# *Electronic Supplementary Information*

## A molecular sponge that exclusively adsorbs acetonitrile

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**General.**

All reagents were of standard analytical grade and were used without further purification. Melting points were obtained with a Mel-Temp capillary apparatus and were not corrected. Compound **1** was prepared for the method according to the literature.[S1] The FAB mass spectra were obtained using a JEOL 600 H mass spectrometer. The $^1$H and $^{13}$C{$^1$H} NMR spectra were measured on a JEOL ECP400 spectrometer and Bruker AVANCE II (400 MHz). The elemental analysis was carried out on a Yanaco MT-6 CHN Micro Corder. TG-DTA was measured on a Rigaku Thermo plus EVO2-TG8121.

**3-Phenyl-2-propynal (1)**
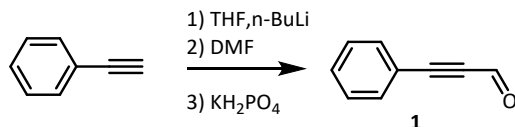


Phenylacetylene (10.9 mL, 99.0 mmol) in absolute tetrahydrofuran (250 mL) was stirred at –40 °C under a nitrogen atmosphere for 30 minutes, then *n*-butyl lithium (70.0 mL, 107 mmol) was added slowly dropwise (temperature: –40 °C to –35 °C) and stirred for 5 minutes. Dry *N,N*-dimethylformamide (16.0 mL, 200 mmol) was added to the reaction mixture and stirred for 10 min. The solution was allowed to stand at room temperature for 12 hr, and then the solution was added to a mixture of 10% potassium dihydrogen phosphate solution (540 mL) and methyl *tert*-butyl ether (500 mL) and stirred for 10 minutes. After the hydrolysis reaction was completed, the mixture was washed with water (200 mL x 2). The aqueous layer was extracted with methyl *tert*-butyl ether (200 mL x 1). The organic layer was combined, dried over sodium sulfate, and filtered through Celite. After removing the organic solvent, the mixture was dried under reduced pressure to give a brown oily mixture. The reaction product was separated and purified by silica gel column chromatography (hexane:ethyl acetate = 9:1) to give compound **1** as a red oil. Yield 91% (11.7 g, lit. 97%[S1]); $^1$H-NMR (400 MHz; CDCl$_3$) $\delta$ 9.43 (s, 1H), 7.61 (dt, $J_{ortho}$ = 7.4 Hz, $J_{metha}$ = 1.5 Hz, 2H), 7.50 (tt, $J_{ortho}$ = 7.4 Hz, $J_{metha}$ = 1.5 Hz, 1H), 7.41 (tt, $J_{ortho}$ = 7.4 Hz, $J_{metha}$ = 1.5 Hz, 2H); FAB-MS (matrix: DTT:TG = 1:1) *m/z* 131 ([M+H]$^+$, 100%); IR (KBr disc) 2855, 2738, 2189, and 1660 cm$^{-1}$.

[S1] Journet, M.; Cai, D.; DiMichele, L. M.; Larsen, R. D. Highly efficient synthesis of α,β-acetylenic aldehydes from terminal alkynes using DMF as the formylating reagent. *Tetrahedron Lett.* **1998**, *39*, 6427-6428.
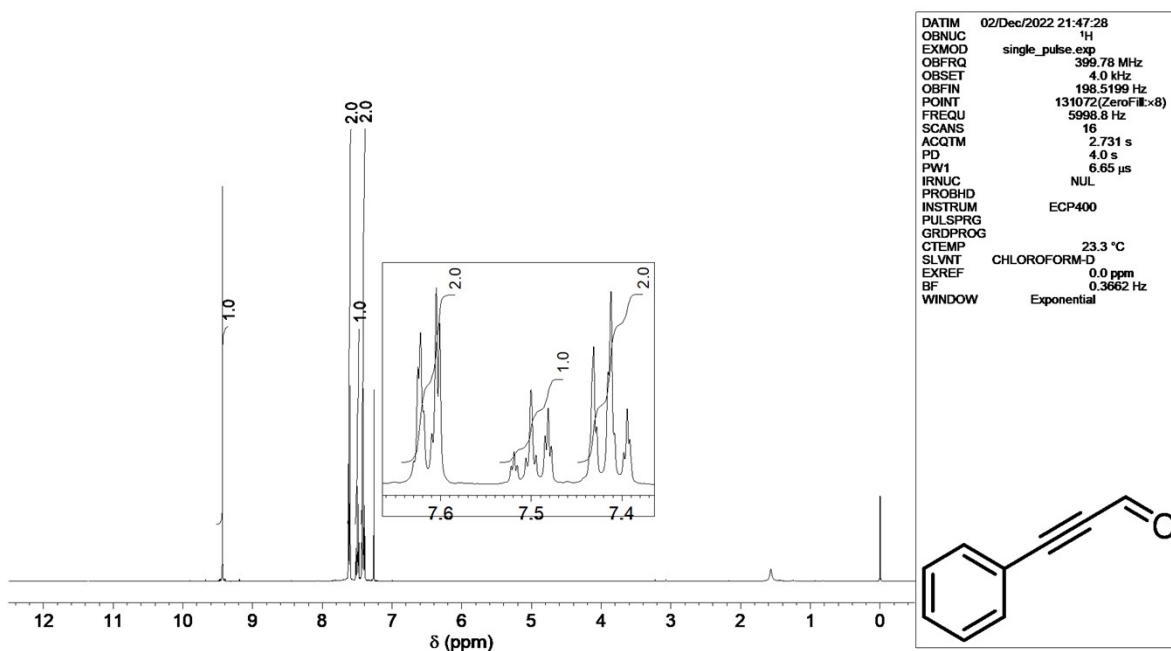
**Fig. S1.** $^1$H NMR spectrum of **1** in CDCl$_3$.
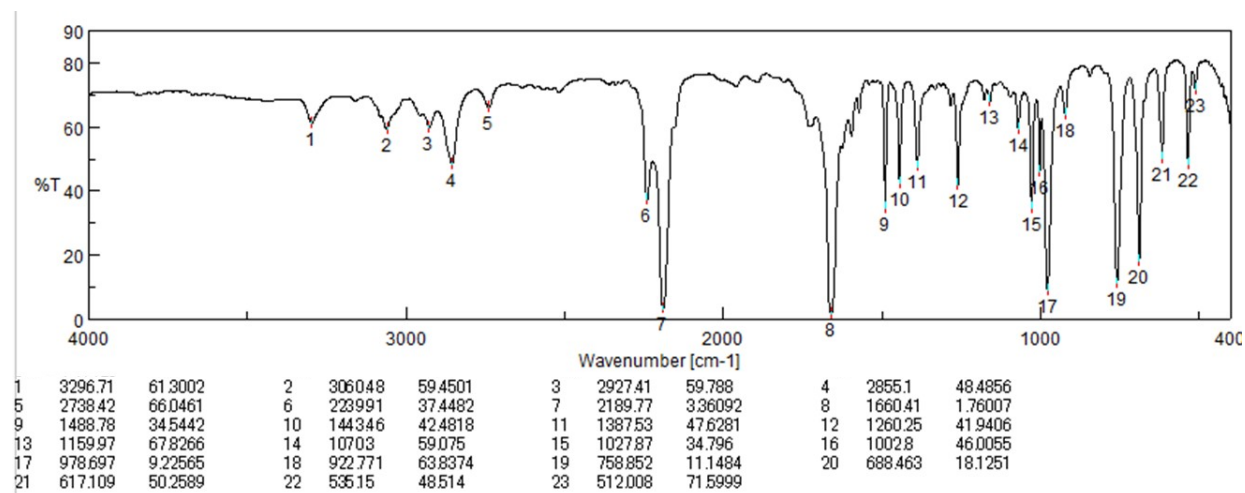


**Fig. S2.** IR spectrum of **1** (KBr disc).

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 3296.71 | 61.3002 | 2 | 3060.48 | 59.4501 | 3 | 2927.41 | 59.788 | 4 | 2855.1 | 48.4856 |
| 5 | 2738.42 | 66.0461 | 6 | 2239.91 | 37.4482 | 7 | 2189.77 | 3.36092 | 8 | 1660.41 | 1.76007 |
| 9 | 1488.78 | 34.5442 | 10 | 1443.46 | 42.4818 | 11 | 1387.53 | 47.6281 | 12 | 1260.25 | 41.9406 |
| 13 | 1159.97 | 67.8266 | 14 | 1070.3 | 59.075 | 15 | 1027.87 | 34.796 | 16 | 1002.8 | 46.0055 |
| 17 | 978.697 | 9.22565 | 18 | 922.771 | 63.8374 | 19 | 758.852 | 11.1484 | 20 | 688.463 | 18.1251 |
| 21 | 617.109 | 50.2589 | 22 | 535.15 | 48.514 | 23 | 512.008 | 71.5999 | | | |

## 1,4,7,10-Tetrakis(3-phenylprop-2-yn-1-yl)-1,4,7,10-tetraazacyclododecane (L)

A mixture of1,4,7,10-tetraazacyclododecane (0.64 g, 3.7 mmol), 1 (2.6 g, 20 mmol), and sodium triacetoxyborohydride
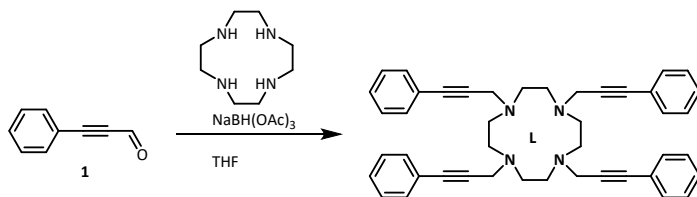


(4.6 g, 22 mmol) in anhydrous tetrahydrofuran (70.0 mL) were stirred at room temperature under nitrogen atmosphere for two days. The reaction mixture was neutralized by adding a saturated aqueous sodium bicarbonate solution and extracted with ethyl acetate (40 mL x 3). The organic layers were combined, dried over anhydrous sodium sulfate, filtered by suction, and removed the organic solvent under reduced pressure. To the residual oil, 5.0 mL of propionitrile was added, and after filtration by suction to obtain crude crystals, which were recrystallized again from propionitrile to give yellow needle-like crystals. After the filtrate was concentrated under reduced pressure, the residual oil was separated and purified by silica gel column chromatography (EtOAc:CH$_3$OH:NH$_3$ aq.=15:1:0.04). The yellow needle-like crystals were obtained by recrystallization with propionitrile. The total weight of these crystals was 1.80 g. Yield 78%; m.p.: 104.7–105.1 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43–7.40 (m, 8H), 7.30–7.27 (m, 12H), 3.70 (s, 8H), 2.86 (s, 16H); $^{13}$C{$^1$H} NMR (100 MHz; solvent peak (77.17 ppm) of CDCl$_3$ was used as a reference) $\delta$ 132.2 (**C**$_{o\text{-Ph}}$), 128.7 (**C**$_{m\text{-Ph}}$), 128.4 (**C**$_{p\text{-Ph}}$), 123.7 (**C**$_{Ph}$-C≡C), 85.6 (C≡C), 85.4 (C≡C), 52.4 (N-**C**H$_2$-C≡C), 45.2 (N-**C**H$_2$**C**H$_2$-N); FAB-MS (matrix: DTT:TG = 1:1) $m/z$ 630 ([M+H]$^+$, 47%); IR (KBr disc) 3048, 2952, 2225, 1596, and 1137 cm$^{-1}$. Anal. Calcd. for C$_{44}$H$_{44}$N$_4$: C, 84.04; H, 7.05; N, 8.91. Found: C, 84.28; H, 6.80; N, 8.92.
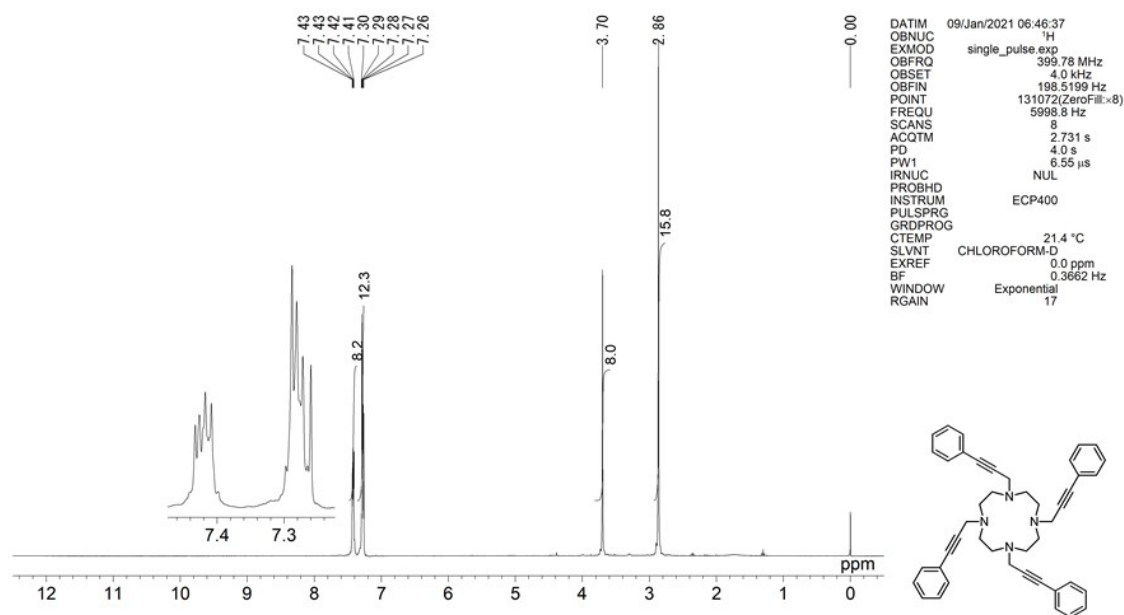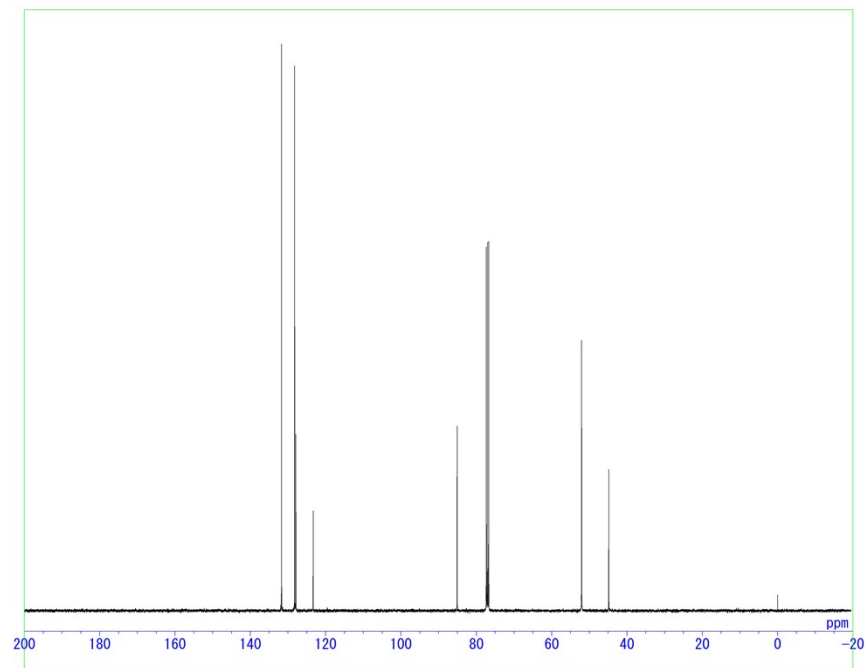


**Fig. S3.** $^1$H NMR spectrum of **L** in CDCl$_3$.

DFILE  C:¥USERS¥HABAT¥APPDATA¥LOCAL¥TEMP¥T
       EMP1_LとL-ANの13C NMR-20221219T082019Z
       -001.ZIP¥LとL-ANの13C NMR¥20221213_YOS
       HIBA_L_13C_CDCL3.RM1
DATIM   13/Dec/2022 19:31:00
COMNT

OBNUC                    13C
EXMOD                 ZGPG30
OBFRQ                   100.61 MHz
OBSET                     0.0 kHz
OBFIN                  10005.84 Hz
POINT                   32768
FREQU                 24038.46 Hz
SCANS                    1024
ACQTM                    1.3631 s
PD                       2.0 s
PW1                      8.0 μs
IRNUC                    OFF
PROBHD   5 MM PABBO BB-1H/D Z-GRD Z104450
INSTRUM               SPECT
PULSPRG               ZGPG30
GRDPROG
CTEMP                   24.45 °C
SLVNT                 CDCL₃
EXREF                    0.0 ppm
BF                       0.25 Hz

**Fig. S4.** $^{13}C\{^1H\}$ NMR spectrum of **L** in CDCl$_3$.



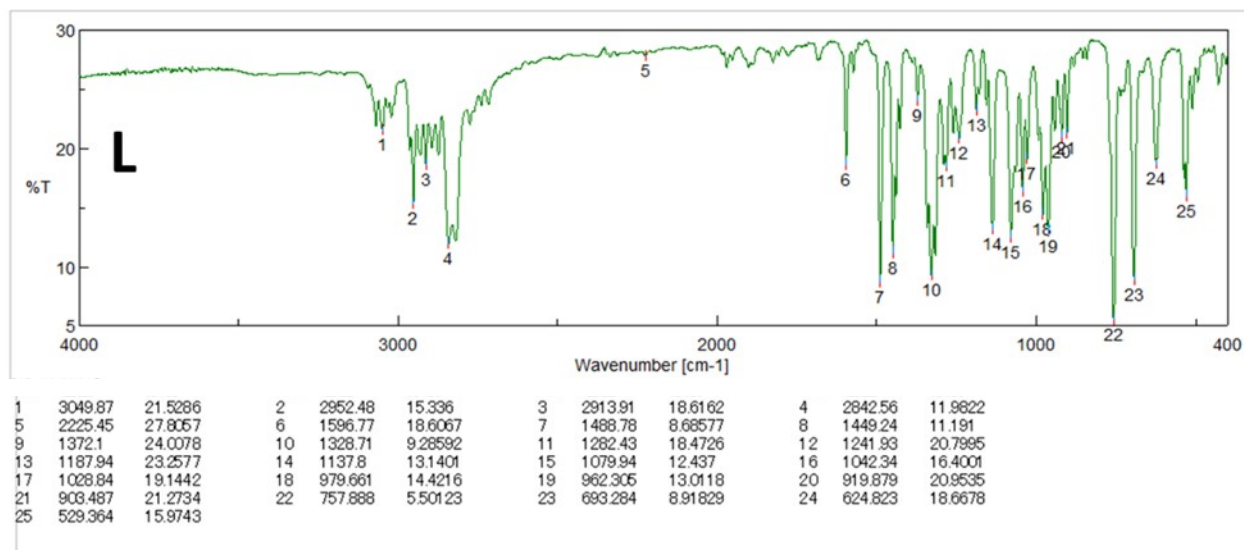| | | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1 | 3049.87 | 21.5286 | 2 | 2952.48 | 15.336 | 3 | 2913.91 | 18.6162 | 4 | 2842.56 | 11.9822 |
| 5 | 2225.45 | 27.8057 | 6 | 1596.77 | 18.6067 | 7 | 1488.78 | 8.68577 | 8 | 1449.24 | 11.191 |
| 9 | 1372.1 | 24.0078 | 10 | 1328.71 | 9.28592 | 11 | 1282.43 | 18.4726 | 12 | 1241.93 | 20.7995 |
| 13 | 1187.94 | 23.2577 | 14 | 1137.8 | 13.1401 | 15 | 1079.94 | 12.437 | 16 | 1042.34 | 16.4001 |
| 17 | 1028.84 | 19.1442 | 18 | 979.661 | 14.4216 | 19 | 962.305 | 13.0118 | 20 | 919.879 | 20.9535 |
| 21 | 903.487 | 21.2734 | 22 | 757.888 | 5.50123 | 23 | 693.284 | 8.91829 | 24 | 624.823 | 18.6678 |
| 25 | 529.364 | 15.9743 | | | | | | | | | |

**Fig. S5.** IR spectrum of **1** (KBr disc).

**CH₃CN (L·AN) inclusion complex (SI video 1).**

Ligand **L** (5.0 mg, 0.0080 mmol) was dissolved in 0.4 mL of acetonitrile and allowed to stand at room temperature. The single crystals of the **L**·CH₃CN inclusion complex were obtained with 94‰ yields. Mp: 99.5–100.0 °C; $^1$H NMR (400 MHz, CDCl₃) $\delta$ 7.43–7.40 (m, 8H), 7.30–7.27 (m, 12H), 3.70 (s, 8H), 2.86 (s, 16H); $^{13}$C{$^1$H} NMR (100 MHz; TMS) $\delta$ 131.7 ($C_{o\text{-Ph}}$), 128.2 ($C_{m\text{-Ph}}$), 127.9 ($C_{p\text{-Ph}}$), 123.3 ($C_{Ph}$-C≡C), 116.3 (C≡N), 85.1 (C≡C), 52.0 (N-$CH_2$-C≡C), 44.8 (N-$CH_2CH_2$-N), 1.9 ($CH_3$C≡N); IR (KBr disc) 3062, 2932, 2240, 1595, and 1111 cm$^{-1}$. Anal. Calcd. for C₄₄H₄₄N₄+CH₃CN: C, 82.47; H, 7.07; N, 10.45. Found: C, 82.40; H, 7.12; N, 10.32.

**Recrystallization of L·AN from a mixture of acetonitrile and dichloromethane (SI video 2).**

**L** of dichloromethane saturated solution was added dropwise slowly to acetonitrile (2.5 mL), and after 1 mL of the saturated solution was added, white powder was precipitated. The precipitated white powder was dried under reduced pressure at room temperature and subjected to elemental analysis. Anal. C₄₄H₄₄N₄+CH₃CN+0.05CH₂Cl₂: C, 82.04; H, 7.04; N, 10.39. Found: C, 82.01; H, 6.93; N, 10.43.
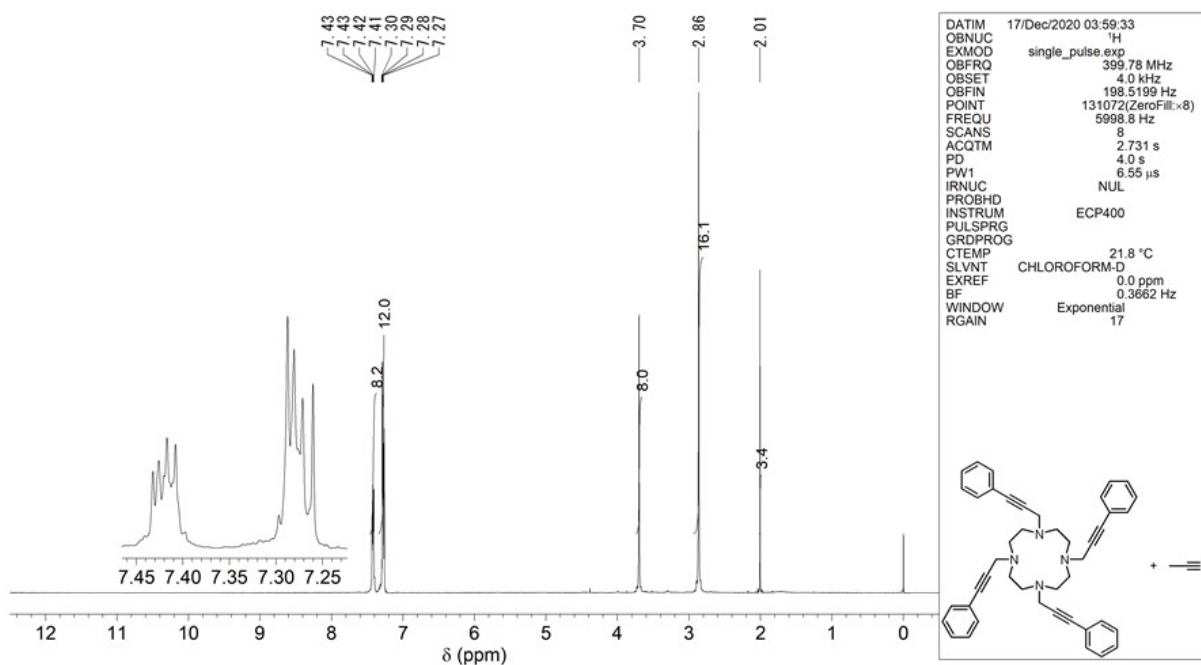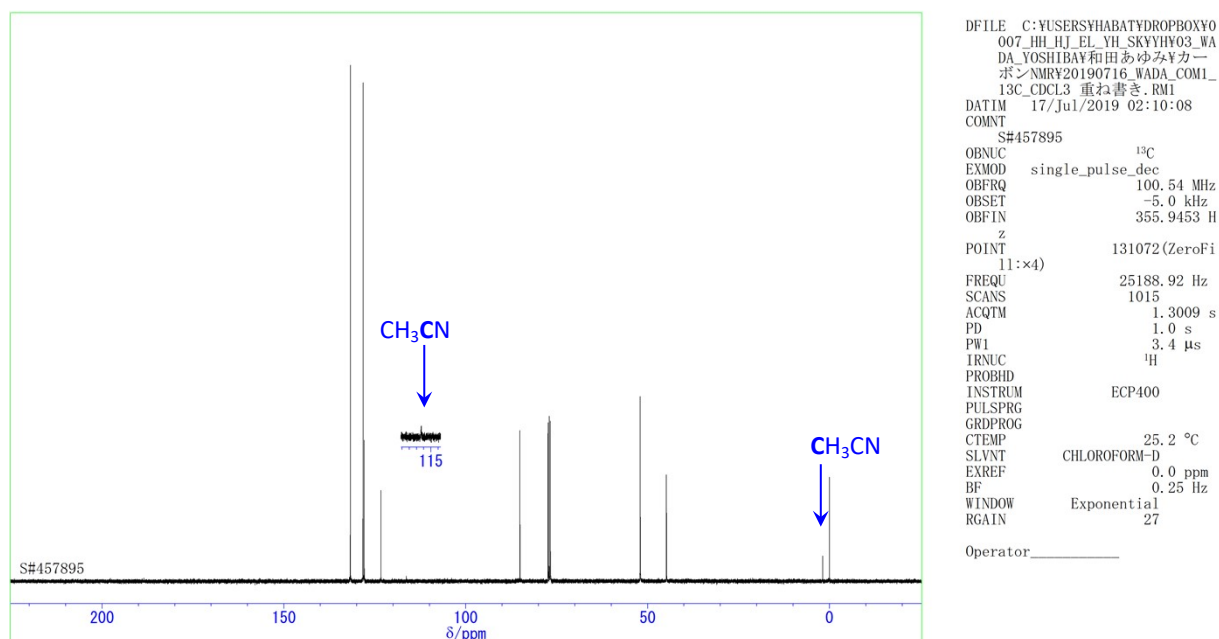


**Fig. S6.** $^1$H NMR spectrum of **L·AN** in CDCl₃.

7

DFILE   C:¥USERS¥HABAT¥DROPBOX¥0
    007_HH_HJ_EL_YH_SK¥YH¥03_WA
    DA_YOSHIBA¥和田あゆみ¥カー
    ボンNMR¥20190716_WADA_COM1_
    13C_CDCL3_重ね書き.RM1
DATIM   17/Jul/2019 02:10:08
COMNT
    S#457895
OBNUC               13C
EXMOD   single_pulse_dec
OBFRQ               100.54 MHz
OBSET               -5.0 kHz
OBFIN               355.9453 H
    z
POINT               131072(ZeroFi
    ll:×4)
FREQU               25188.92 Hz
SCANS               1015
ACQTM               1.3009 s
PD                  1.0 s
PW1                 3.4 μs
IRNUC               1H
PROBHD
INSTRUM             ECP400
PULSPRG
GRDPROG
CTEMP               25.2 ℃
SLVNT   CHLOROFORM-D
EXREF               0.0 ppm
BF                  0.25 Hz
WINDOW  Exponential
RGAIN               27

Operator_____

**Fig. S7.** $^{13}C\{^1H\}$ NMR spectrum of **L·AN** in CDCl$_3$.



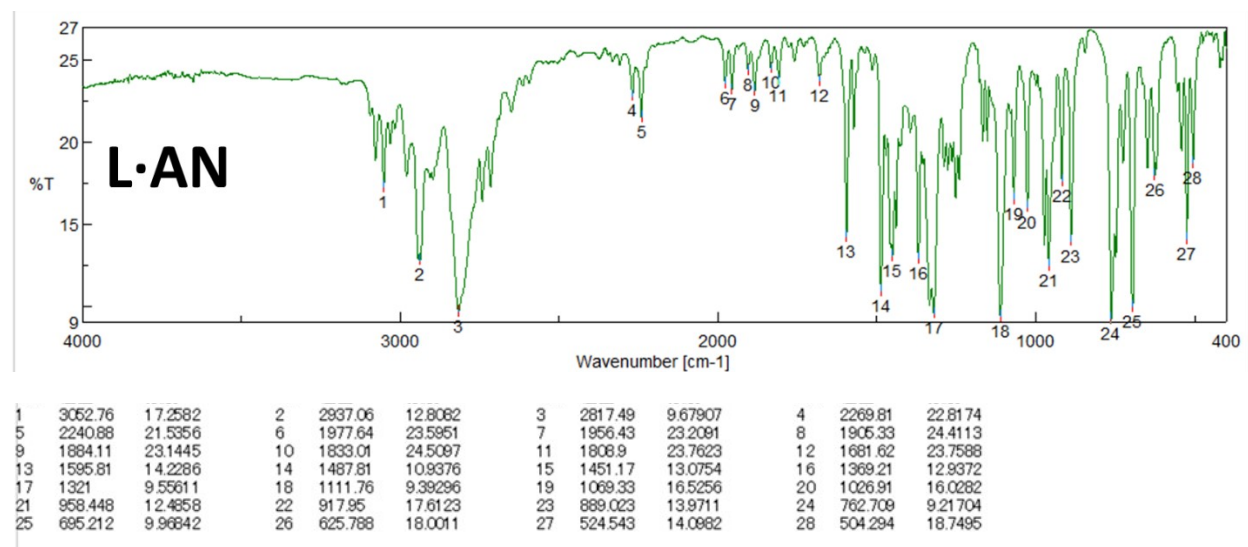| 1 | 3052.76 | 17.2582 | 2 | 2937.06 | 12.8082 | 3 | 2817.49 | 9.67907 | 4 | 2269.81 | 22.8174 |
| 5 | 2240.88 | 21.5356 | 6 | 1977.64 | 23.5951 | 7 | 1956.43 | 23.2091 | 8 | 1905.33 | 24.4113 |
| 9 | 1884.11 | 23.1445 | 10 | 1833.01 | 24.5097 | 11 | 1808.9 | 23.7623 | 12 | 1681.62 | 23.7588 |
| 13 | 1595.81 | 14.2286 | 14 | 1487.81 | 10.9376 | 15 | 1451.17 | 13.0754 | 16 | 1369.21 | 12.9372 |
| 17 | 1321 | 9.55611 | 18 | 1111.76 | 9.39296 | 19 | 1069.33 | 16.5256 | 20 | 1026.91 | 16.0282 |
| 21 | 958.448 | 12.4858 | 22 | 917.95 | 17.6123 | 23 | 889.023 | 13.9711 | 24 | 762.709 | 9.21704 |
| 25 | 695.212 | 9.96842 | 26 | 625.788 | 18.0011 | 27 | 524.543 | 14.0982 | 28 | 504.294 | 18.7495 |

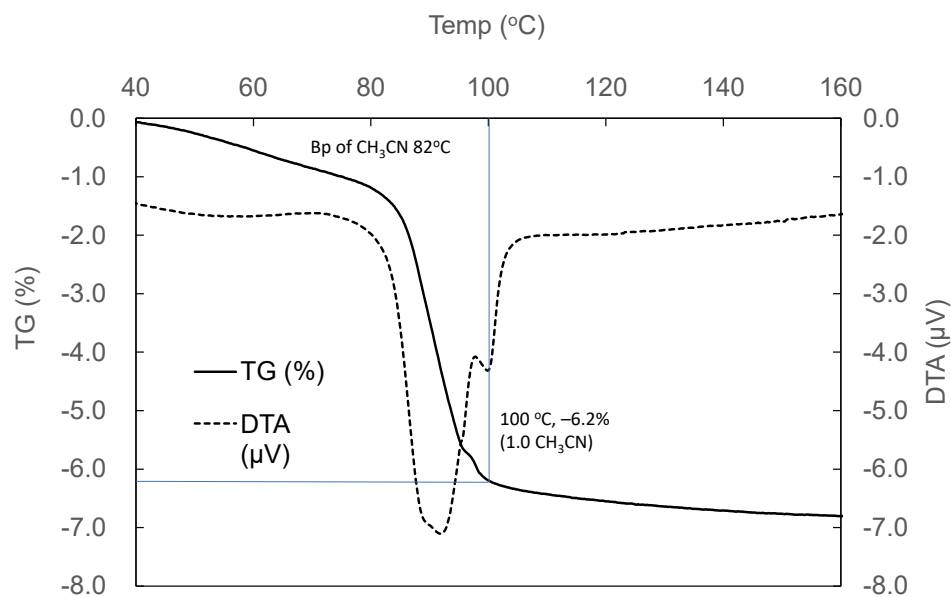**Fig. S8.** IR spectrum of **L·AN** inclusion complex (KBr disc).

**Fig. S9.** TG-DTA of **L·AN** inclusion complex.

**X-ray Crystallographic Analysis.**

X-ray data was collected on a Bruker SMART APEX II ULTRA diffractometer equipped with graphite monochromated Mo $K_{\alpha}$ radiation ($\lambda = 0.71073$ Å) generated by a rotating anode. The cell parameters for the compounds were obtained from a least-squares refinement of the spot. Data collection, data reduction and semi-empirical absorption correction were carried out using the software package of APEX2.[S2] All of the calculations for the structure determination were carried out using the SHELXTL package.[S3] In all cases, nonhydrogen atoms were refined anisotropically and hydrogen atoms were placed in idealized positions and refined isotropically in a riding manner along with their respective parent atoms. Relevant crystal data collection and refinement data for the crystal structures are summarized in Table S1. CCDC 2233509 (**L**) and 2233510 (**L·AN**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[S2] APEX2 Version 2009.1-0 Data collection and Processing Software; Bruker AXS Inc.: Madison, WI, 2008.

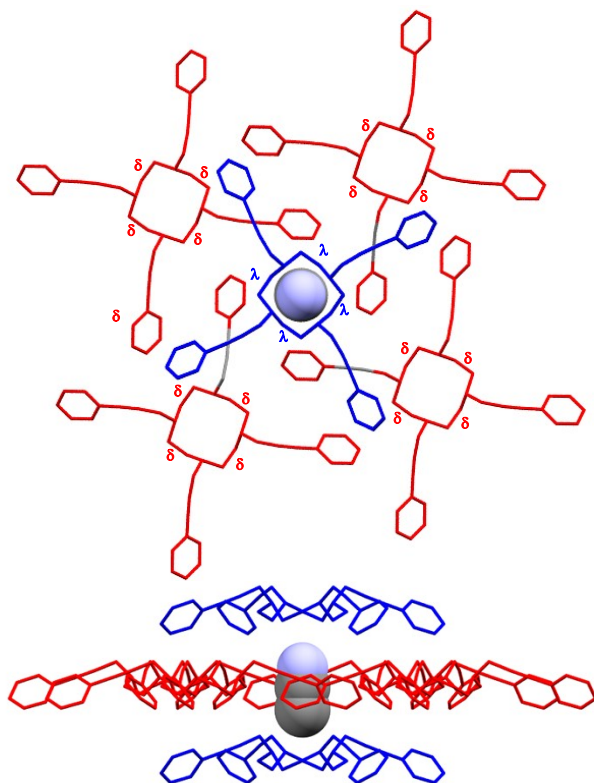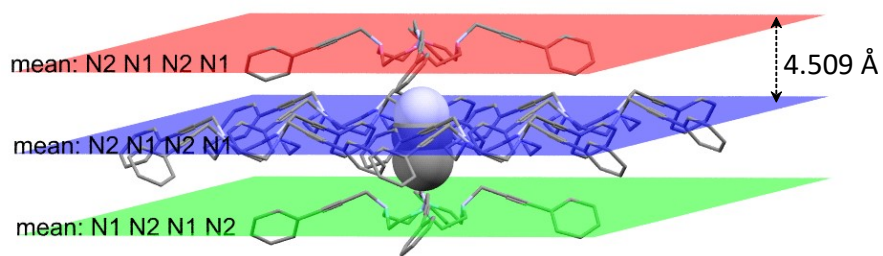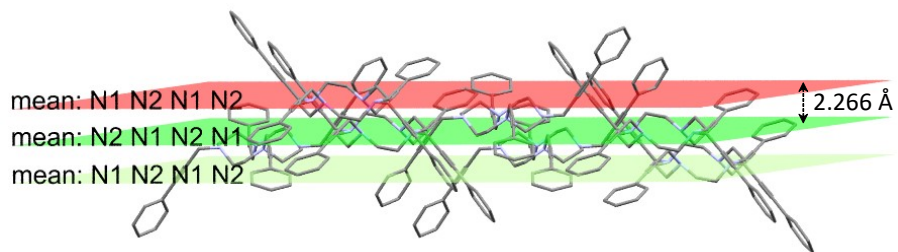[S3] G. M. Sheldrick, *Acta Crystallogr*. 2015, **C71**, 3–8.

**Fig. S10.** Top view and side view of pacing diagram of **L·AN.**



(a)



(b)

**Fig. S11.** Distances of N1-N2-N1'-N2' mean planes of **L·AN** (a) and **L** (b).

**Table S1.** 1,4,7,10-tetrakis(3-phenylprop-2-yn-1-yl)-1,4,7,10-tatraazacyclododecane (**L**).

| | |
|---|---|
| Empirical formula | C44 H44 N4 |
| Formula weight | 628.83 |
| Temperature | 120(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| Unit cell dimensions | a = 10.825(5) Å        a= 90°. |
| | b = 18.151(8) Å        b= 97.156(8)°. |
| | c = 9.211(4) Å         g = 90°. |
| Volume | 1795.7(14) Å$^3$ |
| Z | 2 |
| Density (calculated) | 1.163 Mg/m$^3$ |
| Absorption coefficient | 0.068 mm$^{-1}$ |
| F(000) | 672 |
| Crystal size | 0.244 x 0.135 x 0.065 mm$^3$ |
| Theta range for data collection | 1.896 to 26.000°. |
| Index ranges | -12<=h<=13, -22<=k<=21, -11<=l<=10 |
| Reflections collected | 10326 |
| Independent reflections | 3530 [R(int) = 0.1711] |
| Completeness to theta = 25.242° | 99.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7457 and 0.5659 |
| Refinement method | Full-matrix least-squares on F$^2$ |
| Data / restraints / parameters | 3530 / 0 / 217 |
| Goodness-of-fit on F$^2$ | 1.008 |
| Final R indices [I>2sigma(I)] | R1 = 0.0755, wR2 = 0.1391 |
| R indices (all data) | R1 = 0.2119, wR2 = 0.1969 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.264 and -0.324 e.Å$^{-3}$ |

**Table S2. L·AN** inclusion complex.

| | |
|---|---|
| Empirical formula | C46 H47 N5 |
| Formula weight | 669.89 |
| Temperature | 120(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Tetragonal |
| Space group | P4nc |
| Unit cell dimensions | a = 14.404(7) Å        a= 90°. |
| | b = 14.404(7) Å        b= 90°. |
| | c = 9.018(8) Å        g = 90°. |
| Volume | 1871(2) Å$^3$ |
| Z | 2 |
| Density (calculated) | 1.189 Mg/m$^3$ |
| Absorption coefficient | 0.070 mm$^{-1}$ |
| F(000) | 716 |
| Crystal size | 0.265 x 0.11 x 0.106 mm$^3$ |
| Theta range for data collection | 1.999 to 25.997°. |
| Index ranges | -17<=h<=17, -17<=k<=13, -10<=l<=11 |
| Reflections collected | 9633 |
| Independent reflections | 1794 [R(int) = 0.1687] |
| Completeness to theta = 25.242° | 99.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7457 and 0.5862 |
| Refinement method | Full-matrix least-squares on F$^2$ |
| Data / restraints / parameters | 1794 / 1 / 118 |
| Goodness-of-fit on F$^2$ | 1.072 |
| Final R indices [I>2sigma(I)] | R1 = 0.0786, wR2 = 0.1657 |
| R indices (all data) | R1 = 0.1918, wR2 = 0.2340 |
| Absolute structure parameter | ? |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.161 and -0.226 e.Å$^{-3}$ |

**Fig. S12.** Binding constant for 1:1 complex between **L** and acetonitrile.