Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

# Syntheses of a pillar[4]arene[1]quinone and a difunctionalized pillar[5]arene by partial oxidation

Chengyou Han, Zibin Zhang, Guocan Yu and Feihe Huang*

*Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China.*

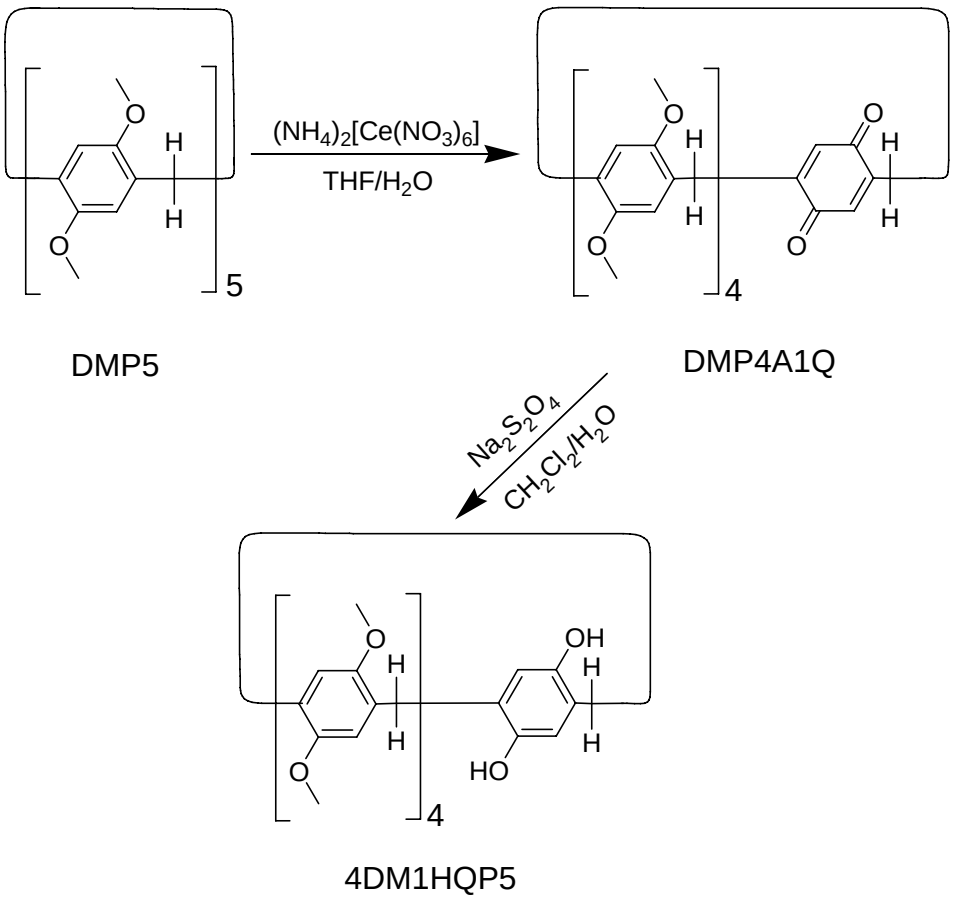
*Fax: +86-571-8795-1895; Tel: +86-571-8795-3189; Email address: fhuang@zju.edu.cn.*

## Electronic Supplementary Information (11 pages)

*1. Materials and Methods:*

1,4-dimethoxypillar[5]arene (DMP5)[S1] and *n*-octylethyl ammonium hexafluorophosphate (**3**)[S2] were synthesized according to literature procedures. Solvents were either employed as purchased or dried according to procedures described in the literature. $^{1}$H NMR spectra were collected on a temperature-controlled 400 MHz spectrometer. $^{13}$C NMR spectra were recorded on a Bruker AVANCE DMX-500 spectrometer at 100 MHz. Low-resolution electrospray ionization (LRESI) mass spectra were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with an ESI interface and an ion trap analyzer.

*2. Synthetic routes for DMP4A1Q and 4DM1HQP5*




**Scheme S1** Synthetic routes for DMP4A1Q and 4DM1HQP5.

*3. Synthesis of DMP4A1Q*

A solution of DMP5 (3.00 g, 4.00 mmol) in THF (100 mL) was stirred in a 250 mL round–bottom flask while an aqueous solution $(NH_4)_2[Ce(NO_3)_6]$ (2.19 g, 4.00 mmol) was added dropwise. The mixture was stirred at room temperature for 24 h. The organic solvent was removed and water layer was extracted by dichloromethane (50 mL × 3). The combined organic phase was washed with water (100 mL) and saturated NaCl solution (100 mL), and dried over anhydrous $Na_2SO_4$. After being filtered and evaporated, the residue was purified by chromatography on silica gel (petroleum ether/dichloromethane, *v*/*v* 4:1 → 2:1) to obtain DMP5 (1.50 g) and red solid DMP4A1Q (430 mg, 30%). M.p. 148.6–149.9 °C. The $^1$H NMR spectrum of DMP4A1Q is shown in Figure S1. $^1$H NMR (400 MHz, $CDCl_3$, room temperature) $\delta$ (ppm): 6.84 (s, 2H), 6.81 (s, 2H), 6.79 (s, 2H), 6.67 (s, 4H), 3.79 (br, 6H), 3.75 (s, 6H), 3.71 (s, 12H), 3.63 (s, 6H), 3.59 (s, 4H). The $^{13}$C NMR spectrum of DMP4A1Q is shown in Figure S2. $^{13}$C NMR (100 MHz, $CDCl_3$, room temperature) $\delta$ (ppm): 188.8, 151.2, 150.9, 150.9, 146.7, 133.5, 129.5, 128.5, 128.0, 123.7, 114.4, 114.4, 113.9, 113.9, 56.1, 56.0, 55.9, 55.9, 55.6, 53.4, 29.5, 28.2. LRESIMS: *m*/*z* 721.0 $[M + H]^+$ (100%). HRESIMS: *m*/*z* calcd for $[M]^+$ $C_{43}H_{44}O_{10}$, 720.2934, found 720.2950, error 2.2 ppm.

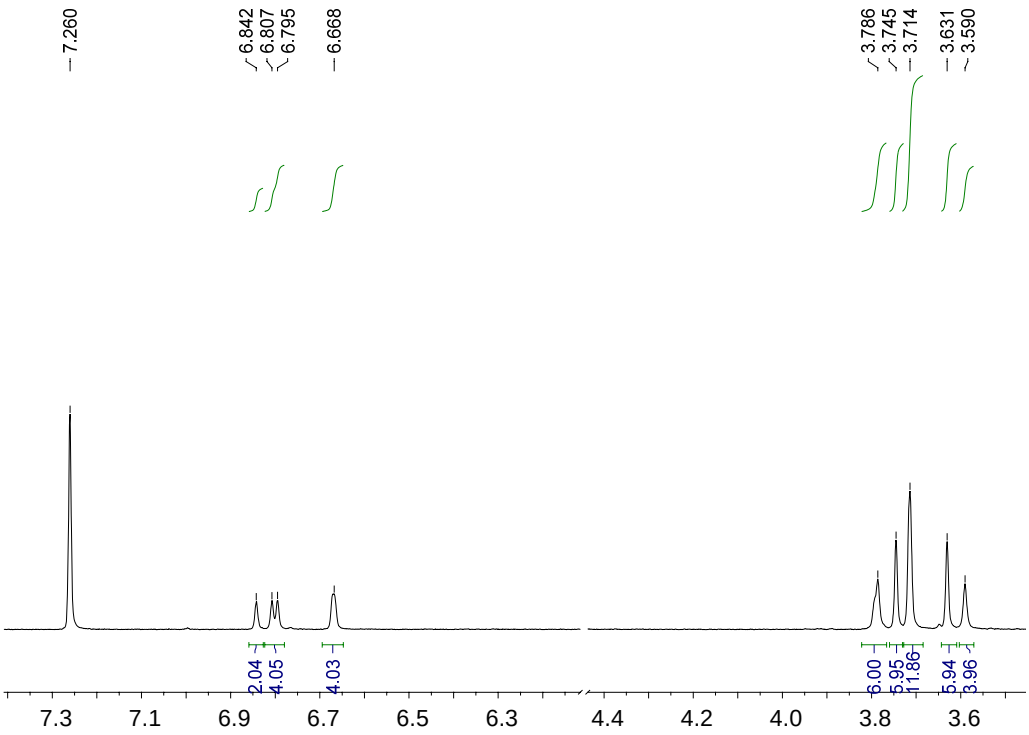



**Fig. S1** $^{1}$H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of DMP4A1Q.

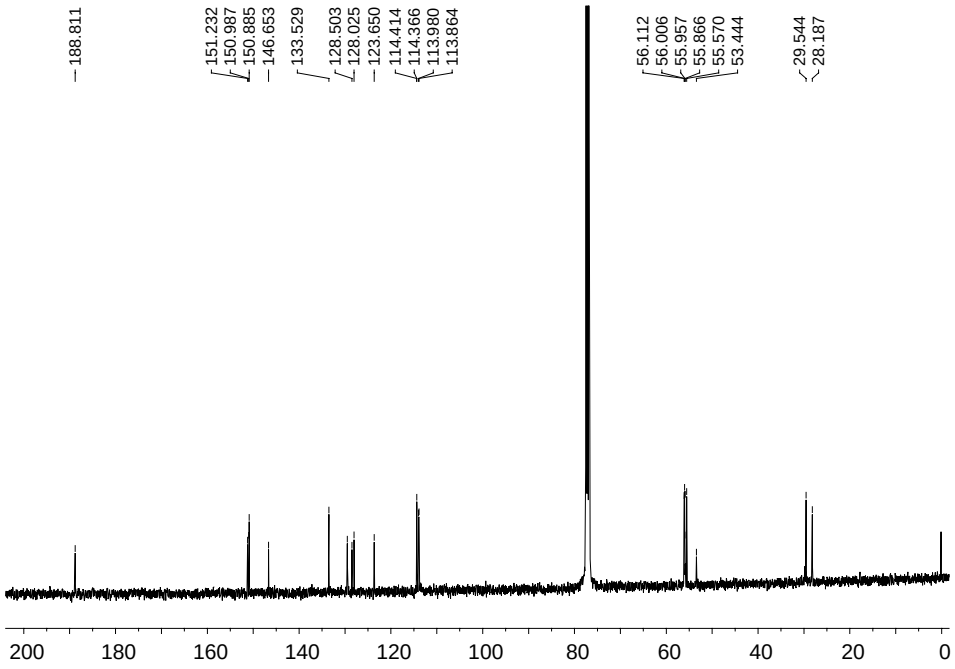



**Fig. S2** $^{13}$C NMR spectrum (100 MHz, $CDCl_3$, room temperature) of DMP4A1Q.

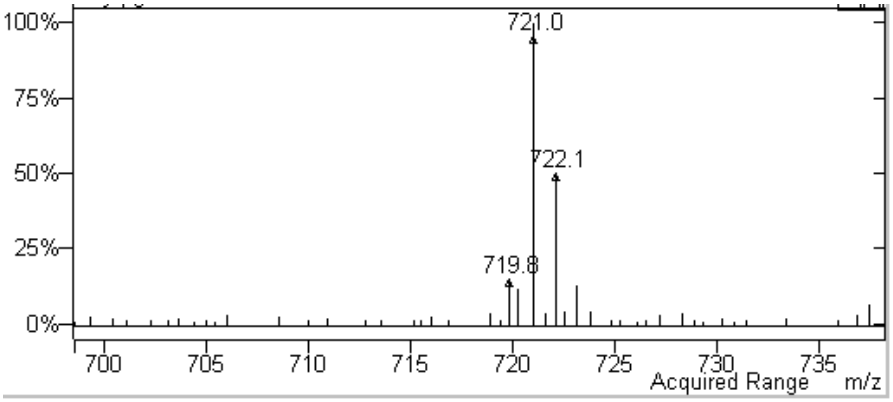



**Fig. S3** LRESI mass spectrum of DMP4A1Q.

*4. Synthesis of 4DM1HQP5*

A solution of DMP4A1Q (200 mg, 0.278 mmol) in $CH_2Cl_2$ (10 mL) was stirred in a 50 mL round–bottom flask while an aquous solution of $Na_2S_2O_4$ (0.960 g, 5.56 mmol) was added. The mixture was stirred roughly at room temperature for 12 h. The water layer was extracted by $CH_2Cl_2$ (50 mL × 3). The combined organic phase was washed with water (100 mL) and saturated NaCl solution (100 mL), and dried over anhydrous $Na_2SO_4$. After being filtered and evaporated, 4DM1HQP5 was obtained as a white solid quantitatively. M.p. 173.8–174.5 °C. The $^1$H NMR spectrum of 4DM1HQP5 is shown in Figure S4. $^1$H NMR (400 MHz, $CDCl_3$, room temperature) $\delta$ (ppm): 7.18 (s, 2H), 6.91 (s, 2H), 6.84 (s, 2H), 6.81 (s, 2H), 6.61 (s, 2H), 6.59 (s, 2H), 3.84 (s, 6H), 3.77 (br, 12H), 3.74 (s, 6H), 3.69 (s, 6H), 3.68 (s, 4H). The $^{13}$C NMR spectrum of 4DM1HQP5 is shown in Figure S5. $^{13}$C NMR (100 MHz, $CDCl_3$, room temperature) $\delta$ (ppm): 152.1, 150.9, 150.8, 148.5, 147.5, 129.3, 128.5, 127.7, 127.2, 126.8, 118.3, 114.7, 114.2, 113.9, 113.2, 56.6, 55.9, 55.9, 55.9, 30.9, 29.9, 29.2. LRESIMS: *m*/*z* 723.1 $[M + H]^+$ (100%). HRESIMS: *m*/*z* calcd for $[M]^+$ $C_{43}H_{46}O_{10}$, 722.3091, found 722.3082, error –1.2 ppm.

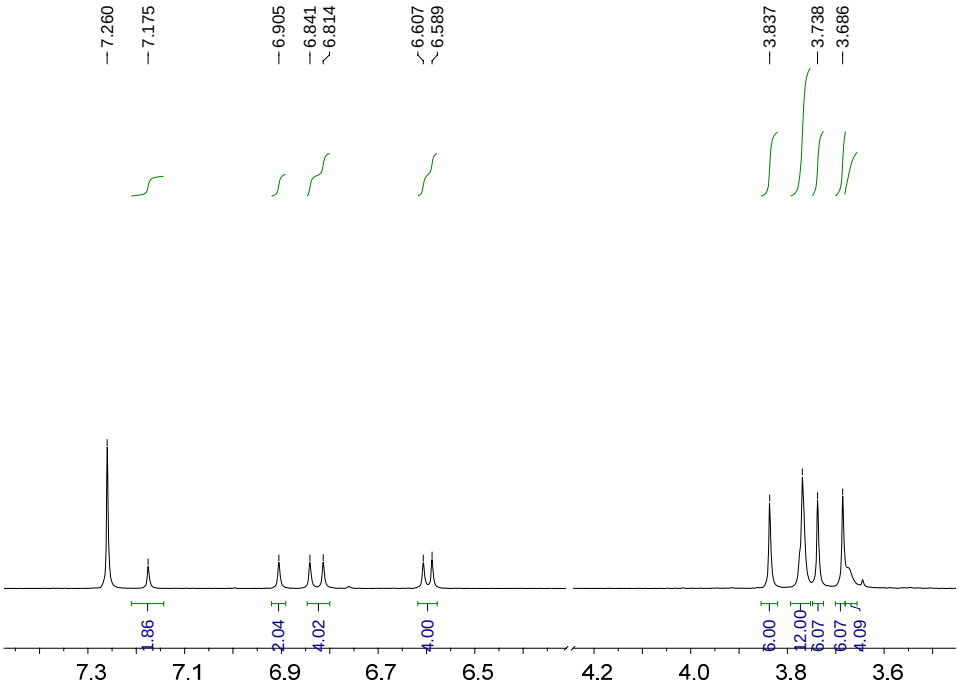



**Fig. S4** $^{1}$H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of 4DM1HQP5.

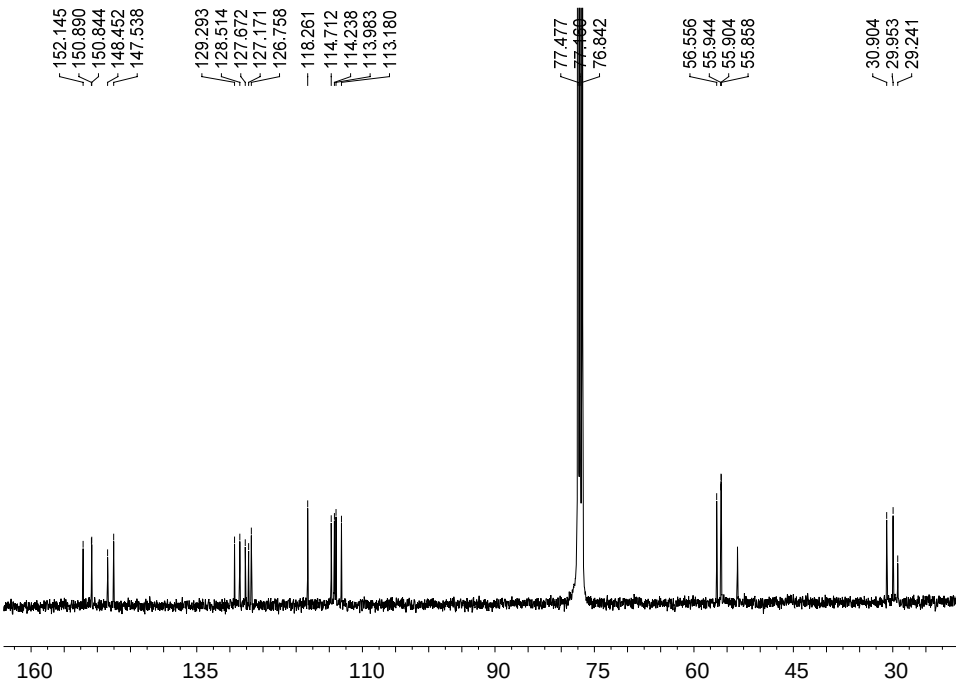



**Fig. S5** $^{13}$C NMR spectrum (100 MHz, $CDCl_3$, room temperature) of 4DM1HQP5.

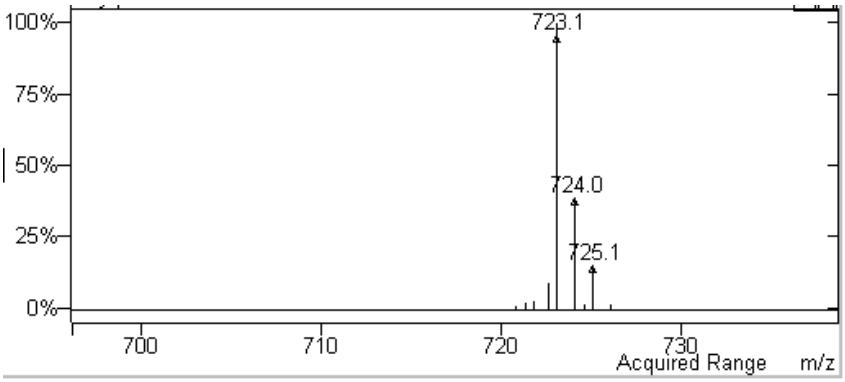



**Fig. S6** LRESI mass spectrum of 4DM1HQP5.

*5. X-ray crystal data of DMP4A1Q and 4DM1HQP5*

Crystal data of DMP4A1Q: yellow, $C_{89}H_{94}Cl_6O_{20}$, *FW* 1696.34, monoclinic, space group $P2_1/c$, $a$ = 36.5565(4), $b$ = 20.67542(18), $c$ = 22.5397(2) Å, $\alpha$ = 90.00°, $\beta$ = 92.9319(9)°, $\gamma$ = 90.00°, $V$ = 17013.7(3) Å$^3$, $Z$ = 8, $D_c$ = 1.325 g cm$^{-3}$, $T$ = 140(2) K, $\mu$ = 2.425 mm$^{-1}$, 102790 measured reflections, 30386 independent reflections, 2103 parameters, 0 restraints, $F$(000) = 7120, $R_1$ = 0.0806, $wR_2$ = 0.1838 (all data), $R_1$ = 0.0654, $wR_2$ = 0.1692 [$I > 2\sigma(I)$], max. residual density 1.418 e•Å$^{-3}$, and goodness-of-fit ($F^2$) = 1.044. CCDC- 893117.

Crystal data of 4DM1HQP5: yellow, $C_{45}H_{50}Cl_4O_{10}$, *FW* 892.65, monoclinic, space group $C2$, $a$ = 21.1700(12), $b$ = 12.0046(5), $c$ = 17.9282(9) Å, $\alpha$ = 90.00°, $\beta$ = 99.384(5)°, $\gamma$ = 90.00°, $V$ = 4495.3(4) Å$^3$, $Z$ = 4, $D_c$ = 1.319 g cm$^{-3}$, $T$ = 140(2) K, $\mu$ = 0.319 mm$^{-1}$, 9225 measured reflections, 4295 independent reflections, 510 parameters, 5 restraints, $F$(000) = 1872, $R_1$ = 0.1332, $wR_2$ = 0.2784 (all data), $R_1$ = 0.1174, $wR_2$ = 0.2693 [$I > 2\sigma(I)$], max. residual density 1.410 e•Å$^{-3}$, and goodness-of-fit ($F^2$) = 1.036. CCDC- 893116.

This journal is © The Royal Society of Chemistry 2012

*6. The determination of the association constant of complex* 4DM1HQP5⊃***3***

To determine the stoichiometry and association constant for the complexation between 4DM1HQP5 and *n*-octylethyl ammonium hexafluorophosphate (**3**), NMR titrations were done with solutions which had a constant concentration of 4DM1HQP5 (2.00 mM) and varying concentrations of **3**. By a non-linear curve-fitting method, the association constant ($K_a$) of 4DM1HQP5⊃**3** was estimated to be about 1.70 (± 0.70) × $10^3$ $M^{-1}$. By a mole ratio plot, a 1:1 stoichiometry was obtained.

The non-linear curve-fitting was based on the equation:[S3]

$$\Delta\delta = (\Delta\delta_\infty/[H]_0)\ (0.5[G]_0 + 0.5([H]_0+1/K_a)-(0.5\ ([G]_0^2+(2[G]_0(1/K_a - [H]_0)) + (1/K_a + [H]_0)^2)^{0.5})) \qquad \text{(Eq. S1)}$$

Where $\Delta\delta$ is the chemical shift change of $H_{20}$ on 4DM1HQP5 at $[G]_0$, $\Delta\delta_\infty$ is the chemical shift change of $H_{20}$ when the host is completely complexed, $[H]_0$ is the fixed initial concentration of the host, and $[G]_0$ is the initial concentration of **3**.

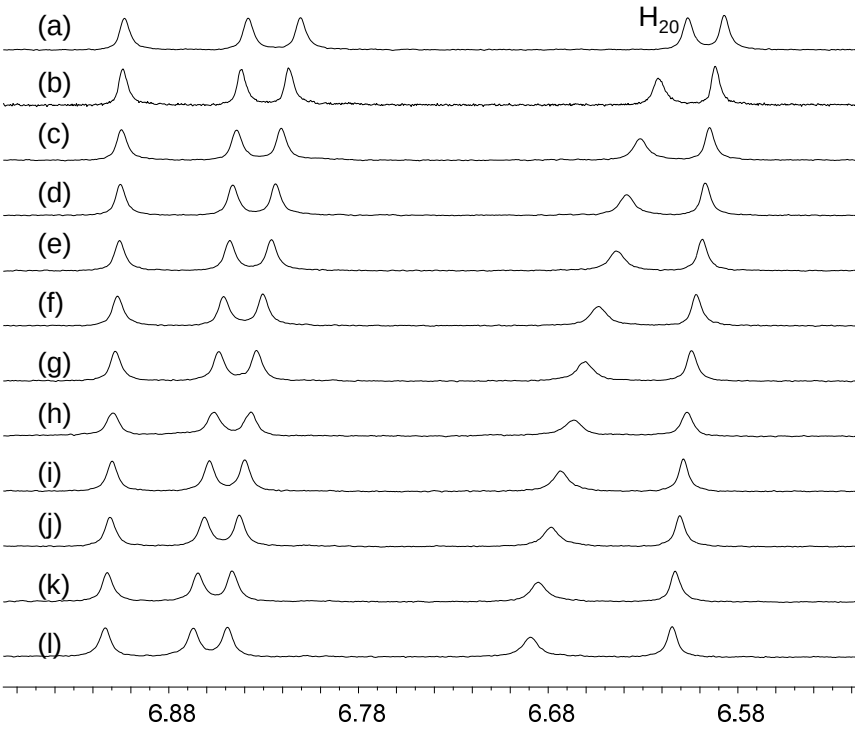



**Fig. S7** Partial $^{1}$H NMR spectra (400 MHz, $CDCl_3$, room temperature) of 4DM1HQP5 at a concentration of 2.00 mM upon addition of **G** (15 mM): (a) 0.00 μL, (b) 10.0 μL to a, (c) 10.0 μL to b, (d) 10.0 μL to c, (e) 10.0 μL to d, (f) 25.0 μL to e, (g) 25.0 μL to f, (h) 25.0 μL to g, (i) 50.0 μL to h, (j) 50.0 μL to i, (k) 100 μL to j, (l) 100 μL to k.

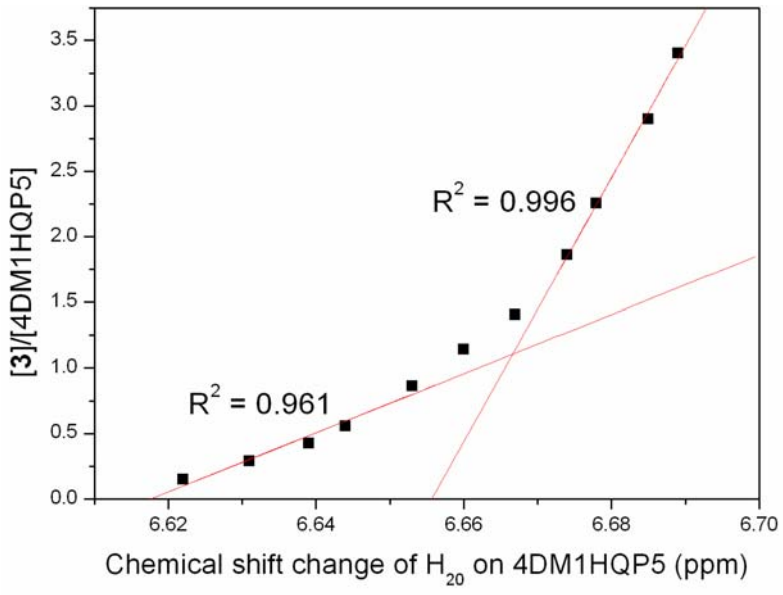



**Fig. S8** Mole ratio plot for the complexation between 4DM1HQP5 and **3**, indicating a 1:1 stoichiometry.

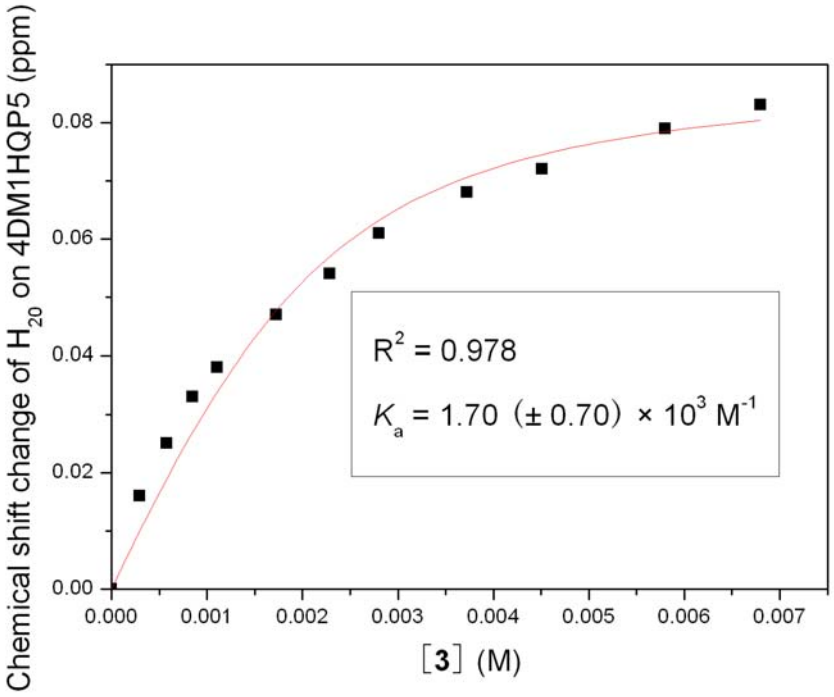



**Fig. S9** The chemical shift change of $H_{20}$ on 4DM1HQP5 upon addition of **3**. The red solid line was obtained from the non-linear curve-fitting using Eq. S1.

*7. Electrospray ionization mass spectrum of a solution of* 4DM1HQP5 *and* ***3***

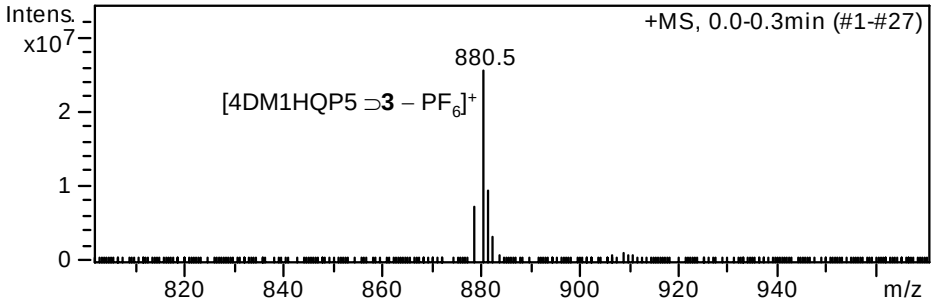



**Fig. S10** Electrospray ionization mass spectrum of a solution of 4DM1HQP5 and **3**.

*References:*

S1. T. Ogoshi, K. Kitajima, T. Aoki, S. Fujinami, T. Yamagishi and Y. Nakamoto, *J. Org. Chem.*, 2010, **75**, 3268–3273.

S2. G. W. Kabalka, G. W. McCollum and S. A. Kunda, *J. Org. Chem.*, 1984, **49**, 1656–1658.

S3. K. A. Connors, *Binding Constants*; Wiley: New York, 1987; P. S. Corbin, Ph.D. Dissertation, University of Illinois at Urbana-Champaign, Urbana, IL, 1999; P. R. Ashton, R. Ballardini, V. Balzani, M. Belohradsky, M. T. Gandolfi, D. Philp, L. Prodi, F. M. Raymo, M. V. Reddington, N. Spencer, J. F. Stoddart, M. Venturi and D. J. Williams, *J. Am. Chem. Soc.*, 1996, **118**, 4931–4951.