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Supplementary Information

Aggregation-Induced Emission Mesogens Formed by Intermolecular Hydrogen Bonding of 4-Alkyl 4'-Cyanobiphenyl Molecules

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Contents

1. DSC analysis

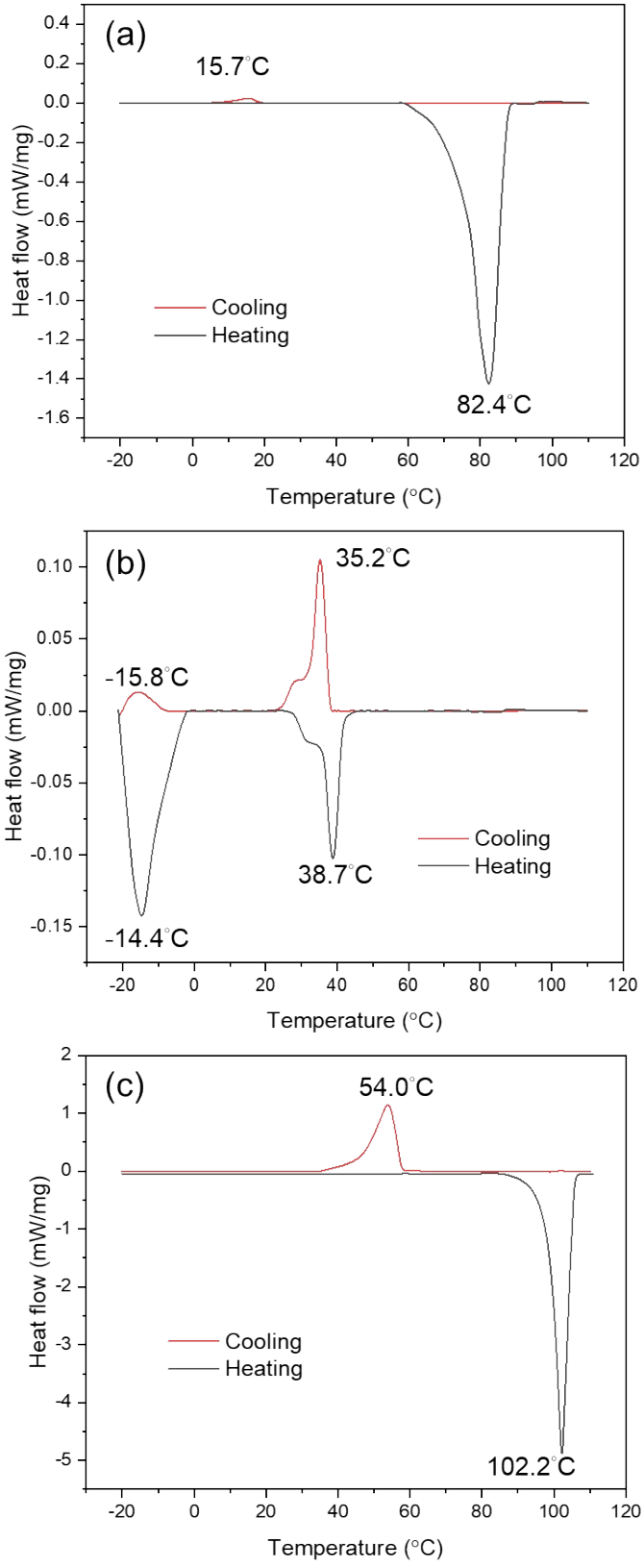

Fig. S1. The DSC thermograms of (a) 2CB-NC2O, (b) 2CB-NC3O, and (c) 2CB-NC4O. The scan rate was 10°C/min.

2. Single Crystal X-ray Structures and Crystal Data

The crystals of complexes 2CB-NC2O and 2CB-NC4O chosen for X-ray diffraction studies are measured in sizes of 0.20 × 0.08 × 0.8 mm and 0.30 × 0.05 × 0.05 mm, respectively. Each crystal was mounted on a glass fiber and quickly coated in epoxy resin. Unit-cell parameters were obtained by least-squares refinement. Diffraction measurements for complexes **2CB-NC2O** and **2CB-NC4O** were carried out on a Bruker SMART Apex CCD diffractometers using graphite-monochromated Mo Kα radiation (λ = 0.7107 Å) and between 2.43° and 25.94° for complex **2CB-NC2O**, between 2.83° and 28.39° for complex **2CB-NC4O**. The space groups were determined on the basis of systematic absences and intensity statistics. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. Anisotropic displacement parameters were determined for all nonhydrogen atoms. Hydrogen atoms were mixed treatment in the least-squares refinment. The following is a list of programs used: data collection and cell refinement, APEX2;[a] data reductions, SAINTPLUS Version 6.63;[b] absorption correction, SADABAS;[c] structural solutions, SHELXS-97;[d] structural refinement, SHELXL-97;[e] graphics and publication materials, Mercury Version 2.3.[f] Full crystal data has been deposited at the Chambridge Crystallographic Data Centre (CCDC2219044 and CCDC2219045).

a. *APEX2*, version 2009.7-0; Bruker AXS, Inc.: Madison, WI, 2007.
b. *SAINTPLUS*: Program for Reduction of Area Detector Data, 1034 version 6.63; Bruker AXS Inc.: Madison, WI, 2007.
c. Sheldrick, G. M. *SADABS: Program for Absorption Correction of 1036 Area Detector Frames*; Bruker AXS Inc.: Madison, WI, 2001.
d. Sheldrick, G. M. *SHELXS-97: Program for Crystal Structure 1038 Solution*; Universitat Go ̈ttingen: Göttingen, Germany, 1997.

e. Sheldrick, G. M., *SHELXL-97: Program for Crystal Structure 1040 Refinement*; Universitat Go ¨ttingen: Göttingen, Germany, 1997.

f. Macrae, C. F.; Edgington, P. R.; McCabe, P.; Pidcock, E.; 1042 Shields, G. P.; Taylor, R.; Towler, M. and van de Streek, J., *J. Appl. Crystallogr.* 2006, **39**, 453−457.

Table S1. Crystal data and structure refinement for **2CB-NC2O**

Identification code	tat6_0m-auto
Empirical formula	C34 H38 N4 O2
Formula weight	534.68
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	a = 9.259(3) Å a= 90°.
	b = 15.873(5) Å b= 96.57(2)°.
	c = 19.879(5) Å g = 90°.
Volume	2902.3(14) Å^3
Z	4
Density (calculated)	1.224 Mg/m^3
Absorption coefficient	0.077 mm^{-1}
F(000)	1144
Crystal size	0.2 x 0.08 x 0.08 mm^3
Theta range for data collection	2.43 to 25.94°.
Index ranges	-9<=h<=11, -19<=k<=18, -24<=l<=24
Reflections collected	33247
Independent reflections	5671 [R(int) = 0.0680]
Completeness to theta = 25.94°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9805 and 0.8272
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5671 / 0 / 377
Goodness-of-fit on F^2	0.918
Final R indices [I>2sigma(I)]	R1 = 0.0634, wR2 = 0.2104
R indices (all data)	R1 = 0.1251, wR2 = 0.2767
Largest diff. peak and hole	0.328 and -0.360 e.Å-3

Table S2. Bond lengths [Å] and angles [°] for **2CB-NC2O**

O(1)-C(1)	1.415(3)	C(12)-C(14)	1.382(4)
O(1)-H(4)	0.87(4)	C(12)-C(13)	1.441(4)
O(2)-C(18)	1.414(4)	C(14)-C(15)	1.377(4)
O(2)-H(3)	0.89(4)	C(14)-H(14)	0.9500
N(1)-C(3)	1.458(3)	C(15)-H(15)	0.9500
N(1)-C(2)	1.461(3)	C(16)-C(17)	1.379(4)
N(2)-C(13)	1.133(4)	C(16)-H(16)	0.9500
N(3)-C(20)	1.463(3)	C(17)-H(17)	0.9500
N(3)-C(19)	1.459(3)	C(18)-C(19)	1.494(4)
N(4)-C(30)	1.147(4)	C(18)-H(18A)	0.9900
C(1)-C(2)	1.503(4)	C(18)-H(18B)	0.9900
C(1)-H(1A)	0.9900	C(19)-H(19A)	0.9900
C(1)-H(1B)	0.9900	C(19)-H(19B)	0.9900
C(2)-H(2A)	0.9900	C(20)-C(21)	1.513(4)
C(2)-H(2B)	0.9900	C(20)-H(20A)	0.9900
C(3)-C(4)	1.512(4)	C(20)-H(20B)	0.9900
C(3)-H(3A)	0.9900	C(21)-C(22)	1.501(4)
C(3)-H(3B)	0.9900	C(21)-H(21A)	0.9900
C(4)-C(5)	1.508(3)	C(21)-H(21B)	0.9900
C(4)-H(4A)	0.9900	C(22)-C(32)	1.378(4)
C(4)-H(4B)	0.9900	C(22)-C(23)	1.388(4)
C(5)-C(17)	1.384(4)	C(23)-C(24)	1.378(4)
C(5)-C(6)	1.388(4)	C(23)-H(23)	0.9500
C(6)-C(7)	1.385(4)	C(24)-C(25)	1.398(4)
C(6)-H(6)	0.9500	C(24)-H(24)	0.9500
C(7)-C(8)	1.392(4)	C(25)-C(31)	1.385(4)
C(7)-H(7)	0.9500	C(25)-C(26)	1.475(4)
C(8)-C(16)	1.390(4)	C(26)-C(34)	1.399(4)
C(8)-C(9)	1.475(4)	C(26)-C(27)	1.395(4)
C(9)-C(15)	1.390(4)	C(27)-C(28)	1.372(4)
C(9)-C(10)	1.395(4)	C(27)-H(27)	0.9500
C(10)-C(11)	1.376(4)	C(28)-C(29)	1.396(4)
C(10)-H(10)	0.9500	C(28)-H(28)	0.9500
C(11)-C(12)	1.386(4)	C(29)-C(33)	1.385(4)
C(11)-H(11)	0.9500	C(29)-C(30)	1.437(4)

C(31)-C(32)	1.375(4)
C(31)-H(31)	0.9500
C(32)-H(32)	0.9500
C(33)-C(34)	1.369(4)
C(33)-H(33)	0.9500
C(34)-H(34)	0.9500

C(1)-O(1)-H(4)	112(2)
C(18)-O(2)-H(3)	113(3)
C(3)-N(1)-C(2)	111.1(2)
C(20)-N(3)-C(19)	111.6(2)
O(1)-C(1)-C(2)	112.8(2)
O(1)-C(1)-H(1A)	109.0
C(2)-C(1)-H(1A)	109.0
O(1)-C(1)-H(1B)	109.0
C(2)-C(1)-H(1B)	109.0
H(1A)-C(1)-H(1B)	107.8
N(1)-C(2)-C(1)	112.3(2)
N(1)-C(2)-H(2A)	109.1
C(1)-C(2)-H(2A)	109.1
N(1)-C(2)-H(2B)	109.1
C(1)-C(2)-H(2B)	109.1
H(2A)-C(2)-H(2B)	107.9
N(1)-C(3)-C(4)	112.6(2)
N(1)-C(3)-H(3A)	109.1
C(4)-C(3)-H(3A)	109.1
N(1)-C(3)-H(3B)	109.1
C(4)-C(3)-H(3B)	109.1
H(3A)-C(3)-H(3B)	107.8
C(5)-C(4)-C(3)	115.4(2)
C(5)-C(4)-H(4A)	108.4
C(3)-C(4)-H(4A)	108.4
C(5)-C(4)-H(4B)	108.4
C(3)-C(4)-H(4B)	108.4
H(4A)-C(4)-H(4B)	107.5
C(17)-C(5)-C(6)	117.1(2)
C(17)-C(5)-C(4)	119.8(2)
C(6)-C(5)-C(4)	123.1(2)
C(7)-C(6)-C(5)	121.2(3)
C(7)-C(6)-H(6)	119.4
C(5)-C(6)-H(6)	119.4
C(6)-C(7)-C(8)	121.6(2)
C(6)-C(7)-H(7)	119.2
C(8)-C(7)-H(7)	119.2
C(7)-C(8)-C(16)	117.1(2)
C(7)-C(8)-C(9)	121.3(2)
C(16)-C(8)-C(9)	121.5(2)
C(15)-C(9)-C(10)	117.1(2)
C(15)-C(9)-C(8)	121.8(2)
C(10)-C(9)-C(8)	121.1(2)
C(11)-C(10)-C(9)	121.6(2)
C(11)-C(10)-H(10)	119.2
C(9)-C(10)-H(10)	119.2
C(12)-C(11)-C(10)	120.2(3)
C(12)-C(11)-H(11)	119.9
C(10)-C(11)-H(11)	119.9
C(11)-C(12)-C(14)	119.1(2)
C(11)-C(12)-C(13)	120.0(3)
C(14)-C(12)-C(13)	120.8(3)
N(2)-C(13)-C(12)	177.6(3)
C(15)-C(14)-C(12)	120.2(3)
C(15)-C(14)-H(14)	119.9
C(12)-C(14)-H(14)	119.9
C(14)-C(15)-C(9)	121.7(3)
C(14)-C(15)-H(15)	119.1
C(9)-C(15)-H(15)	119.1
C(17)-C(16)-C(8)	121.0(2)
C(17)-C(16)-H(16)	119.5
C(8)-C(16)-H(16)	119.5
C(16)-C(17)-C(5)	122.1(2)
C(16)-C(17)-H(17)	119.0
C(5)-C(17)-H(17)	119.0
O(2)-C(18)-C(19)	112.5(3)
O(2)-C(18)-H(18A)	109.1
C(19)-C(18)-H(18A)	109.1
O(2)-C(18)-H(18B)	109.1

C(19)-C(18)-H(18B) 109.1
H(18A)-C(18)-H(18B) 107.8
N(3)-C(19)-C(18) 112.5(2)
N(3)-C(19)-H(19A) 109.1
C(18)-C(19)-H(19A) 109.1
N(3)-C(19)-H(19B) 109.1
C(18)-C(19)-H(19B) 109.1
H(19A)-C(19)-H(19B) 107.8
N(3)-C(20)-C(21) 113.1(2)
N(3)-C(20)-H(20A) 109.0
C(21)-C(20)-H(20A) 109.0
N(3)-C(20)-H(20B) 109.0
C(21)-C(20)-H(20B) 109.0
H(20A)-C(20)-H(20B) 107.8
C(22)-C(21)-C(20) 114.6(2)
C(22)-C(21)-H(21A) 108.6
C(20)-C(21)-H(21A) 108.6
C(22)-C(21)-H(21B) 108.6
C(20)-C(21)-H(21B) 108.6
H(21A)-C(21)-H(21B) 107.6
C(32)-C(22)-C(23) 116.8(2)
C(32)-C(22)-C(21) 122.9(2)
C(23)-C(22)-C(21) 120.3(2)
C(24)-C(23)-C(22) 122.2(3)
C(24)-C(23)-H(23) 118.9
C(22)-C(23)-H(23) 118.9
C(23)-C(24)-C(25) 120.8(3)
C(23)-C(24)-H(24) 119.6
C(25)-C(24)-H(24) 119.6
C(31)-C(25)-C(24) 116.3(2)
C(31)-C(25)-C(26) 121.4(2)
C(24)-C(25)-C(26) 122.2(2)
C(34)-C(26)-C(27) 117.4(2)
C(34)-C(26)-C(25) 121.7(2)
C(27)-C(26)-C(25) 120.9(2)
C(28)-C(27)-C(26) 121.3(3)
C(28)-C(27)-H(27) 119.3
C(26)-C(27)-H(27) 119.3
C(27)-C(28)-C(29) 120.2(3)
C(27)-C(28)-H(28) 119.9
C(29)-C(28)-H(28) 119.9
C(33)-C(29)-C(28) 119.2(3)
C(33)-C(29)-C(30) 121.5(3)
C(28)-C(29)-C(30) 119.3(3)
N(4)-C(30)-C(29) 178.1(4)
C(25)-C(31)-C(32) 122.4(3)
C(25)-C(31)-H(31) 118.8
C(32)-C(31)-H(31) 118.8
C(22)-C(32)-C(31) 121.4(3)
C(22)-C(32)-H(32) 119.3
C(31)-C(32)-H(32) 119.3
C(34)-C(33)-C(29) 120.1(3)
C(34)-C(33)-H(33) 119.9
C(29)-C(33)-H(33) 119.9
C(33)-C(34)-C(26) 121.7(3)
C(33)-C(34)-H(34) 119.2
C(26)-C(34)-H(34) 119.2

Symmetry transformations used to generate equivalent atoms:

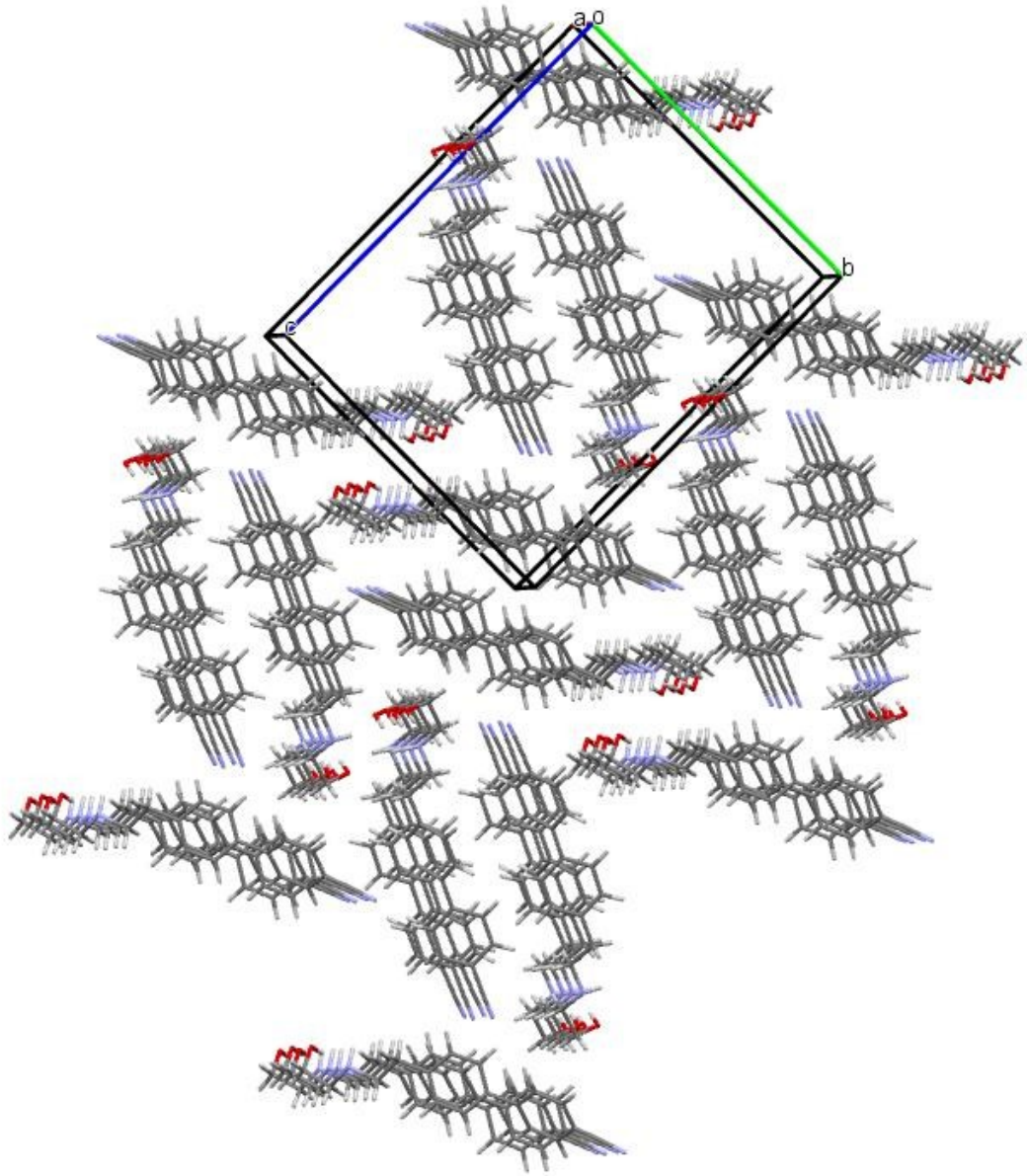

Fig. S2. The packing diagram of 2CB-NC2O alone with an axis in the size of 2*2*2 unit cell.

Table S3. Crystal data and structure refinement for **2CB-NC4O**

Identification code	tat21b_0m-auto
Empirical formula	C19 H22 N2 O
Formula weight	294.39
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P21/n
Unit cell dimensions	a = 9.161 Å a= 90°.

	b = 6.008 Å b= 90.32°.
	c = 28.752 Å g = 90°.
Volume	1582.5 $Å^3$
Z	4
Density (calculated)	1.236 Mg/m^3
Absorption coefficient	0.077 mm^{-1}
F(000)	632
Crystal size	0.3 x 0.05 x 0.05 mm^3
Theta range for data collection	2.83 to 28.39°.
Index ranges -	12<=h<=10, -6<=k<=8, -38<=l<=32
Reflections collected	17358
Independent reflections	3900 [R(int) = 0.1345]
Completeness to theta = 28.39°	98.3 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3900 / 0 / 206
Goodness-of-fit on F^2	1.168
Final R indices [I>2sigma(I)]	R1 = 0.0928, wR2 = 0.2161
R indices (all data)	R1 = 0.1401, wR2 = 0.2571
Largest diff. peak and hole	0.415 and -0.395 $e.Å^{-3}$

Table S4. Bond lengths [Å] and angles [°] for **2CB-NC4O**

C(1)-O(1)	1.417(4)	C(5)-H(11)	0.9900
C(1)-C(2)	1.517(4)	C(6)-C(7)	1.511(4)
C(1)-H(2)	0.9900	C(6)-H(12)	0.9900
C(1)-H(3)	0.9900	C(6)-H(13)	0.9900
C(2)-C(3)	1.525(4)	C(7)-C(17)	1.393(5)
C(2)-H(4)	0.9900	C(7)-C(8)	1.405(4)
C(2)-H(5)	0.9900	C(8)-C(9)	1.386(4)
C(3)-C(4)	1.521(4)	C(8)-H(14)	0.9500
C(3)-H(6)	0.9900	C(9)-C(10)	1.389(5)
C(3)-H(7)	0.9900	C(9)-H(15)	0.9500
C(4)-N(1)	1.465(4)	C(10)-C(16)	1.408(4)
C(4)-H(8)	0.9900	C(10)-C(11)	1.484(4)
C(4)-H(9)	0.9900	C(11)-C(19)	1.399(5)
C(5)-N(1)	1.473(4)	C(11)-C(12)	1.402(4)
C(5)-C(6)	1.517(5)	C(12)-C(13)	1.382(4)
C(5)-H(10)	0.9900	C(12)-H(16)	0.9500

C(13)-C(14)	1.389(5)
C(13)-H(17)	0.9500
C(14)-C(18)	1.394(5)
C(14)-C(15)	1.447(5)
C(15)-N(2)	1.142(4)
C(16)-C(17)	1.380(4)
C(16)-H(18)	0.9500
C(17)-H(19)	0.9500
C(18)-C(19)	1.380(5)
C(18)-H(20)	0.9500
C(19)-H(21)	0.9500
N(1)-H(22)	0.96(4)
O(1)-H(1)	0.82(5)

O(1)-C(1)-C(2)	112.3(3)
O(1)-C(1)-H(2)	109.1
C(2)-C(1)-H(2)	109.1
O(1)-C(1)-H(3)	109.1
C(2)-C(1)-H(3)	109.1
H(2)-C(1)-H(3)	107.9
C(1)-C(2)-C(3)	112.4(3)
C(1)-C(2)-H(4)	109.1
C(3)-C(2)-H(4)	109.1
C(1)-C(2)-H(5)	109.1
C(3)-C(2)-H(5)	109.1
H(4)-C(2)-H(5)	107.9
C(4)-C(3)-C(2)	114.1(3)
C(4)-C(3)-H(6)	108.7
C(2)-C(3)-H(6)	108.7
C(4)-C(3)-H(7)	108.7
C(2)-C(3)-H(7)	108.7
H(6)-C(3)-H(7)	107.6
N(1)-C(4)-C(3)	109.9(2)
N(1)-C(4)-H(8)	109.7
C(3)-C(4)-H(8)	109.7
N(1)-C(4)-H(9)	109.7
C(3)-C(4)-H(9)	109.7
H(8)-C(4)-H(9)	108.2
N(1)-C(5)-C(6)	109.4(2)
N(1)-C(5)-H(10)	109.8
C(6)-C(5)-H(10)	109.8
N(1)-C(5)-H(11)	109.8
C(6)-C(5)-H(11)	109.8
H(10)-C(5)-H(11)	108.2
C(7)-C(6)-C(5)	116.7(3)
C(7)-C(6)-H(12)	108.1
C(5)-C(6)-H(12)	108.1
C(7)-C(6)-H(13)	108.1
C(5)-C(6)-H(13)	108.1
H(12)-C(6)-H(13)	107.3
C(17)-C(7)-C(8)	117.3(3)
C(17)-C(7)-C(6)	118.6(3)
C(8)-C(7)-C(6)	124.1(3)
C(9)-C(8)-C(7)	120.6(3)
C(9)-C(8)-H(14)	119.7
C(7)-C(8)-H(14)	119.7
C(8)-C(9)-C(10)	121.8(3)
C(8)-C(9)-H(15)	119.1
C(10)-C(9)-H(15)	119.1
C(9)-C(10)-C(16)	117.7(3)
C(9)-C(10)-C(11)	122.5(3)
C(16)-C(10)-C(11)	119.8(3)
C(19)-C(11)-C(12)	117.6(3)
C(19)-C(11)-C(10)	121.2(3)
C(12)-C(11)-C(10)	121.1(3)
C(13)-C(12)-C(11)	121.3(3)
C(13)-C(12)-H(16)	119.4
C(11)-C(12)-H(16)	119.4
C(12)-C(13)-C(14)	119.8(3)
C(12)-C(13)-H(17)	120.1
C(14)-C(13)-H(17)	120.1
C(13)-C(14)-C(18)	120.0(3)
C(13)-C(14)-C(15)	120.6(3)
C(18)-C(14)-C(15)	119.4(3)
N(2)-C(15)-C(14)	178.2(4)
C(17)-C(16)-C(10)	120.3(3)

C(17)-C(16)-H(18)	119.8	C(18)-C(19)-C(11)	121.6(3)
C(10)-C(16)-H(18)	119.8	C(18)-C(19)-H(21)	119.2
C(16)-C(17)-C(7)	122.2(3)	C(11)-C(19)-H(21)	119.2
C(16)-C(17)-H(19)	118.9	C(4)-N(1)-C(5)	113.2(2)
C(7)-C(17)-H(19)	118.9	C(4)-N(1)-H(22)	107(3)
C(19)-C(18)-C(14)	119.6(3)	C(5)-N(1)-H(22)	107(2)
C(19)-C(18)-H(20)	120.2	C(1)-O(1)-H(1)	114(3)
C(14)-C(18)-H(20)	120.2		

Symmetry transformations used to generate equivalent atoms:

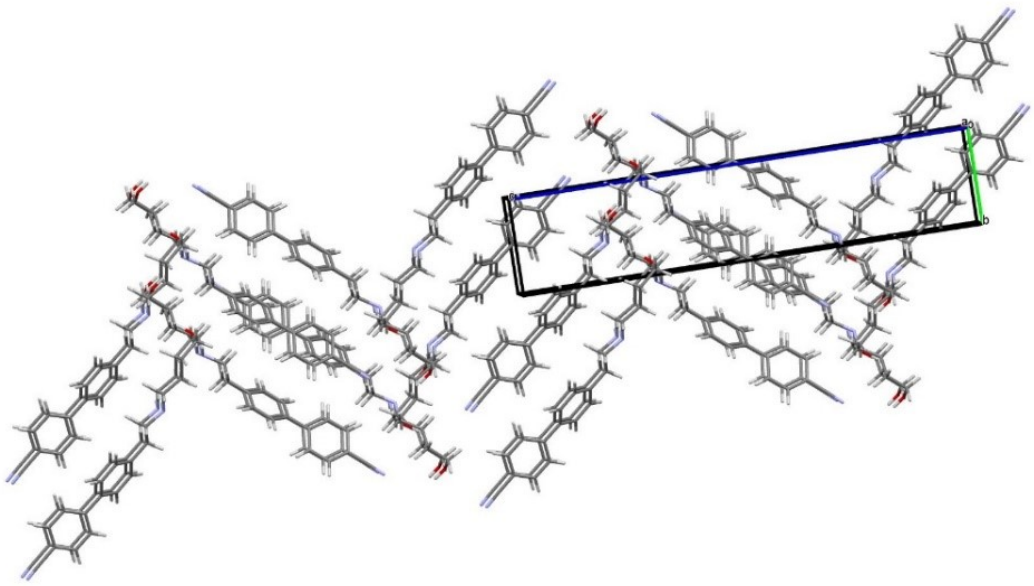

Fig. S3. The packing diagram of 2CB-NC4O alone with an axis in the size of 2*2*2 unit cell.

3. Synthesis and Characterization of the Molecules

Synthesis of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzeneethanol (1)

In a nitrogen atmosphere, a mixture of bis(pinacolato)diboron (3.04 g, 11.9 mmol) and $Pd(dppf)Cl_2•CH_2Cl_2$ (0.406 g, 0.497 mmol) in 1,4-dioxane was degassed with nitrogen for 30 min, and then 2-(4-bromophenyl)ethanol was added in flask by syringe. The mixture was heated up to react at 100 ℃ for 24 h. After cooling, the mixture was filtered over celite and washed with ethyl acetate. The filtrate was extracted with ethyl acetate and DI water. The organic phase was dried over $MgSO_4$ and concentrated by rotary evaporation. The residue was purified by column chromatography on silica gel with hexanes: ethyl acetate (30% to 70% ethyl acetate, by volume) as the eluent. Compound **1** was obtained as a yellow solid.

Synthesis of 4'-(2-hydroxyethyl)-(1,1'-biphenyl)-4-carbonitrile (2)

In a nitrogen atmosphere, a mixture of 4-bromobenzonitrile (0.176 g, 0.967 mmol), **1** (0.200 g, 0.806 mmol), $Pd(PPh_3)_4$ (46.6 mg, 40.3 μmol) and K_2CO_3 (0.667 g, 4.84 mmol) in a mixed solvent containing 4.8 mL toluene, 4.8 mL ethanol and 2.4 mL DI water was allowed to react at reflux condition for 2.5 h. After that, the reaction mixture was cooled down to room temperature and then extracted twice with ethyl acetate and DI water. The organic phase was dried over $MgSO_4$ and concentrated by rotary evaporation. The residue was purified by column chromatography on silica gel with hexanes: ethyl acetate (20% to 50% ethyl acetate, by volume) as the eluent. Compound **2** was obtained as a white solid (88.9% yield). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 7.71 (d, J = 8.2 Hz, 2H), 7.66 (d, J = 8.2 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 3.92 (t, J = 5.9 Hz, 2H), 2.93 (t, J = 6.5 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 145.36, 139.40, 137.31, 132.57, 129.77, 127.51, 127.34, 118.92, 110.71, 63.43, 38.76; HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{15}H_{13}NO$: 223.0997, found 223.0993.

Synthesis of 4'-(2-bromoethyl)-(1,1'-biphenyl)-4-carbonitrile (3)

In a nitrogen atmosphere, a mixture of tetrabromomethane (0.297 g, 0.896 mmol) and **2** (0.100 g, 0.448 mmol) in 7.5 mL dichloromethane was cooled down to 0 ℃, and then triphenylphosphine (0.235 g, 0.896 mmol) was added. The reaction mixture was allowed to react at room temperature for 1 h. After that, the reaction mixture was concentrated by rotary evaporation. The crude product was purified by column chromatography on silica gel with hexanes: dichloromethane (50% dichloromethane, by volume) as the eluent. Compound **3** was obtained as a white solid (89.8% yield). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 7.72 (d, J = 8.1 Hz, 2H), 7.68 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 3.62 (t, J = 7.4 Hz, 2H), 3.23 (t, J = 7.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 145.19, 139.48, 137.75, 132.58, 129.43, 127.54, 127.39, 118.89, 110.86, 38.82, 32.61; HRMS (FAB) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{13}BrN$: 286.0231, found 286.0235.

Synthesis of 2CB-NC2O, 2CB-NC3O, and 2CB-NC4O

Compound 2CB-NC2O, 2CB-NC3O, and 2CB-NC4O were synthesized according to the same procedures. Only the preparation of 2CB-NC2O was described in detail.

Synthesis of 2CB-NC2O

In a nitrogen atmosphere, a mixture of ethanolamine (0.630 mL, 10.5 mmol) and **3** (0.500 g, 1.75 mmol) in 2 mL ethanol was allowed to react at reflux condition overnight. After that, the reaction mixture was concentrated by rotary evaporation and then the crude product was purified by column chromatography on silica gel with MeOH: dichloromethane (95% dichloromethane, by volume) as the eluent. Compound **2CB-NC2O** was obtained as a yellow solid (65.1% yield). ^{1}H NMR (600 MHz, MeOD-d_4, ppm): δ 7.80-7.77 (m, 4H), 7.63 (d, J = 7.7 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 3.67 (t, J = 5.4 Hz, 2H), 3.23 (m, 4H), 2.79 (t, J = 5.5 Hz, 2H); ^{13}C NMR (150 MHz, MeOD-d_4, ppm): δ 146.98, 141.71, 138.65, 133.93, 130.73,

128.82, 128.58, 119.97, 111.86, 61.30, 52.24, 51.72, 36.25; HRMS (FAB) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{19}N_2O$: 267.1497, found 267.1493.

Synthesis of 2CB-NC3O

A yellow-green viscous liquid (80.6% yield). ^{1}H NMR (600 MHz, MeOD-d_4, ppm): δ 7.80-7.76 (m, 4H), 7.62 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 3.62 (t, J = 6.2 Hz, 2H), 3.32-3.30 (m, 4H), 2.76 (t, J = 7.1 Hz, 2H), 1.76-1.72 (m, 2H); ^{13}C NMR (150 MHz, MeOD-d_4, ppm): δ 146.82, 141.70, 138.43, 133.76, 130.55, 128.65, 128.40, 119.82, 111.68, 61.47, 51.86, 47.90, 36.14, 32.74; HRMS (FAB) *m/z*: $[M]^+$ calcd for $C_{18}H_{21}N_2O$: 281.1654, found 281.1647.

Synthesis of 2CB-NC4O

A yellow solid (53.4% yield). ^{1}H NMR (600 MHz, MeOD-d_4, ppm): δ 7.80-7.77 (m, 4H), 7.63 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 3.56 (t, J = 6.1 Hz, 2H), 2.91-2.86 (m, 4H), 2.66 (t, J = 6.8 Hz, 2H), 1.62-1.53 (m, 4H); ^{13}C NMR (150 MHz, MeOD-d_4, ppm): δ 146.84, 141.78, 138.43, 133.76, 130.54, 128.66, 128.40, 119.82, 111.70, 62.72, 51.80, 50.32, 36.20, 31.55, 27.06; HRMS (FAB) *m/z*: $[M]^+$ calcd for $C_{19}H_{23}N_2O$: 295.1810, found 295.1805.

4. Theoretical Calculation

The theoretical calculations of the bimolecular structure for 2CB-NC2O, 2CB-NC3O, 2CB-NC4O, and 5CB were calculated by the Gaussian 16 software. The molecular model is optimized by the density functional theory (DFT) B3LYP-D3 with the basis set of 6-31g(d)+ for C/H/O/N atoms.[1]

References:

1. J. Witte, M. Goldey, J. B. Neaton, M. H.-Gordon, *J. Chem. Theory Comput.* 2015, **11**, 1481−1492.

5. ^{1}H and ^{13}C NMR spectra

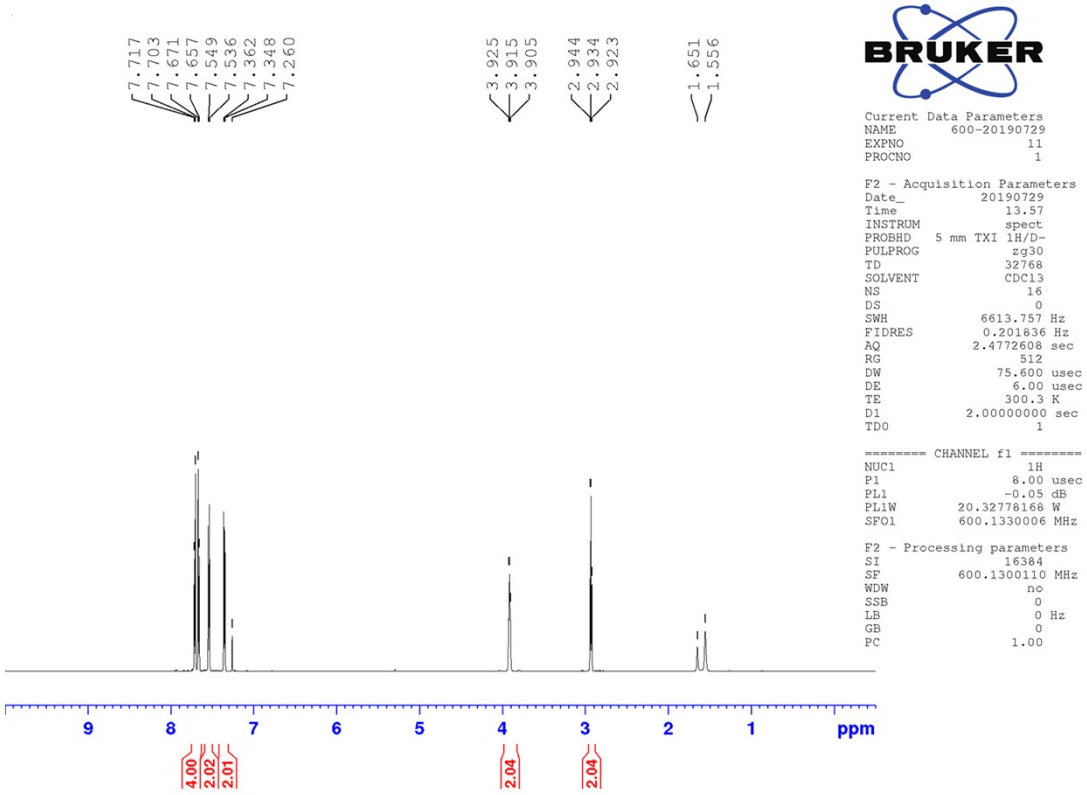

Fig. S4. ^{1}H NMR spectra of **2** in $CDCl_3$.

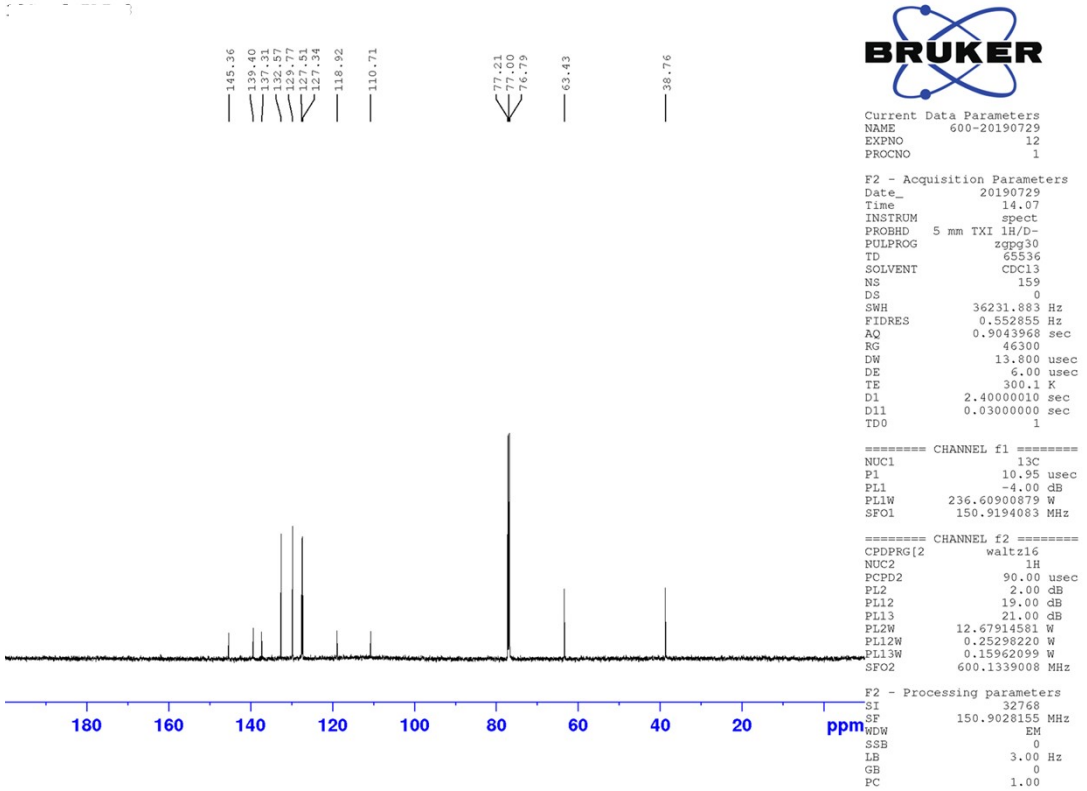

Fig. S5. ^{13}C NMR spectra of **2** in $CDCl_3$.

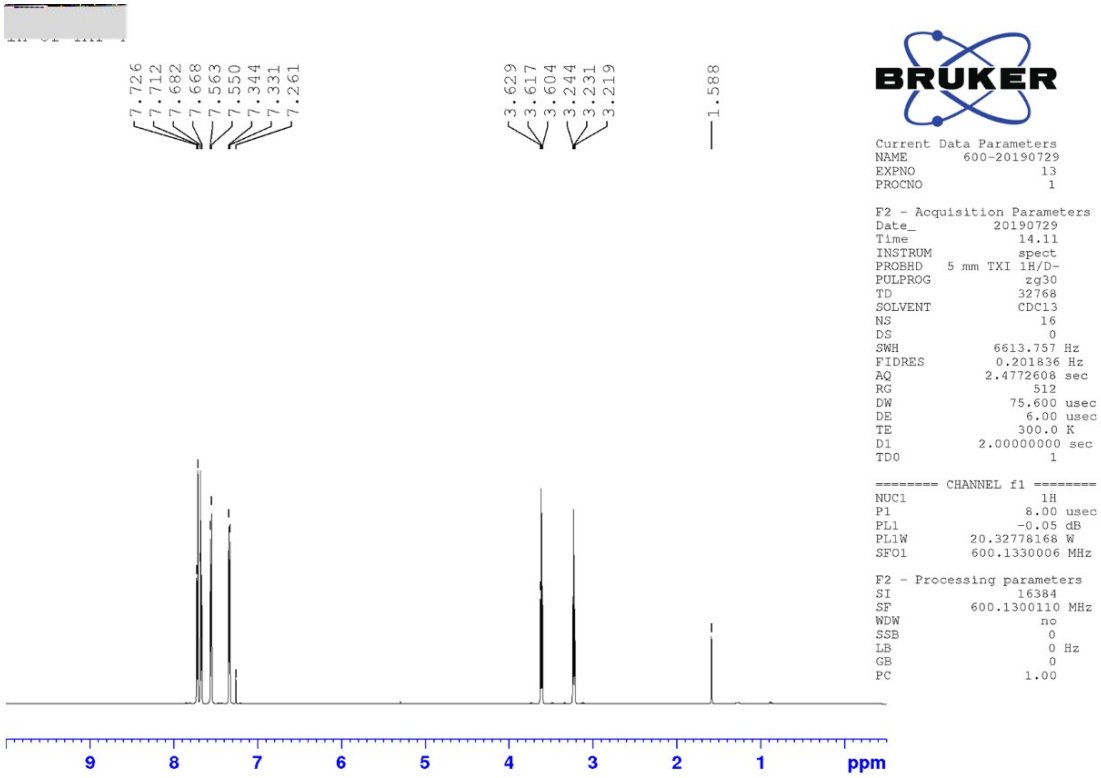

Fig. S6. ^{1}H NMR spectra of **3** in $CDCl_3$.

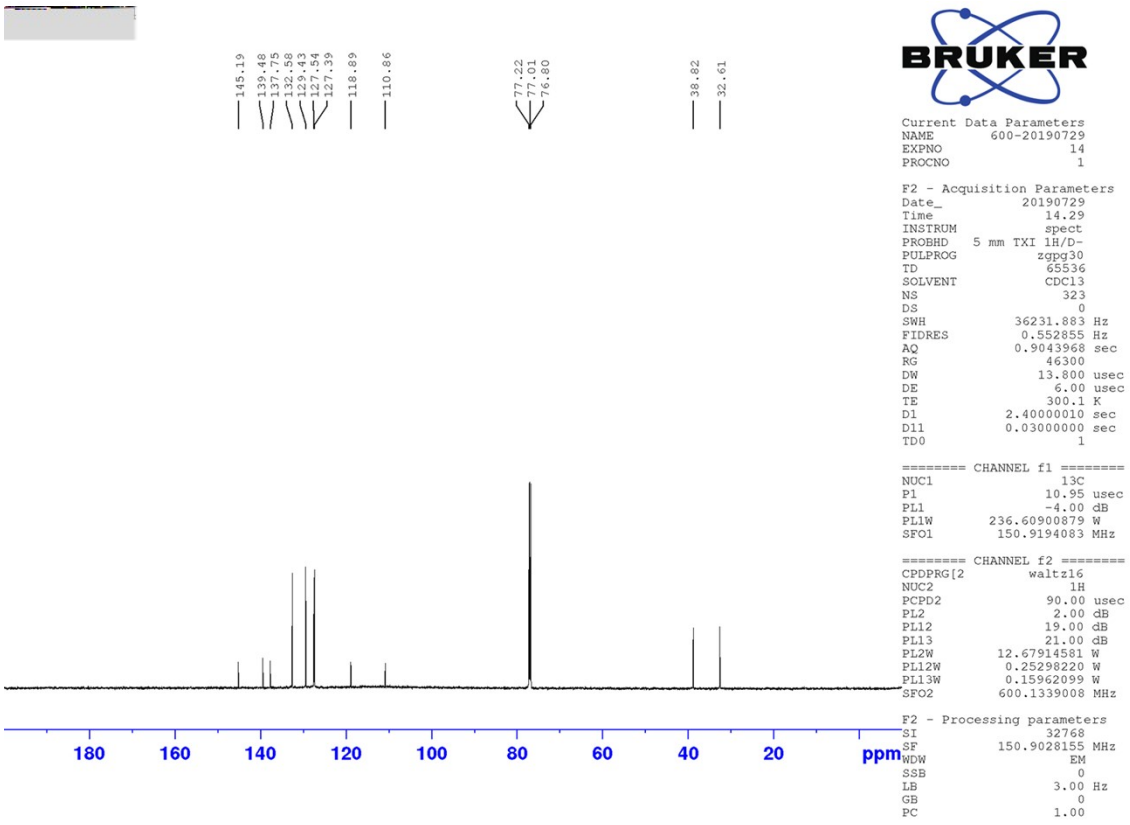

Fig. S7. ^{13}C NMR spectra of **3** in $CDCl_3$.

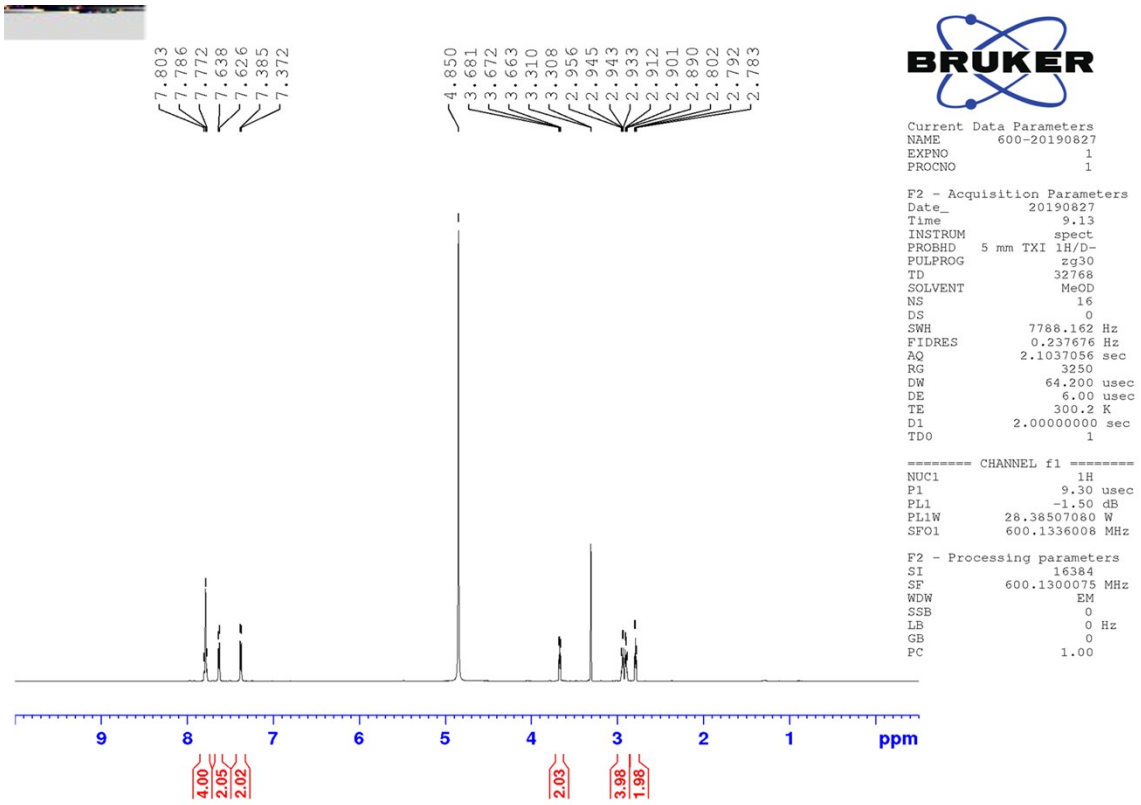

Fig. S8. [1]H NMR spectra of **2CB-NC2O** in MeOD-d_4.

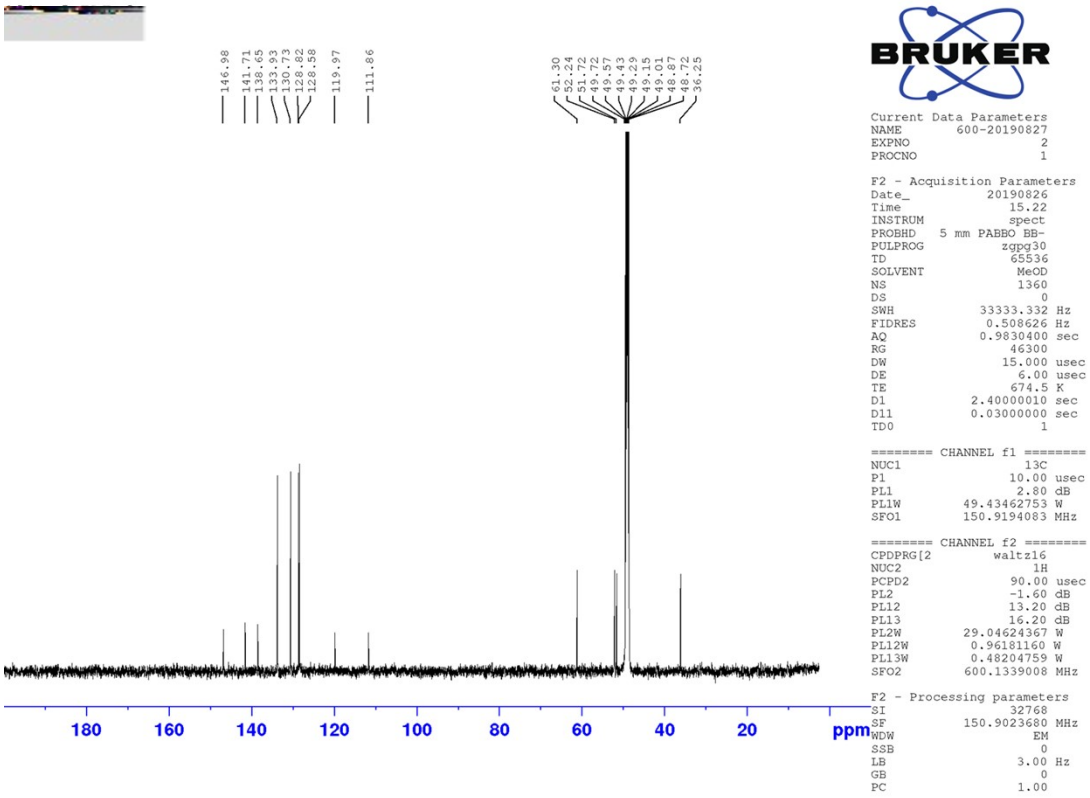

Fig. S9. [13]C NMR spectra of **2CB-NC2O** in MeOD-d_4.

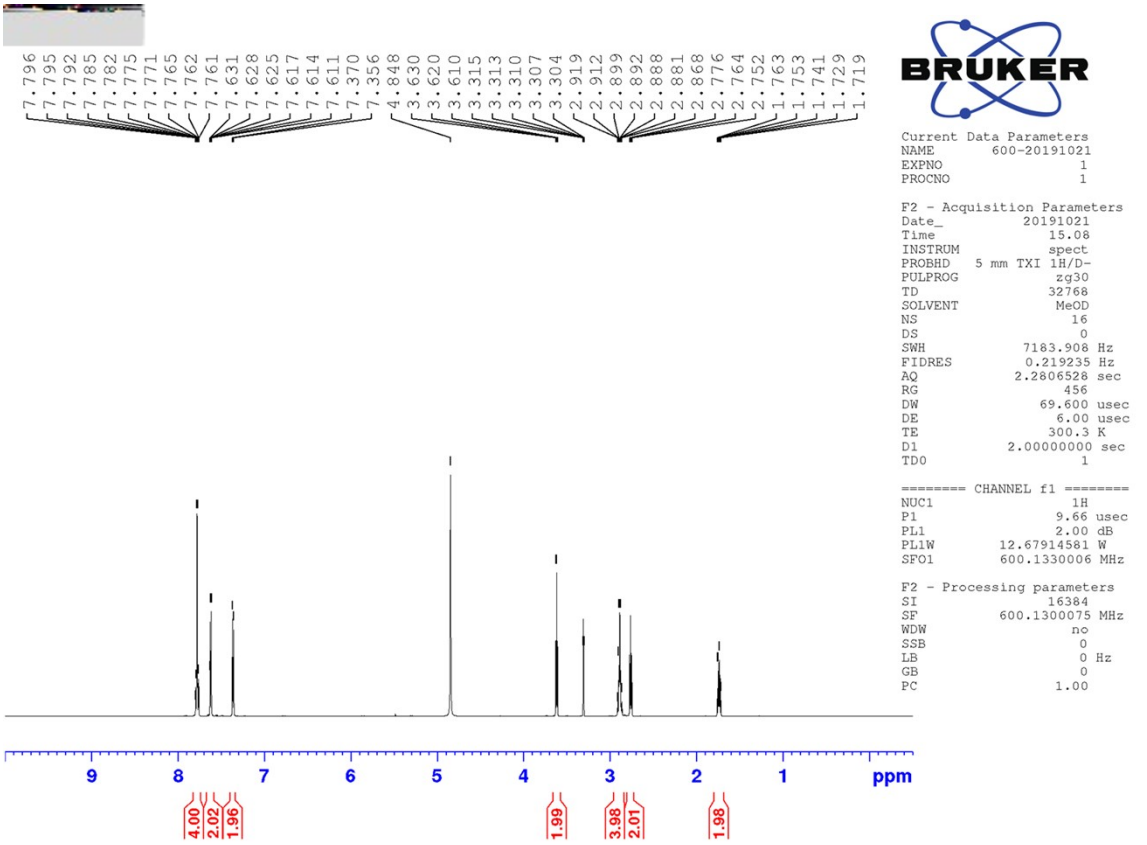

Fig. S10. [1]H NMR spectra of **2CB-NC3O** in MeOD-d_4.

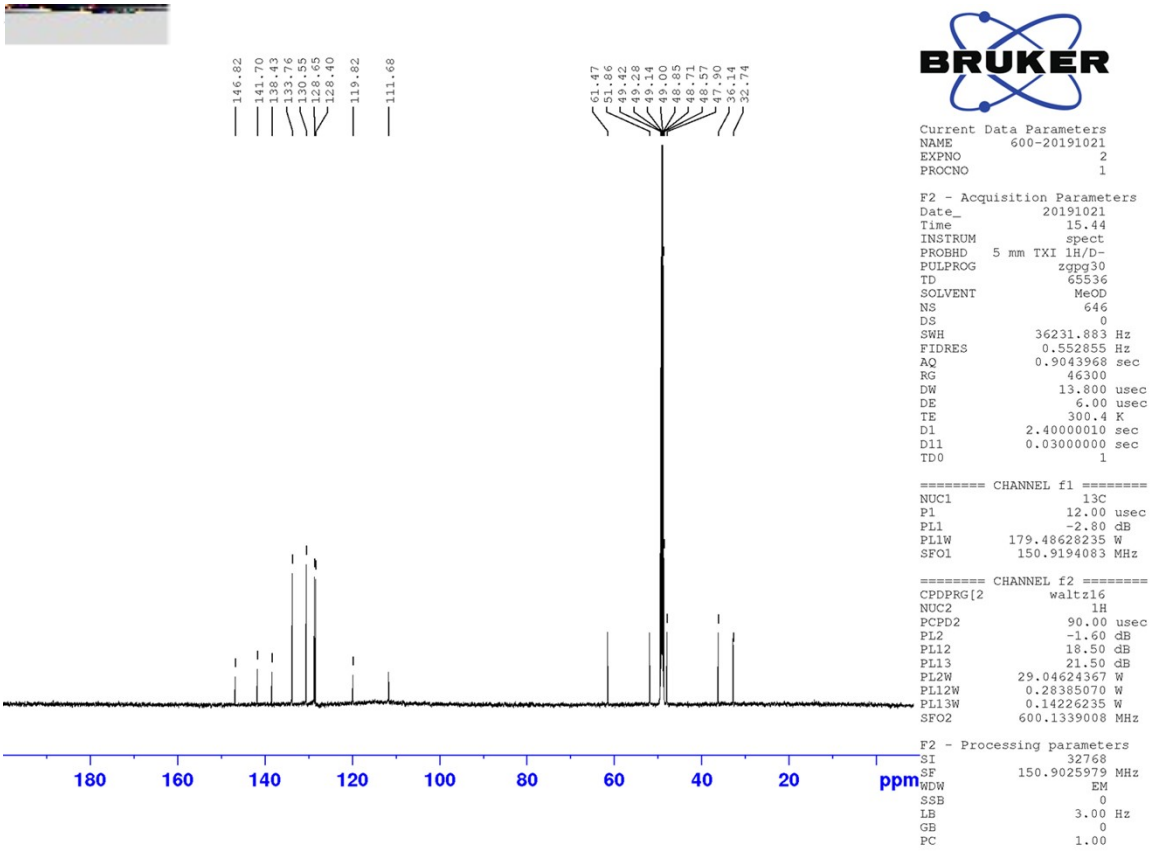

Fig. S11. [13]C NMR spectra of **2CB-NC3O** in MeOD-d_4.

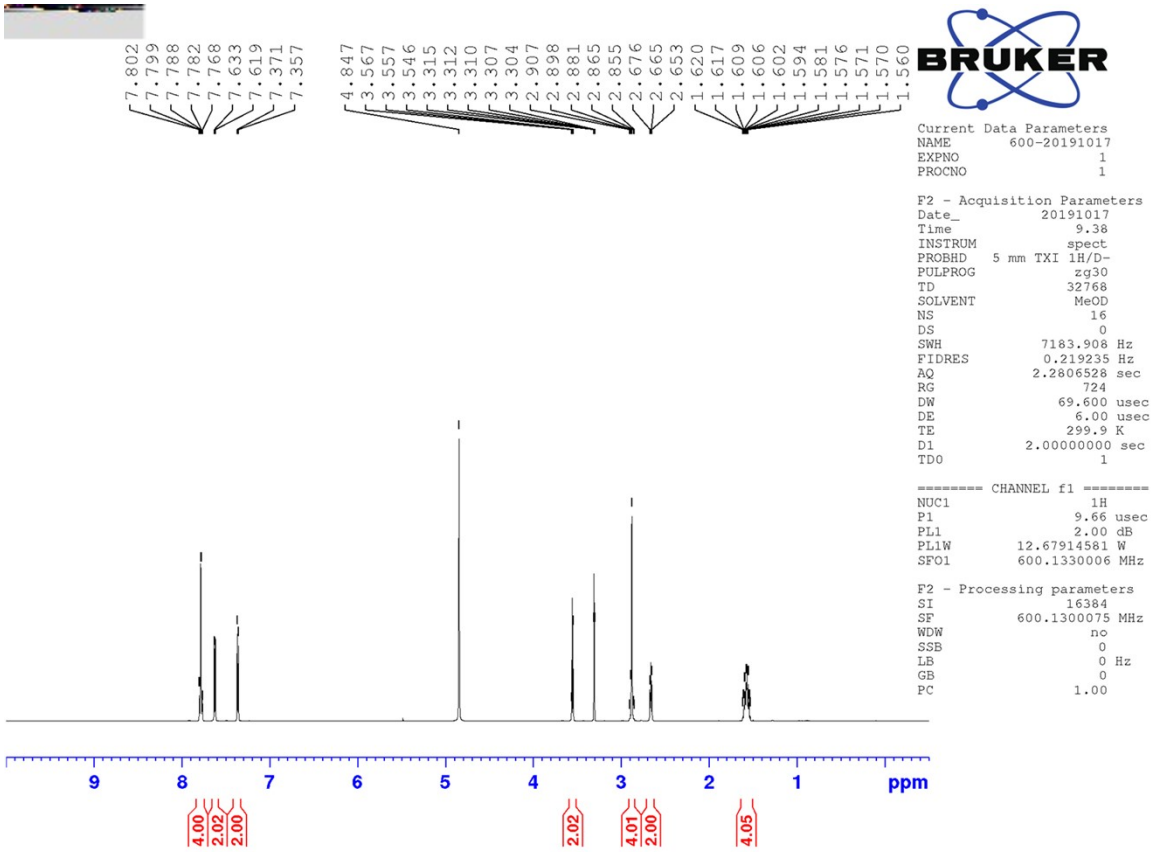

Fig. S12. [1]H NMR spectra of **2CB-NC4O** in MeOD-d_4.

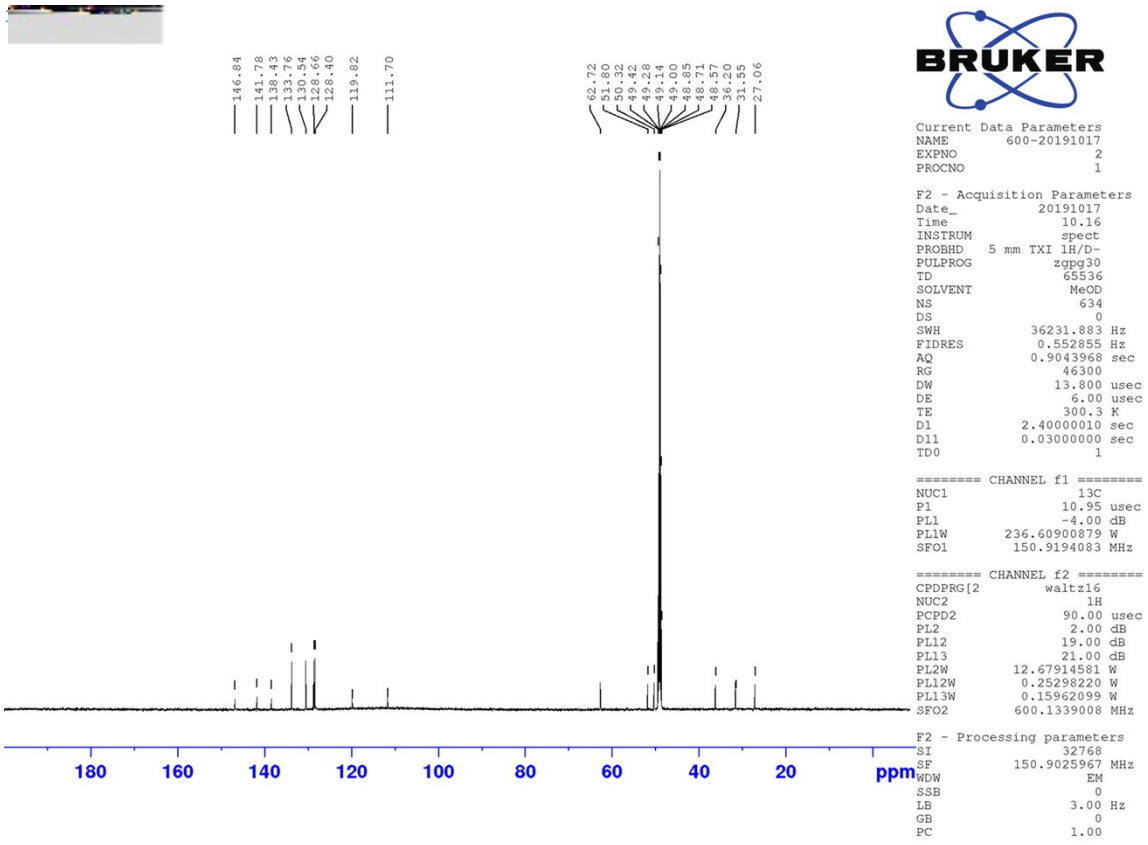

Fig. S13. [13]C NMR spectra of **2CB-NC4O** in MeOD-d_4.