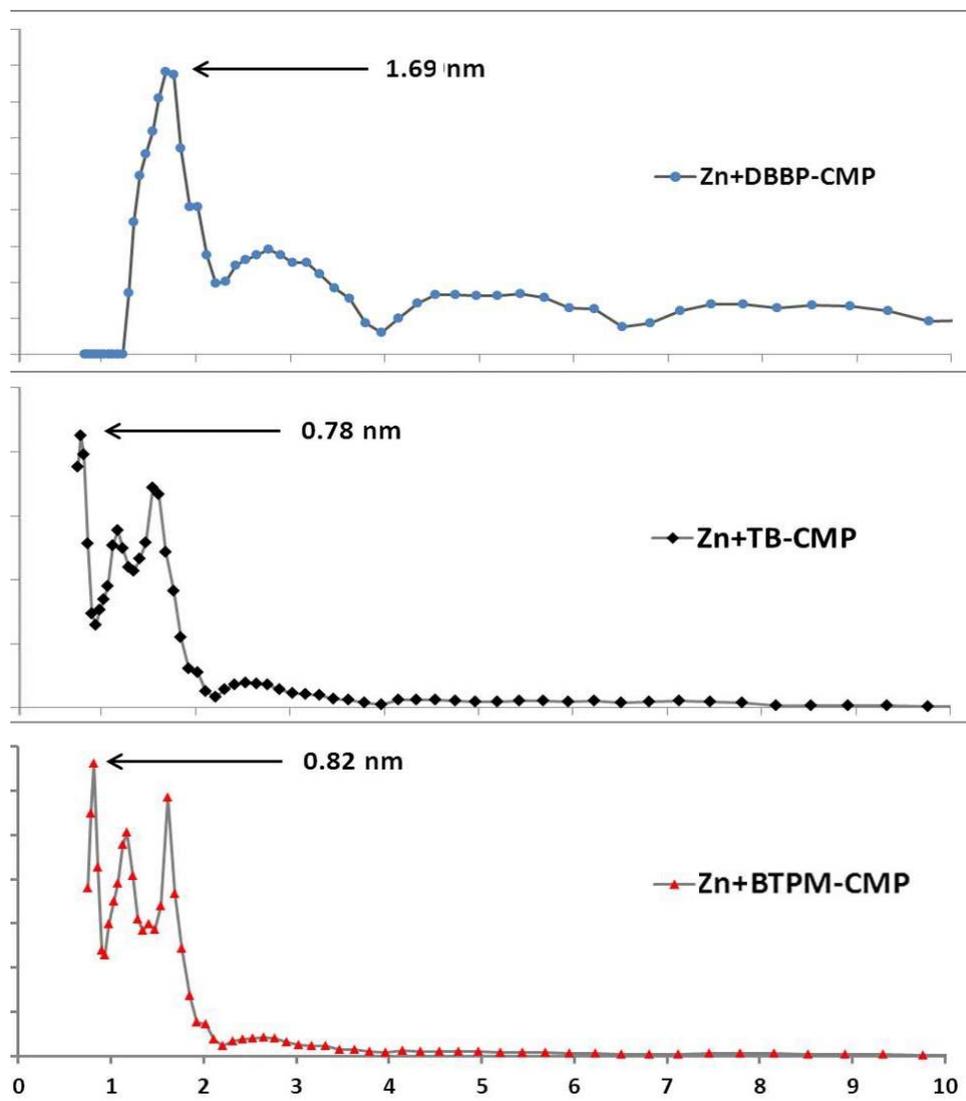


Figure S7 Pore size distributions for CMP spheres from the adsorption branch of the N_2 isotherms by NLDFT method.

9. Fourier transform infrared (FT-IR) spectra.

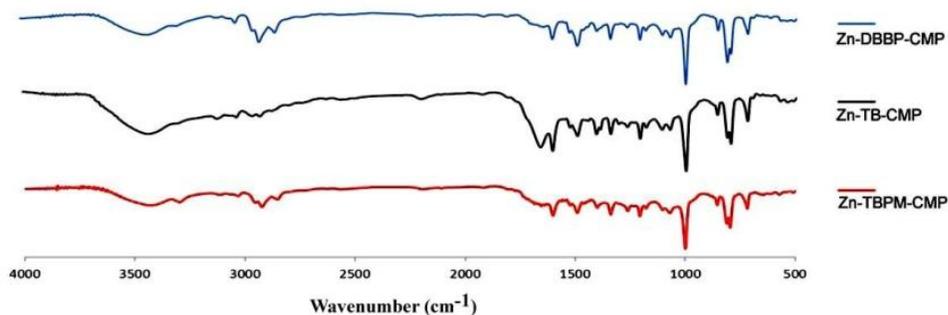


Figure S8 FT-IR spectrum of the CMP spheres. The spectra were recorded as KBr pellets.

10. TEM images of the bulky Zn+TB-CMP obtained at different time.

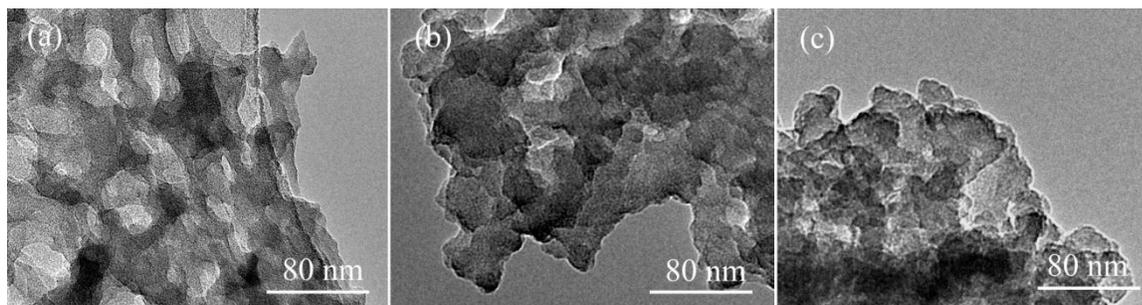


Figure S9 TEM images of the bulky Zn+TB-CMPs obtained at reaction time of (b) 1 h, (c) 4 h, (d) 12 h (CHCl_3 , 25°C , N_2).

11. ^1H NMR spectra for the reaction solutions at different time.

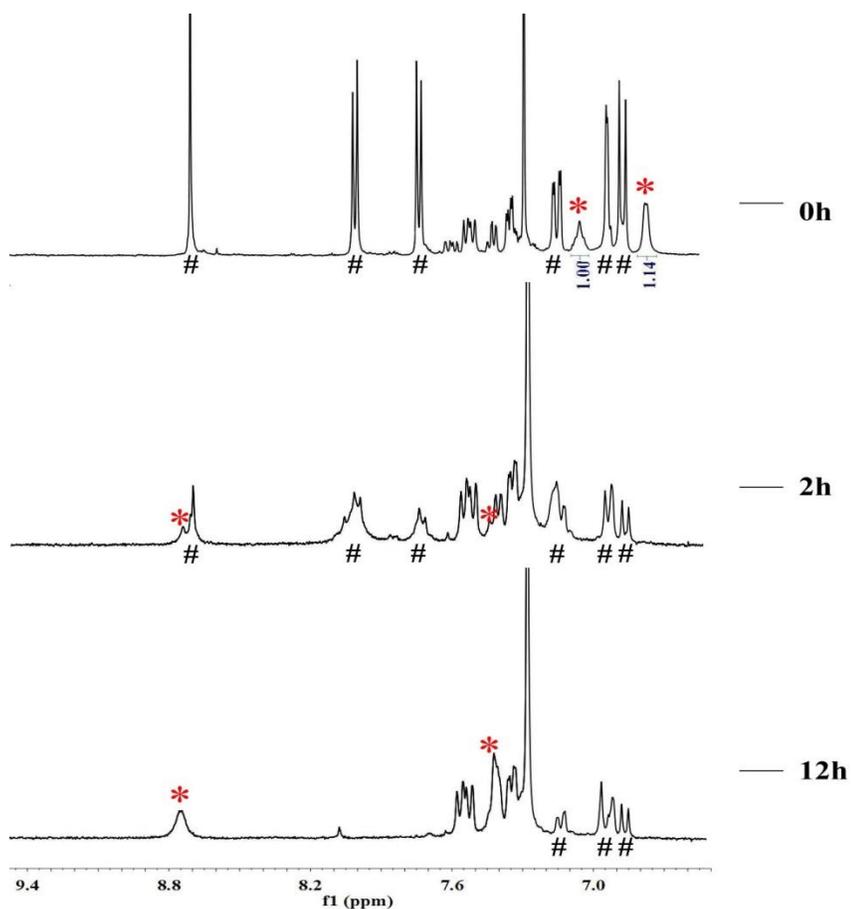


Figure S10 ^1H NMR spectrum of the reaction solutions at reaction time of (0 h), (2 h), (12 h). * peaks of bipyridine, # peaks of TP-Zn and TB.

12. Reference

1. S. Drouet, A. Merhi, D. Yao, M. P. Cifuentes, M. G. Humphrey, M. Wielgus, J. Olesiak-Banska, K. Matczyszyn, M. Samoc, F. Paul and C. O. Paul-Roth, *Tetrahedron*, 2012, **68**, 10351-10359.
2. A. Hansson, J. Jensen, Ola F. Wendt and K. Wärnmark, *Eur. J. Org. Chem.*, 2003, **16**, 3179-3188.
3. J. L. Shaw, S. A. Garrison, E. A. Alemán, C. J. Ziegler and D. A. Modarelli, *J. Org. Chem.*, 2004, **69**, 7423-7427.
4. B. H. Kaae, K. Harpsøe, T. Kvist, J. M. Mathiesen, C. Møck, D. Gloriam, H. N. Jimenez, M. A. Uberti, S. M. Nielsen, B. Nielsen, H. Bräuner-Osborne, P. Sauerberg, R. P. Clausen and U. Madsen, *ChemMedChem*, 2012, **7**, 440-451.
5. Z. Wang, S. Yuan, A. Mason, B. Reprogle, D. J. Liu and L. Yu, *Macromolecules*, 2012, **45**, 7413-7419.