Supplementary Material (ESI) for New Journal of Chemistry

Electronic Supplementary Information (ESI)

A programmed hydrogen bonding array self-assembles into a polymeric pipper-like architecture

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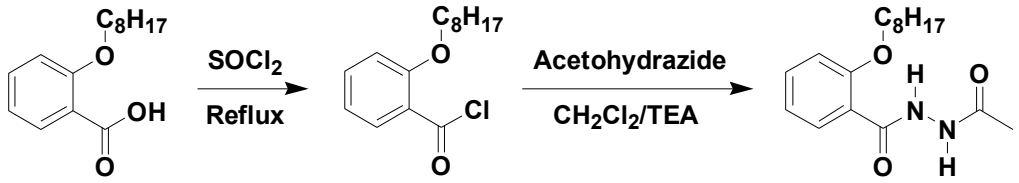
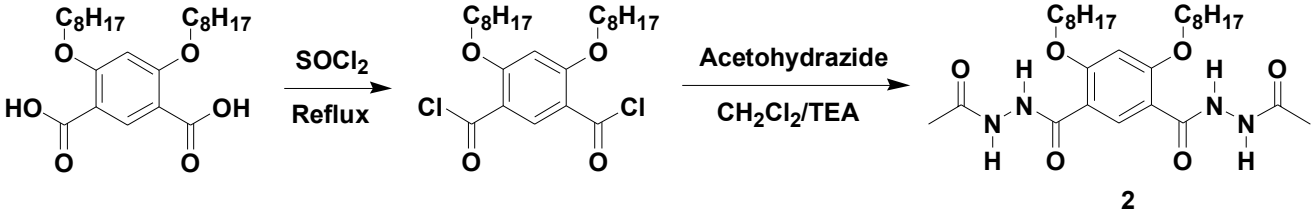


1

***N′*-Acetyl-2-(octyloxy)benzohydrazide (1)**: 2-Octyloxybenzoic acid[1] (1.00 g, 4 mmol) was dissolved in thionyl chloride (10 mL), and the mixture was heated under reflux with a calcium chloride drying tube for 8 hours. The excess thionyl chloride was removed under reduced pressure. The crude acid chloride was directly used for the next step without further purification. A solution of the above-prepared acid chloride in CH_2Cl_2 (10 mL) was dropwise added to a solution of acetohydrazide (0.6 g, 8 mmol) and triethylamine (1.1 mL, 8 mmol) in CH_2Cl_2 (10 mL) over a period of 10 minutes with ice-water bath equipped. Then the ice-water bath was removed, and the reaction mixture was stirred at room temperature for 1 hour. More CH_2Cl_2 (30 mL) was added. The solution was then washed with diluted 2N HCl (20 mL), saturated Na_2CO_3 aqueous solution (20 mL) and saturated brine (20 mL) successively. The organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated under reduce pressure. The crude product was recrystallized from methanol to give 1.18 g (96.4 %) of **1** as a white solid. Mp: 102-3 ˚C. ^{1}H NMR ($CDCl_3$): δ 11.04 (d, *J*=7.4 Hz, 1H, **H**-N), 10.31 (d, *J*=7.3 Hz, 1H, **H**-N), 8.18 (q, *J*=1.2 Hz, 7.7 Hz, 1H, **H**-Ar), 7.49 (t, *J*=8.3 Hz, 1H, **H**-Ar), 7.07 (t, *J*=7.5 Hz, 1H, **H**-Ar), 7.00 (d, *J*=8.3 Hz, 1H, **H**-Ar), 4.17 (t, *J*=6.7 Hz, 2H, C**H**$_2$O), 2.16 (s, 3H, COC**H**$_3$), 2.00-2.06 (m, 2H, C**H**$_2$), 1.48-1.53 (m, 2H, C**H**$_2$), 1.36-1.41 (m, 2H, C**H**$_2$), 1.27-1.32 (m, 6H, C**H**$_2$), 0.88 (t, *J*=6.6 Hz, 3H, C**H**$_3$). ^{13}C NMR ($CDCl_3$): δ 165.2, 160.1, 157.3, 133.5, 131.8, 121.1, 118.7, 112.3, 69.6, 31.8, 29.21, 29.15, 28.9, 26.0, 22.6, 20.6, 14.1. IR (KBr, cm^{-1}): 3345.89, 3190.65, 2923.56, 2853.17, 1605.45, 1475.28, 1286.29, 1230.36. MS (EI): *m/z* 306 (M^+), 233 (100), 121. Elemental analysis calcd (%) for $C_{17}H_{26}N_2O_3$: C 66.64, H 8.55, N 9.14; found: C 66.66, H 8.70, N 8.99.



***N*^{1}′, *N*^{3}′-Diacetyl-4,6-bis(octyloxy)benzene-1,3-dihydrazide** (**2**): This compound was prepared as a white solid (96.7 %) from 4,6-bis (octyloxy)benzene-1,3-dioic acid[2] and acetohydrazide according to the procedure described for **1**. Mp: 201-2 ˚C. ^{1}H NMR ($CDCl_3$): δ 10.65 (d, *J*=7.6 Hz, 2H, **H**-N), 9.55 (d, *J*=7.4 Hz, 2H, **H**-N), 9.00 (s, 1H, Ar-**H**), 6.51 (s, 1H, Ar-**H**), 4.21 (t, *J*=6.7 Hz, 4H, C**H**$_2$O), 2.15 (s, 6H, COC**H**$_3$), 2.04-2.08 (m, 4H, C**H**$_2$), 1.50-1.56 (m, 4H, C**H**$_2$), 1.38-1.44 (m, 4H, C**H**$_2$), 1.24-1.35 (m, 12H, C**H**$_2$), 0.89 (t, *J*=6.8 Hz, 6H, C**H**$_3$). ^{13}C NMR ($CDCl_3$): δ 165.0, 161.0, 159.1, 136.7, 112.4, 96.23, 70.3, 31.8, 29.2, 29.1, 28.8, 26.0, 22.6, 20.7, 14.1. IR (KBr, cm^{-1}): 3325.64, 3204.15, 2957.3, 2927.41, 2854.13, 1618.95, 1543.74, 1484.67, 1400.07, 1282.43, 1264.11. MS (EI): *m/z* 534 (M^+), 461 (100). Elemental analysis ca lcd (%) for $C_{28}H_{46}N_4O_6$: C 62.90, H 8.67, N 10.48; found: C 62.77, H 8.71, N 10.52.

(1) Zhao, X.; Wang, X.-Z.; Jiang, X.-K.; Chen, Y.-Q.; Li, Z.-T.; Chen, G.-J. *J. Am. Chem. Soc.* **2003**, *125*, 15128-15139.

(2) Yuan, L.; Feng, W.; Yamato, K.; Sanford, A. R.; Xu, D.; Guo, H.; Gong, B. *J. Am. Chem. Soc.* **2004**, *126*, 11120-11121.

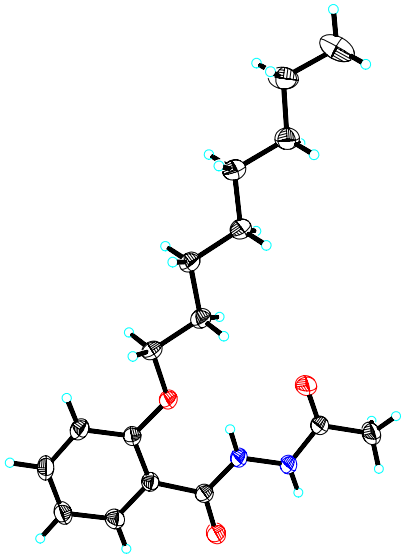


Figure S1. Thermal ellipsoid representation of X–ray structure of **1.**

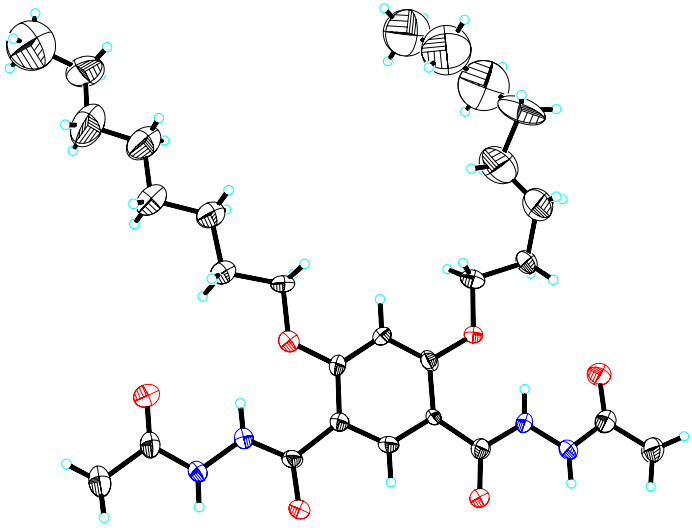


Figure S2. Thermal ellipsoid representation of X–ray structure of **2.**

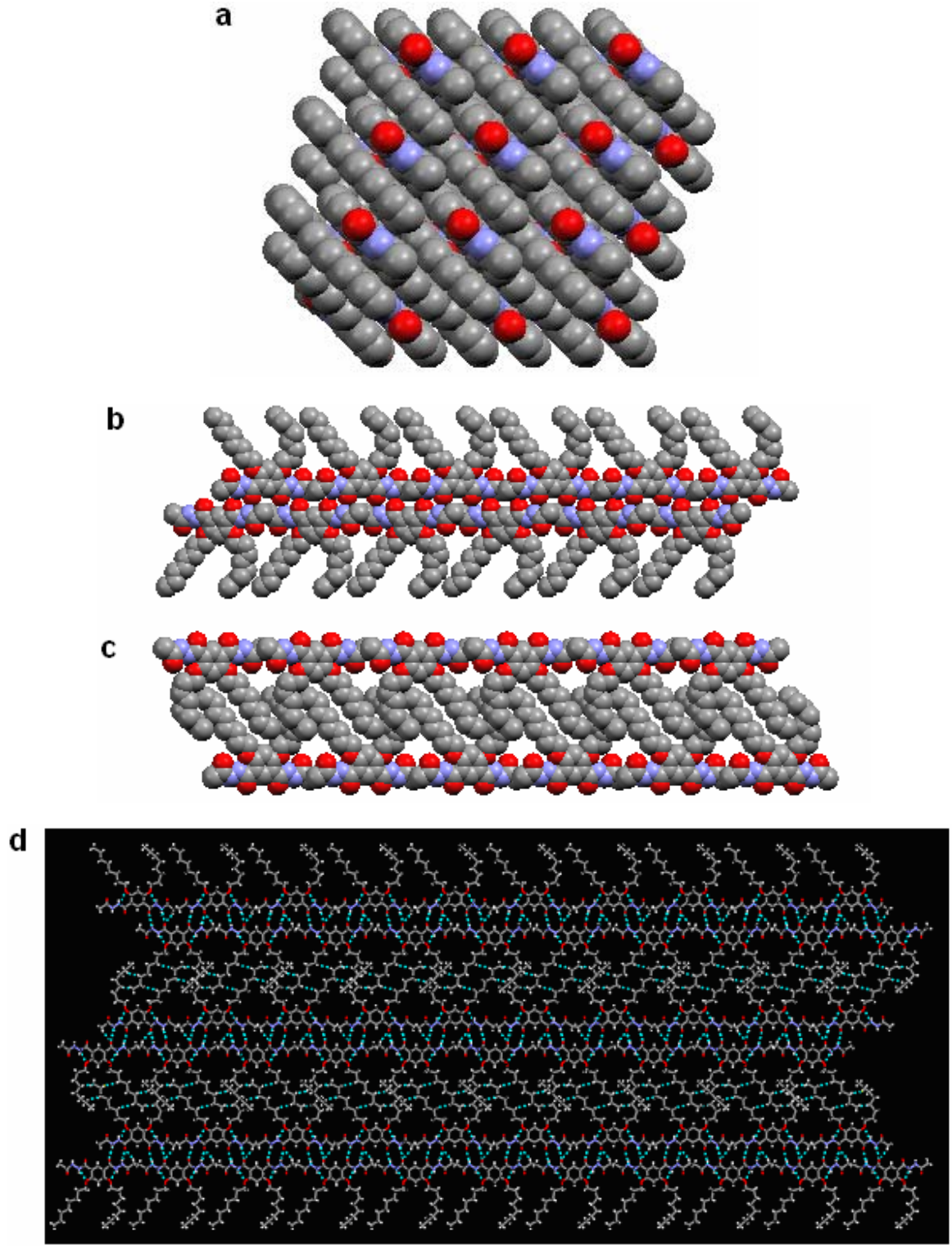


Figure S3. (a) Crystal packing of **1** viewed along the *b*-axis. Crystal packing of **2** viewed along the *a*-axis: (b) zipper locked by hydrogen bonding and (c) zipper locked by van der Waals interaction. (d) Illustration of lamellar structure of **2**.

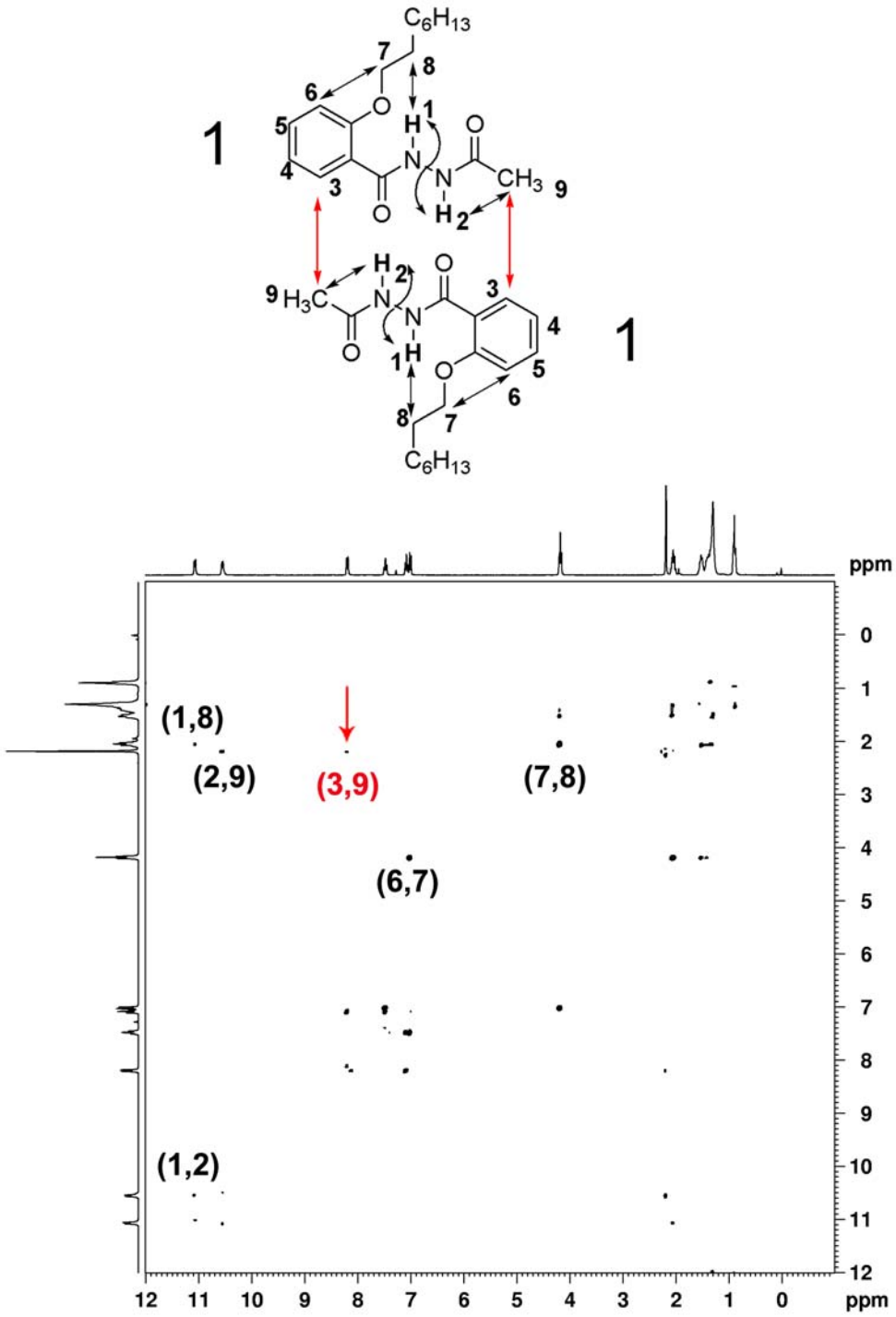


Figure S4. NOESY spectrum of **1** (300 MHz, $CDCl_3$).

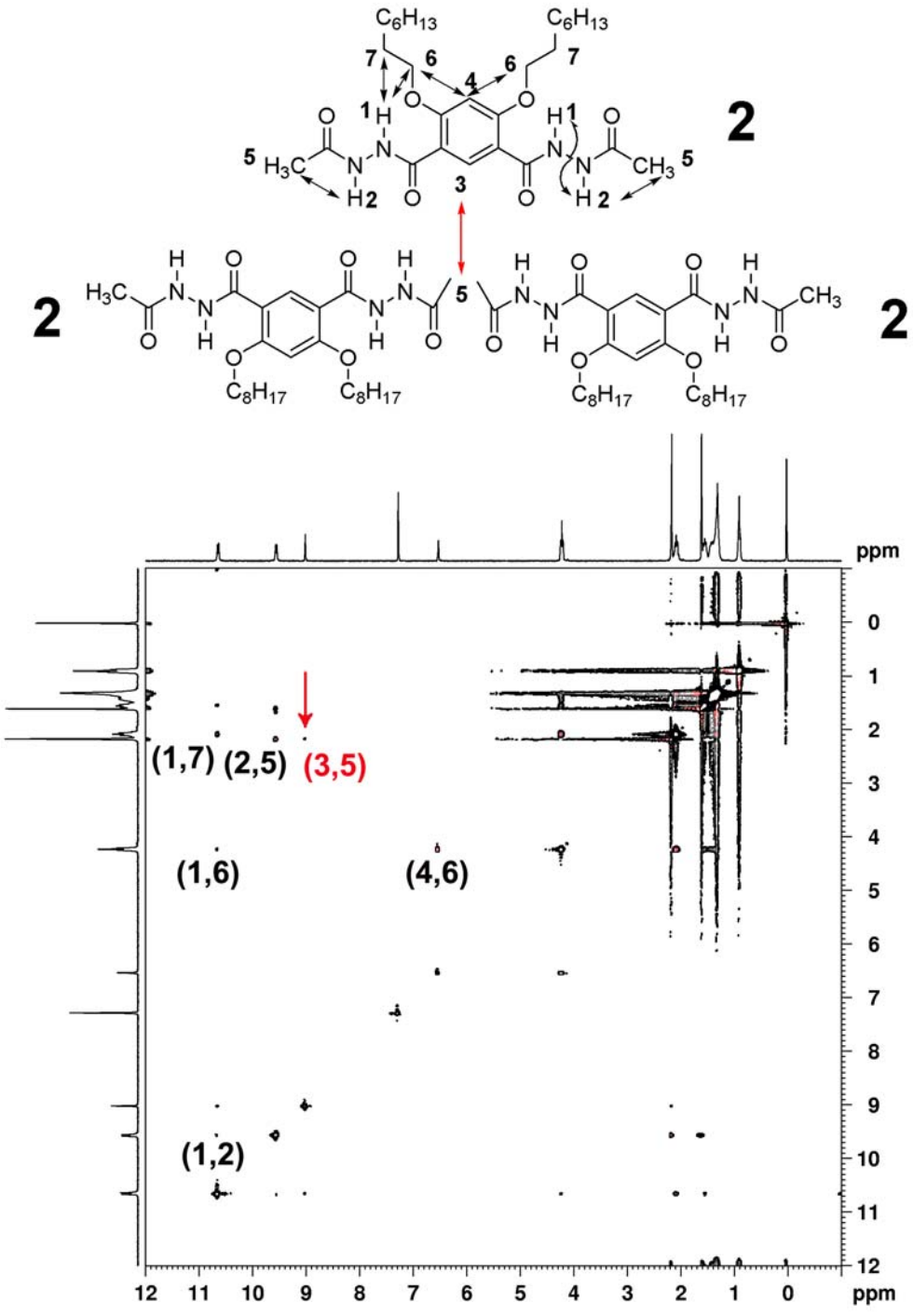
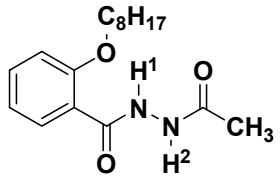


Figure S5. NOESY spectrum of **2** (300 MHz, $CDCl_3$).



1

Table S1. Chemical shifts of H^1 and H^2 at different concentrations.

Concenration (mM)	200	100	50	40	30	20	10	5	2.5	1	0.5
Chemical shift of H^1 (ppm)[a]	11.060	11.043	11.007	10.989	10.983	10.965	10.936	10.906	10.890	10.878	10.872
Chemical shift of H^2 (ppm)	10.547	10.310	9.962	9.831	9.732	9.555	9.281	9.028	8.890	8.794	8.756

(a) TMS as inner standard.

Nonlinear regression analysis is based on the following equation:[3,4]

$$A + A \rightleftharpoons AA$$

$$K_d = \frac{[AA]}{[A]^2}$$

$$[A] = [A]_0 - 2[AA]$$

$$[AA] = \frac{4K_d[A]_0 + 1 - \sqrt{8K_d[A]_0 + 1}}{8K_d}$$

$$\delta_{obs} = \frac{2[AA]}{[A]_0}\delta_d + \frac{[A]}{[A]_0}\delta_f$$

$$= \delta_f + (\delta_d - \delta_f)\frac{4K_d[A]_0 + 1 - \sqrt{8K_d[A]_0 + 1}}{4K_d[A]_0}$$

$[A]$: the concentration of unbound free species

$[A]_0$: the total concentration

$[AA]$: the concentration of dimer

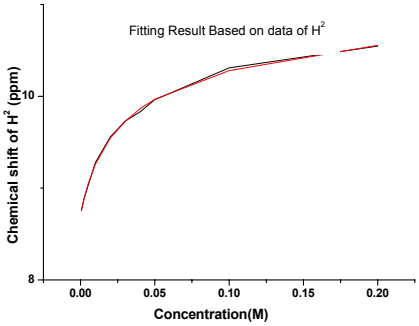
K_d : the dimerization constant

δ_d : the limiting bound chemical shift of the dimer

δ_f : the free chemical shift

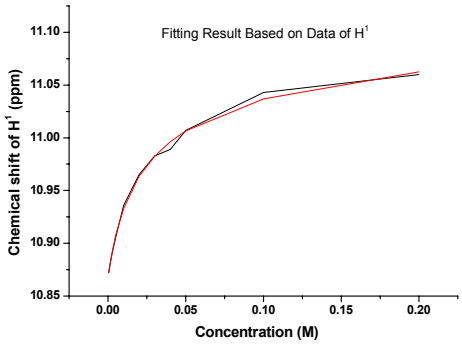
δ_{obs} : chemical shift measured by experiment

The dimerization constant was obtained by fitting the NMR data into the above equation with Origin's nonlinear regression method (Version: Origin 6.1) based on Levenberg-Marquardt (LM) algorithm on a PC computer.



$$\delta_f = 8.71 \pm 0.01$$
$$\delta_d = 11.45 \pm 0.05$$
$$K_d = 15.60 \pm 0.93 M^{-1}$$

Figure S6. Fitting result based on H^2. Black: experimental data; Red: fitting result.

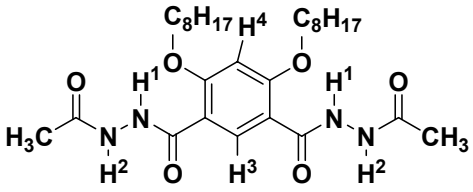


$$\delta_f = 10.867 \pm 0.003$$
$$\delta_d = 11.144 \pm 0.008$$
$$K_d = 20.66 \pm 2.35 M^{-1}$$

Figure S7. Fitting result based on H^1. Black: experimental data; Red: fitting result.

(3) Wilcox, C. S. In *Frontiers in Supramolecular Organic Chemistry and Photochemistry*; Schneider, H.-J., Durr, H., Eds.; VCH: New York, 1991; pp123-143.

(4) Bisson, A. P.; Carver, F. J.; Eggleston, D. S.; Haltiwanger, R. C.; Hunter, C. A.; Livingstone, D. L.; McCabe, J. F.; Rotger, C.; Rowan, A. E. *J. Am. Chem. Soc.* **2000**, *122*, 8856-8868.



2

Table S2. Chemical shifts of H^1 and H^2 at different concentrations.

Concenration (mM)	5	4.5	4	3.5	3	2.5	2	1.5	1	0.5
Chemical shift of H^1 (ppm)[a]	10.627	10.627	10.624	10.620	10.616	10.611	10.605	10.597	10.588	10.578
Chemical shift of H^2 (ppm)	9.419	9.396	9.366	9.320	9.286	9.224	9.158	9.130	8.986	8.897

a: TMS as inner standard.

The association constant for chain extension of the aggregate was obtained by fitting the NMR data into the above equation with Origin's nonlinear regression method (Version: Origin 6.1) based on Levenberg-Marquardt (LM) algorithm on a PC computer.

$$[Agg] = [A]_0\{1 - \frac{2}{1+\sqrt{1+4K_a[A]_0}}\}$$

$$[A] = [A]_0 - [Agg]$$

$$\delta_{obs} = \frac{[Agg]}{[A]_0}\delta_b + \frac{[A]}{[A]_0}\delta_f$$

$$= \delta_f + (\delta_f - \delta_b)\frac{2}{1+\sqrt{4K_a[A]_0+1}}$$

$[A]_0$: the total concentration

$[A]$: the concentration of sites which are unbound

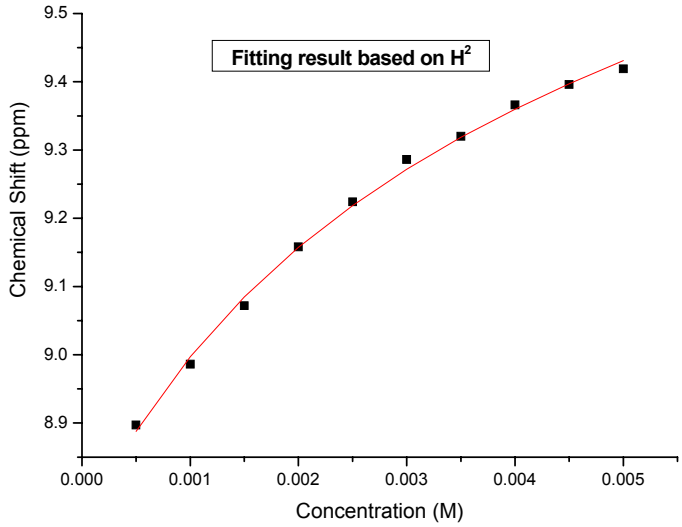
$[Agg]$: the concentration of sites involved in intermolecular interactions in the aggregate

K_a : the association constant for chain extension of the aggregate

δ_b : the limiting bound chemical shift of the bound sites in the aggregate

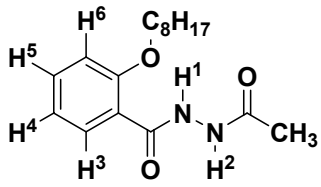
δ_f : the free chemical shift

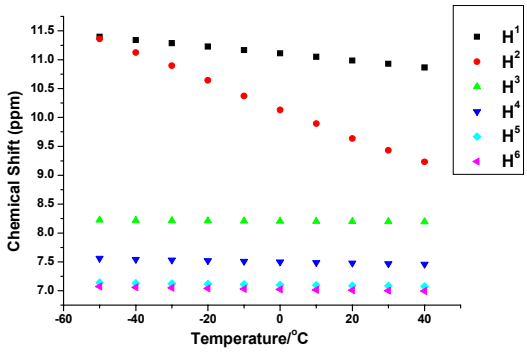
δ_{obs} : chemical shift measured by experiments



$$\delta_f = 8.742 \pm 0.024$$
$$\delta_b = 10.636 \pm 0.165$$
$$K_a = 179.561 \pm 38.604 M^{-1}$$

Figure S8. Fitting result based on H^2. Black: experimental data; Red: fitting result.

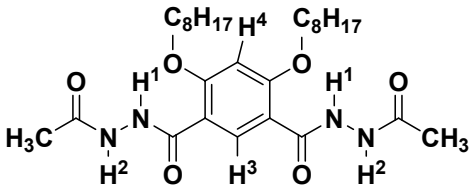




Temperature coefficient of $\mathbf{H^1}$: -5.92×10^{-3} ppm/K.

Temperature coefficient of $\mathbf{H^2}$: -2.41×10^{-2} ppm/K.

Figure S9. Chemical shifts of protons of **1** at different temperatures. TMS as inner standard.



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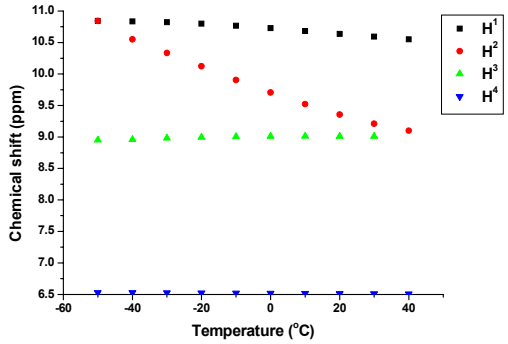

Temperature coefficient of $\mathbf{H^1}$: -3.4×10^{-3} ppm/K.

Temperature coefficient of $\mathbf{H^2}$: -1.94×10^{-2} ppm/K.

Figure S10. Chemical shifts of protons of **2** at different temperatures. TMS as inner standard.