Electronic Supplementary Information

for

High-Yield Synthesis of [m]Biphenyl-Extended Pillar[n]arenes for Efficient Selective Inclusion of toluene and *m*-xylene in the Solid State

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1. Methods

Starting materials and reagents were purchased from Aladdin and used as received. ¹H and ¹³C NMR spectra were recorded at 298 K on a Bruker AVANCEIII 500MHz instrument at room temperature. Chemical shifts were referred to TMS. Mass spectra were recorded on Bruker Daltonics Autoflex Speed Series: High-Performance MALDI-TOF Systems. Single-crystal X-ray diffraction data for the complexes were recorded on a Rigaku RAXIS-PRID diffractometer using the ω -scan mode with graphite-monochromator Mo K α radiation ($\lambda = 0.71073$ Å).

2. Experimental section

Synthesis of MDM:

To a solution of 1,4-dimethoxybenzene (138 g, 1 mol) in 300 mL dichloromethane, aluminum chloride (26.6)g, 0.2 mol) was added. The solution of 4,4'-bis(chloromethyl)-1,1'-biphenyl (25 g, 0.1 mol) in 250 mL dichloromethane was added dropwise for one hour. The resulting mixture was stirred at room temperature for another hour until quenched with water. Organic layer was washed with water and brine, concentrated and purified through reduced pressure distillation to remove 1,4-dimethoxybenzene. The residue was purified by flash column chromatography on silica gel (petroleum ether : DCM = 2:1) to give the product as white powder (21 g, 46%).

¹H NMR (500 MHz, CDCl₃): δ 7.46 (d, J = 8.1 Hz, 4H), 7.25 (d, J = 8.0 Hz, 4H), 6.78 (d, J = 8.4 Hz, 2H), 6.74-6.64 (m, 4H), 3.96 (s, 4H), 3.76 (s, 6H), 3.70 (s, 6H); ¹³C NMR (126 MHz, CDCl₃): δ 153.58, 151.74, 139.67, 138.77, 130.88, 129.32, 126.97, 116.93, 111.47, 111.30, 56.09, 55.68, 35.69; MS (EI): C₃₀H₃₀O₄ calcd. m/z, 454.21, found m/z 454.31.

Synthesis of macrocycles:

Paraformaldehyde (0.9 g, 30 mmol) and **MDM** (4.56 g, 10 mmol) were added to a DCM solution (500 mL) in a 1 L flask. The resulting solution was stirred under nitrogen protection with boron trifluoride diethyl etherate (1.5 mL, 12 mmol) added. After stirred for 25 minutes at room temperature, the reaction was quenched with sodium hydroxide

solution. The organic layer was washed with water and brine, concentrated and purified by silica gel chromatography.

[2]Bp-ExP6 (2.3 g, 50%) was obtained after recrystallization from chloroform and acetone and dried under vacuum. ¹H NMR (500 MHz, CDCl₃): δ 7.37 (d, *J* = 8.1 Hz, 8H), 7.20 (d, *J* = 8.1 Hz, 8H), 6.94 (s, 4H), 6.69 (s, 4H), 3.93 (s, 8H), 3.88 (s, 4H), 3.77 (s, 12H), 3.71 (s, 12H); ¹³C NMR (126 MHz, CDCl₃): δ 151.43, 151.22, 140.30, 138.62, 128.84, 128.49, 127.24, 126.80, 114.75, 113.69, 56.13, 56.08, 35.89, 30.25; MALDI-TOF: C₆₂H₆₀O₈ calcd. m/z 932.43, found m/z 932.278.

[3]Bp-ExP9 (isolated yield: ca. 1.2%) was obtained after recrystallization from chloroform and methanol in refrigerator and dried under vacuum. ¹H NMR (500 MHz, CDCl₃) δ 7.43 (d, *J* = 7.9 Hz, 12H), 7.22 (d, *J* = 7.9 Hz, 12H), 6.66 (s, 6H), 6.63 (s, 6H), 3.95 (s, 12H), 3.90 (s, 6H), 3.72 (s, 18H), 3.64 (s, 18H); ¹³C NMR (126 MHz, CDCl₃) δ 151.52, 151.28, 140.19, 138.55, 129.06, 128.00, 127.64, 126.77, 113.92, 113.49, 56.20, 56.14, 35.62, 29.74; MALDI-TOF: C₉₃H₉₀O₁₂ calcd. m/z 1399.65, found m/z 1398.974.

[2]Bp-ExP7 (isolated yield: ca. 0.1%) was obtained after dried under vacuum. ¹H NMR (500 MHz, CDCl₃): δ 7.40 (dq, J = 8.6, 2.5 Hz, 8H), 7.20 (d, J = 8.0 Hz, 8H), 6.70 (s, 2H), 6.68 (s, 2H), 6.66 (s, 2H), 6.62 (s, 2H), 6.57 (s, 2H), 3.95 (s, 4H), 3.94 (s, 4H), 3.89 (s, 6H), 3.73 (s, 6H), 3.72 (s, 6H), 3.66 (s, 6H), 3.64 (s, 6H), 3.60 (s, 6H); ¹³C NMR (126 MHz, CDCl₃): δ 151.59, 151.53, 151.38, 151.31, 140.17, 140.09, 138.53, 138.50, 128.94, 128.92, 128.10, 127.53, 127.51, 127.29, 126.69, 126.66, 114.29, 114.02, 113.89, 113.65, 113.50, 56.25, 56.16, 56.15, 56.06, 35.94, 35.89, 30.29; MALDI-TOF: C₇₁H₇₀O₁₀ calcd. m/z 1082.50, found m/z 1083.191.

[2]Bp-ExP5 (isolated yield about 0.1%) was obtained after dried under vacuum. ¹H NMR (500 MHz, CDCl₃): δ 7.32 (d, J = 7.9 Hz, 4H), 7.27 (d, J = 7.9 Hz, 4H), 7.18 (d, J = 7.9 Hz, 4H), 7.07 (d, J = 7.8 Hz, 4H), 6.93 (s, 2H), 6.70 (s, 2H), 6.65 (s, 2H), 3.90 (s, 4H), 3.89 (s, 4H), 3.85 (s, 2H), 3.74 (s, 6H), 3.72 (s, 6H), 3.69 (s, 6H); ¹³C NMR (126 MHz, CDCl₃): δ 151.37, 151.11, 151.00, 140.85, 140.44, 138.43, 138.30, 129.13, 128.86, 128.63, 128.52, 127.87, 126.71, 126.66, 114.83, 114.19, 113.56, 56.36, 56.15, 56.11, 35.80, 35.57, 30.06; MALDI-TOF: C₅₃H₅₀O₆ calcd. m/z 782.36, found m/z 781.8.

3. Characterization and Crystal Structure Analysis

Compound	toluene⊂[2]Bp-ExP6	<i>m</i> -xylene⊂[2]Bp-ExP6
Empirical formula	$C_{76}H_{76}O_8$	$C_{78}H_{80}O_8$
Formula weight	1117.37	1145.42
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
$a/ m \AA$	11.4425(7)	11.3535(13)
$b/{ m \AA}$	11.4934(8)	11.5292(13)
$c/{ m \AA}$	13.0446(9)	13.4501(15)
α/deg.	74.0060(10)	70.421(2)
b/deg.	71.9220(10)	73.067(2)
γ/deg.	78.8180(10)	78.916(2)
V/Å ³	1556.65(18)	1578.1(3)
Ζ	1	1
$D_{ m calcd}/ m g\cdot m cm^{-3}$	1.192	1.205
m/mm^{-1}	0.076	0.076
<i>F</i> (000)	596.0	612
Theta range/deg.	1.69 to 26.02	1.66 to 26.04
Reflections collected	8354	8484
R(int)	0.0245	0.0287
R1, wR2 [obs I > 2σ (I)]	0.0686, 0.1624	0.0560, 0.1309
R1, wR2 (all data)	0.1069, 0.1937	0.0933, 0.1532
CCDC number	1448579	1450376

Table S1. Single crystal data



Figure S1. Comparison of ¹H NMR spectra between MDM and [2]Bp-ExP6 in CDCl₃.



Figure S2. Cavity size of [2]Bp-ExP6 in toluene⊂[2]Bp-ExP6.



Figure S3. Cavity size of [2]Bp-ExP6 in *m*-xylene⊂[2]Bp-ExP6.



Figure S4. Dihedral angle of dimethoxybenzene rings and the plane of six methylene bridges in toluene⊂[2]Bp-ExP6.



Figure S5. Dihedral angle of dimethoxybenzene rings and the plane of six methylene bridges in m-xylene \subset [2]Bp-ExP6.



Figure S6. Dihedral angle of biphenyl in toluene⊂[2]Bp-ExP6.



Figure S7. Dihedral angle of biphenyl in *m*-xylene⊂[2]**Bp-ExP6.**



Figure S8. Illustration of $\pi \cdots \pi$ interaction in toluene \subset [2] Bp-ExP6 (i and ii in Fig. 3).



Figure S9. Illustration of $\pi \cdots \pi$ interaction in *m*-xylene \subset [2]Bp-ExP6 (i and ii in Fig. 3).



Figure S10. Illustration of $\pi \cdots \pi$ interaction in toluene **[2]Bp-ExP6.**



Figure S11. Illustration of $\pi \cdots \pi$ interaction in *m*-xylene **C**[2]**Bp-ExP6.**



Figure S12. Illustration of C-H··· π interaction in toluene \subset [2]Bp-ExP6.



Figure S13. Illustration of C-H $\cdots\pi$ interaction in *m*-xylene \subset [2]Bp-ExP6.



Figure S14. Illustration of C-H··· π and C-H···O interactions in toluene **[2]Bp-ExP6**.



Figure S15. Illustration of C-H··· π and C-H···O interactions in *m*-xylene \subset [2]Bp-ExP6.



Figure S16. Illustration of C-H $\cdots\pi$ interaction in toluene \subset [2]Bp-ExP6.



Figure S17. Illustration of C-H··· π interaction in *m*-xylene⊂[2]Bp-ExP6.



Figure 1. Illustration of C-H…O interaction in toluene⊂[2]Bp-ExP6.



Figure S19. Illustration of C-H…O interaction in *m*-xylene⊂[2]Bp-ExP6.



Figure S20. The crystal structure of [2]Bp-ExP6 view along c axis.



Figure S21. ¹H NMR spectrum of MDM in CDCl₃.



Figure S22. ¹³C NMR spectrum of MDM in CDCl_{3.}



Figure S23. MS (EI) spectrum of MDM.



Figure S24. ¹H NMR spectrum of [2]Bp-ExP6 in CDCl₃.



Figure S25. DEPTQ ¹³C NMR spectrum of [2]Bp-ExP6 in CDCl_{3.}



Figure S26. MALDI-TOF-MS spectrum of [2]Bp-ExP6.



Figure S27. ¹H NMR spectrum of [3]Bp-ExP9 in CDCl₃.



Figure S28. ¹³C NMR spectrum of [3]Bp-ExP9 in CDCl_{3.}



Figure S29. MALDI-TOF-MS spectrum of [3]Bp-ExP9.



Figure S30. ¹H NMR spectrum of [2]Bp-ExP7 in CDCl₃.



Figure S31. DEPTQ¹³C NMR spectrum of [2]Bp-ExP7 in CDCl₃.



Figure S32 MALDI-TOF-MS spectrum of [2]Bp-ExP7.



Figure S33. ¹H NMR spectrum of [2]Bp-ExP5 in CDCl₃.



Figure S34. DEPQ ¹³C NMR spectrum of [2]Bp-ExP5 in CDCl_{3.}



Figure S35. MALDI-TOF-MS spectrum of [2]Bp-ExP5.