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Host-Guest Interactions Manipulated Self-Assembly of Pyridinium-Tailored Naphthalene

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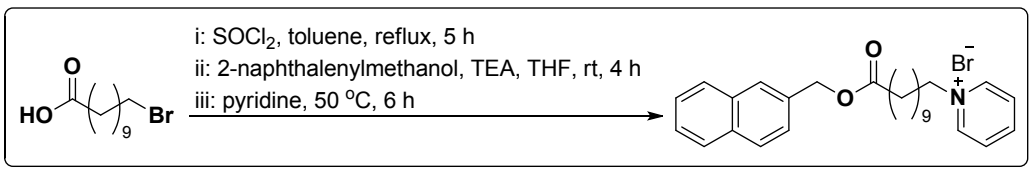
Content

Experimental Section

NMR spectra were obtained by using a Varian Mercury 300/400 apparatus; ESI-MS spectra were recorded using a Micromass QTOF apparatus; MALDI-TOF MS analysis was performed using a Bruker Ultraflex I TOF/TOF mass spectrometer; UV-Vis spectra were measured on Agilent Technologies 95-03 spectrometers; Fluorescence spectra was measured on Varian Cary Eclipse Fluorescence Spectrophotometer; SEM was performed on Variable Pressure Tescan Vega3 SBU. For sample preparation: two drops of the solution were placed on a silicon surface, air-dried, and then was coated by gold before the test. AFM was measured in air on NanoScope IIIA MultiMode AFM (Veeco). For sample preparation: a few drops of the solution were placed on a silicon surface, and then the excess solution was removed by absorption onto filter paper. Finally, the sample was air-dried before test; OM and FM observation were performed on Olympus IX81 fluorescence microscope. The samples were prepared by applying one drop of the test solution onto the glass surface and then covered by a cover slip; The X-ray powder diffraction patterns were recorded using BrukerD8 Discover diffractometer (λ = 0.15406 nm). The Bragg peaks were extracted from the XRPD data and the layer thickness *d* could be obtained according to the Bragg Equation, $d = \lambda/2\sin\theta$. The samples were prepared by placing a few drops of the solution on a silicon surface, and evaporating at room temperature.

1-(1-[11-(naphthalen-2-ylmethoxy)-11-oxoundecyl] pyridinium bromide (2-NP)



$SOCl_2$ (8 mL) was added into a solution of 11-bromoundecanoic acid (2.69 g, 10.0 mmol) in dry toluene (10 mL), and then the mixture was refluxed for 5 h. After removing all the solvents under reduced pressure, the crude was re-dissolved by dry

tetrahydrofuran (THF, 5 mL). The mixture was added dropwise into a solution of 2-naphthalenylmethanol (1.58 g, 10.0 mmol) and triethylamine (TEA, 1.5 mL) in dry THF (20 mL), and stirred at room temperature for 4 h. After that, the solvent was removed under reduced pressure, and re-dissolved by dichloromethane. The organic layer was washed by water, brine, dried with sodium sulfate, filtered, and followed by the removal of the solvent under vacuum. Finally, the crude was dissolved in pyridine (10 mL), and stirred at 50 ^{o}C for 6 h. The solvent was removed under reduced pressure, crystallized in ether, filtered, dried under vacuum to afford a white solid, **2-NP**, 3.65 g, yield 75%; MS-ESI (+) m/z: 404; HRMS (ESI): m/z calcd for $C_{27}H_{34}NO_2$: 404.2590; found: 404.2591; mp. 101-102 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6), δ 9.15 (2H, dd, J = 6.8, 1.2 Hz, pyridinium-H), 8.61 (1H, t, J = 8.0 Hz, pyridinium-H), 8.17 (2H, t, J = 7.2 Hz pyridinium-H), 7.90 (4H, m, naphthalene-H), 7.51 (3H, m, naphthalene-H), 5.24 (2H, s, OCH_2), 4.61 (2H, t, J = 7.4 Hz, NCH_2), 2.36 (2H, t, J = 7.4 Hz, CH_2CO), 1.88 (2H, m, CH_2), 1.53 (2H, m, CH_2), 1.20 (12H, m, CH_2); ^{13}C NMR (100 MHz, DMSO-d_6,) δ 172.85 (C=O), 145.47, 144.74, 128.07 (5C, pyridinium-C), 133.87, 132.68, 132.52, 127.76, 127.59, 126.68, 126.38, 126.25, 125.87 (10C, naphthalene-C), 65.40, 60.66, 33.48, 30.73, 28.72, 28.67, 28.60, 28.39, 28.33, 25.35, 24.47.

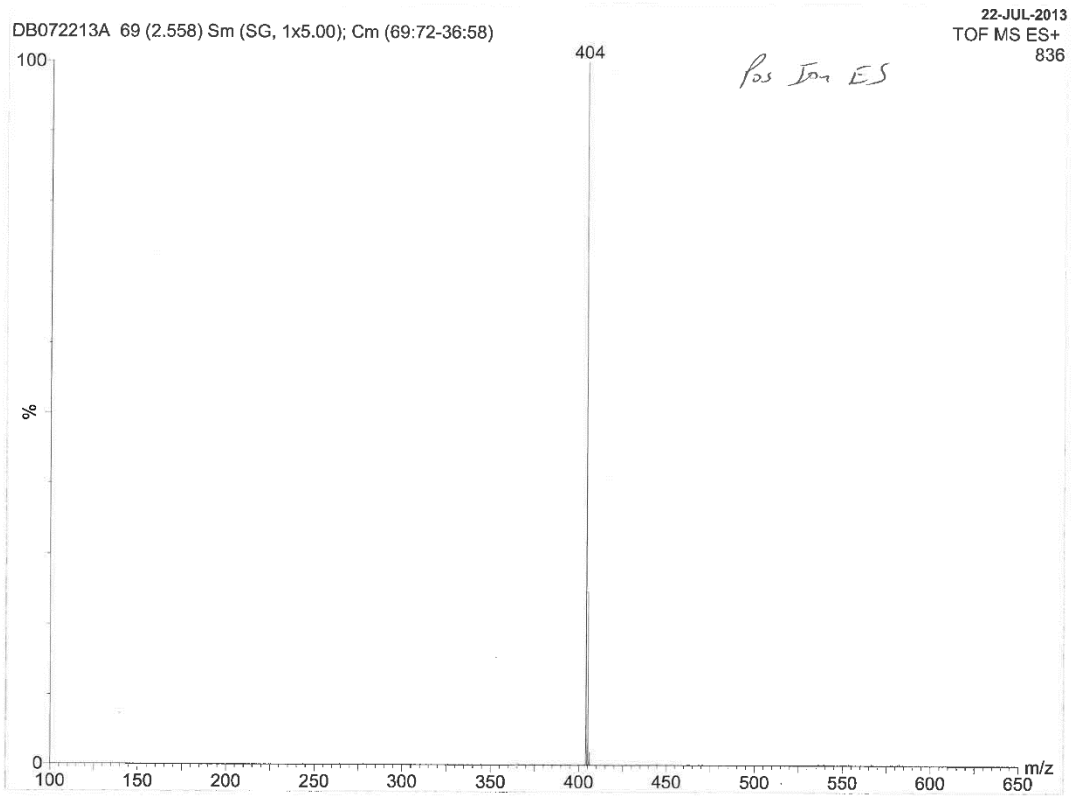


Figure S1. ESI-MS (+) Spectrum of **2-NP**

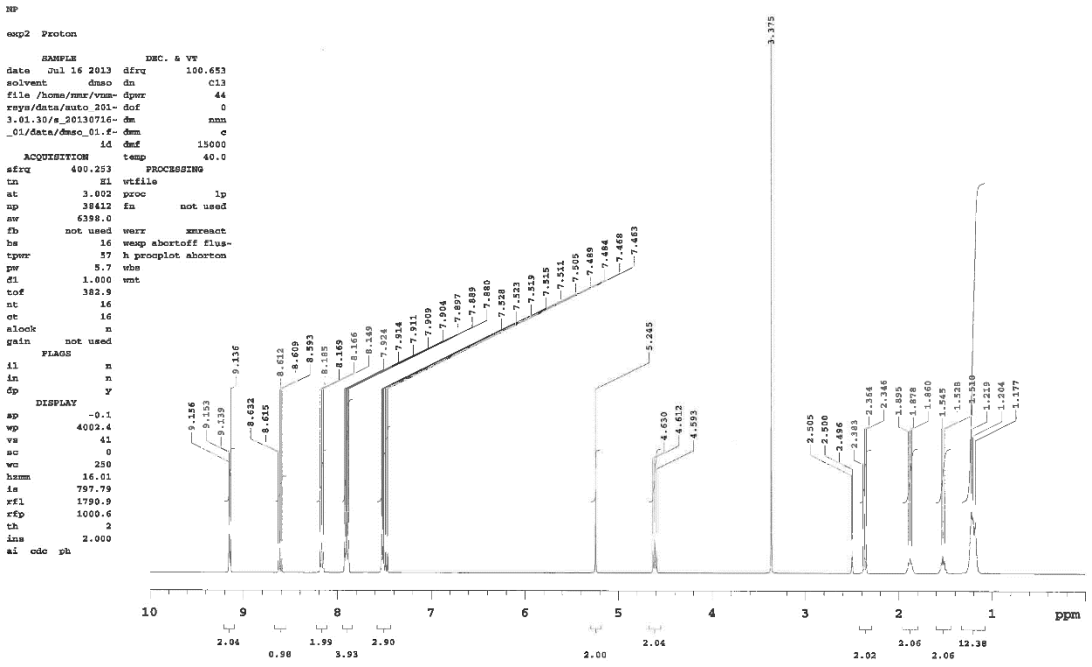


Figure S2. ^{1}H NMR Spectrum (DMSO-d_6, 400 MHz) of **2-NP**

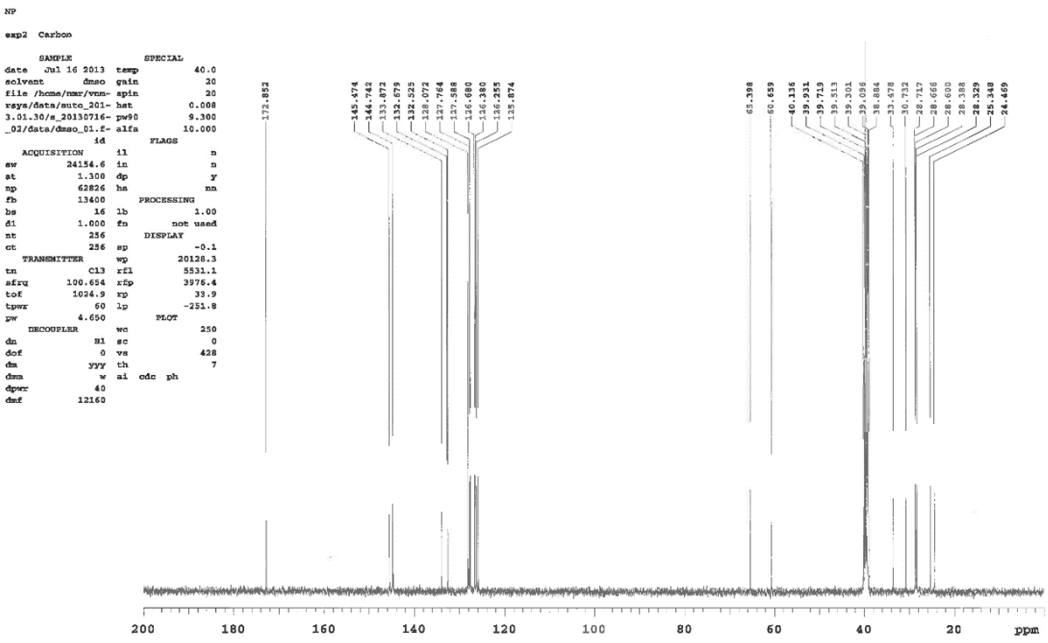


Figure S3. ^{13}C NMR Spectrum (DMSO-d_6, 100 MHz) of **2-NP**

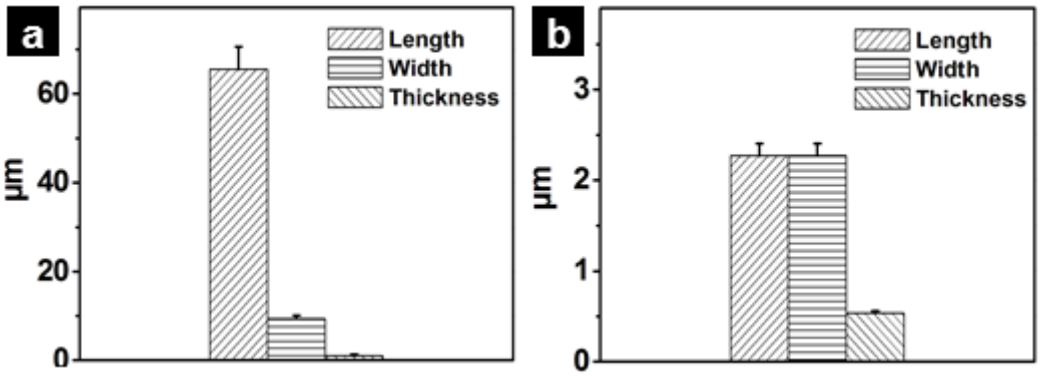


Figure S4. Statistical analysis of the final assemblies of (a) **2-NP** and (b) **2-NP/CB[8]**.

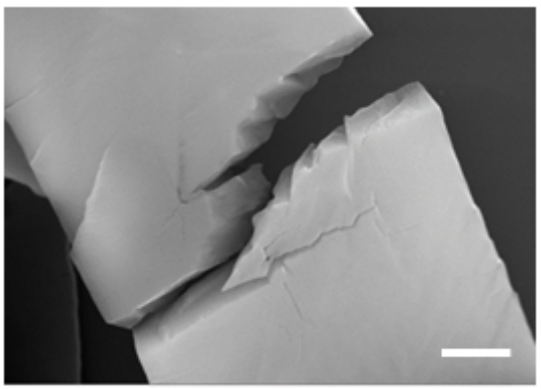


Figure S5. SEM image of the broken assembly of **2-NP** (conc. 2.5×10^{-2} M). Scale bar is 2 μm.

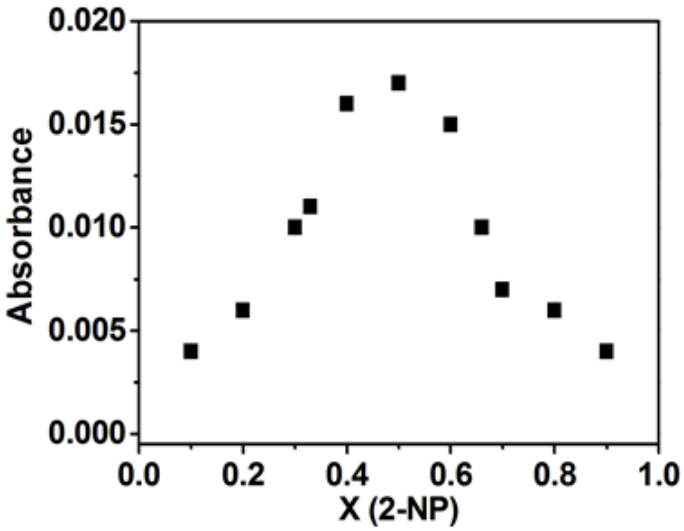


Figure S6. Job's plots of **2-NP**/**CB[8]**. The intensity of UV-Vis absorbance at 336 nm; Conc. **2-NP** = **CB[8]** = 0.1 mM, "X" is the molar ratio of the **2-NP** in the total concentration.

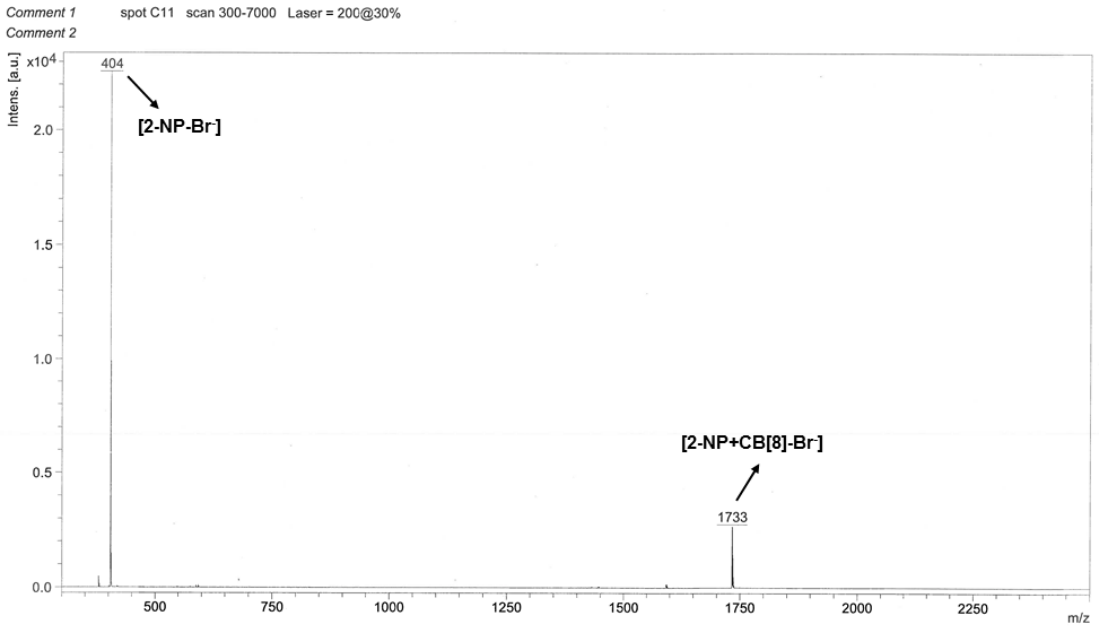


Figure S7. MALDI-TOF MS Spectrum of **2-NP/CB[8]** (molar ratio, 1:1).

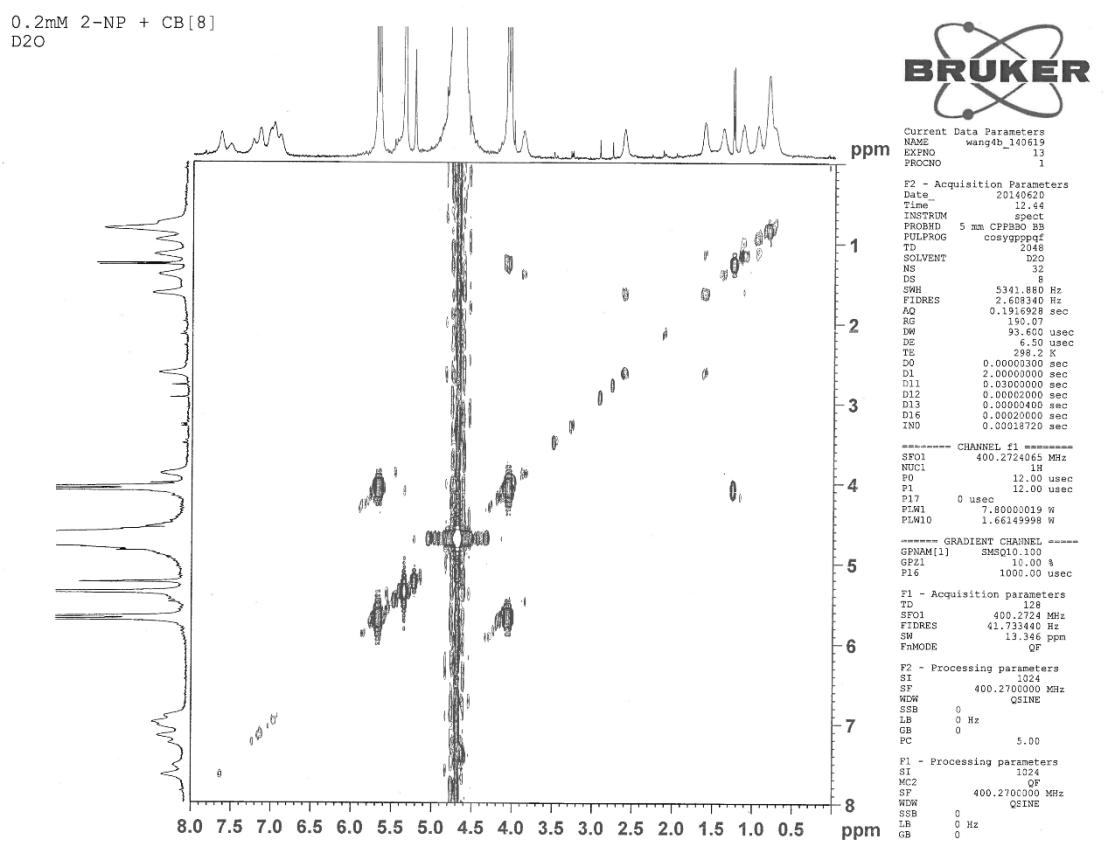


Figure S8. 2D-COSY Spectrum (D_2O, 400 MHz) of **2-NP/CB[8]** (0.2 mM, molar ratio, 1:1).

Table S1. The chemical shift of **2-NP** after added **CB[8]** (molar ratio, 1:1).

Protons	H_1	H_2	H_3	n_1, n_4, n_5, n_8	n_3	n_6, n_7	11	1	2	3-6	7	8	9	10
Before	8.71	8.00	8.49	7.96	7.58	7.58	5.37	4.47	1.85	1.16	1.16	1.16	1.64	2.47
After	7.75	7.26	7.63	7.07	7.34	7.07	5.33	3.98	1.49	0.93	1.06	1.25	1.73	2.72
Δδ (ppm)	-0.96	-0.74	-0.86	-0.89	-0.24	-0.51	-0.04	-0.49	-0.36	-0.23	-0.10	0.09	0.09	0.25

X-Ray Structure Determination, $(C_{27}H_{34}NO_2)(H_2O)(Br)$ (2-NP)

X-ray intensity data from a colorless needle crystal were collected at 100(2) K using a Bruker SMART APEX diffractometer (Mo Kα radiation, λ = 0.71073 Å).[1] The raw area detector data frames were reduced and corrected for absorption effects using the SAINT+ and SADABS programs.[1] Final unit cell parameters were determined by least-squares refinement of 9252 reflections from the data set. Direct methods structure solution, difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXS/L[2] within OLEX2.[3]

The compound crystallizes in the triclinic system. The space group *P*-1 (No. 2) was determined by structure solution. The asymmetric unit consists of one $C_{27}H_{34}NO_2^+$ cation, one bromide anion and a water molecule. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to carbon were located in difference maps before being placed in geometrically idealized positions and included as riding atoms. The water hydrogens were located in a difference map and refined isotropically with their O-H distances restrained to be similar. The largest residual electron density peak in the final difference map is 0.75 $e^-/Å^3$, located 0.92 Å from the bromine atom.

[1] SMART Version 5.630, SAINT+ Version 6.45 and SADABS Version 2.10. Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2003.

[2] Sheldrick, G.M. *Acta Cryst.* , 2008, **A64**, 112-122.

[3] Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard J. A. K. and Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.*, 2009, **42**, 339-341.

Table 1 Crystal data and structure refinement for **2-NP**

Identification code	**2-NP**
Empirical formula	$C_{27}H_{36}BrNO_3$
Formula weight	502.48
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	7.5480(11)
b/Å	8.2091(12)
c/Å	20.886(3)
α/°	92.198(3)
β/°	95.579(3)
γ/°	101.425(3)
Volume/Å^3	1260.3(3)
Z	2
ρ_{calc}mg/mm^3	1.324
μ/mm^{-1}	1.658
F(000)	528.0
Crystal size/mm^3	0.54 × 0.22 × 0.05
2Θ range for data collection	3.92 to 55.58°
Index ranges	$-9 \le h \le 9$, $-10 \le k \le 10$, $-27 \le l \le 27$
Reflections collected	22971
Independent reflections	5920[R(int) = 0.0319]
Data/restraints/parameters	5920/1/297
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0314, wR_2 = 0.0778

Final R indexes [all data]	$R_1 = 0.0360$, $wR_2 = 0.0800$
Largest diff. peak/hole / e Å^{-3}	0.75/-0.27

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^3$) for **2-NP**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Br1	5391.8(2)	3072.68(19)	980.89(8)	22.46(7)
O3	2864(2)	5650.1(17)	351.7(7)	28.8(3)
O1	6184.0(17)	4120.9(14)	5546.4(6)	23.8(3)
O2	7267.3(16)	3731.2(14)	4601.5(6)	20.0(2)
N1	10009.2(19)	19129.2(16)	8985.3(6)	18.4(3)
C1	7122(2)	4654.7(19)	5136.9(8)	17.6(3)
C2	8213(2)	6401.2(19)	5140.1(8)	19.3(3)
C3	8572(2)	7273.5(19)	5814.2(8)	20.1(3)
C4	9043(2)	9168.0(19)	5818.2(8)	19.5(3)
C5	9202(2)	9974.1(19)	6499.5(8)	19.9(3)
C6	9431(2)	11862.8(19)	6527.0(8)	20.6(3)
C7	9487(2)	12579.4(19)	7214.5(8)	20.1(3)
C8	9643(2)	14467(2)	7273.7(8)	21.0(3)
C9	9674(2)	15078.0(19)	7974.6(8)	21.1(3)
C10	9783(2)	16945(2)	8086.7(8)	21.5(3)
C11	9722(2)	17318.5(19)	8801.1(8)	21.4(3)
C12	8659(2)	19943(2)	8828.6(8)	21.7(3)
C13	8841(3)	21595(2)	9022.9(8)	24.1(4)
C14	10438(3)	22415(2)	9379.1(8)	24.4(4)

C15	11818(3)	21565(2)	9525.6(9)	25.7(4)
C16	11576(2)	19910(2)	9324.6(8)	22.2(3)
C17	6140(2)	2075.8(19)	4549.5(8)	19.3(3)
C18	6056(2)	1317.8(19)	3878.3(8)	17.4(3)
C19	5857(2)	-376.2(19)	3785.0(8)	17.6(3)
C20	5691(2)	-1149.8(19)	3156.4(8)	16.9(3)
C21	5491(2)	-2904.3(19)	3050.3(8)	20.0(3)
C22	5395(2)	-3600(2)	2438.8(8)	22.2(3)
C23	5469(2)	-2597(2)	1904.2(8)	22.3(3)
C24	5624(2)	-909(2)	1990.5(8)	20.6(3)
C25	5731(2)	-143.9(19)	2620.8(8)	17.2(3)
C26	5901(2)	1604.2(19)	2728.5(8)	19.7(3)
C27	6059(2)	2314.3(19)	3339.6(8)	19.4(3)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **2-NP**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka\times b\times U_{12}]$

Atom	$\mathbf{U_{11}}$	$\mathbf{U_{22}}$	$\mathbf{U_{33}}$	$\mathbf{U_{23}}$	$\mathbf{U_{13}}$	$\mathbf{U_{12}}$
Br1	22.38(10)	24.56(9)	21.63(10)	4.79(6)	1.35(6)	7.48(7)
O3	32.9(8)	30.4(7)	28.3(7)	7.6(6)	9.4(6)	15.0(6)
O1	28.9(7)	23.2(6)	18.1(6)	-0.6(5)	4.5(5)	1.9(5)
O2	19.5(6)	17.8(5)	21.7(6)	-4.0(4)	4.9(5)	1.5(4)
N1	20.6(7)	17.3(6)	17.9(7)	-0.1(5)	5.0(5)	3.9(5)
C1	18.2(8)	18.8(7)	16.9(8)	-0.7(6)	-0.7(6)	7.9(6)
C2	19.5(8)	18.8(7)	19.8(8)	-0.8(6)	3.2(6)	4.3(6)
C3	23.1(8)	18.5(7)	18.2(8)	-0.3(6)	0.2(6)	4.1(6)
C4	20.4(8)	19.0(7)	18.1(8)	-1.2(6)	0.0(6)	3.1(6)
C5	22.3(8)	18.5(7)	17.9(8)	-0.5(6)	0.8(6)	2.5(6)
C6	21.9(8)	18.3(7)	20.5(8)	-0.9(6)	0.8(6)	2.2(6)

C7	21.9(8)	17.3(7)	19.7(8)	-1.2(6)	1.7(6)	1.2(6)
C8	22.6(9)	17.9(7)	21.3(8)	-1.2(6)	2.2(7)	1.5(6)
C9	23.7(9)	17.3(7)	21.5(8)	-0.2(6)	2.6(7)	2.3(6)
C10	24.1(9)	17.6(7)	22.5(8)	-0.2(6)	4.0(7)	3.0(6)
C11	25.3(9)	14.9(7)	24.4(8)	0.5(6)	5.1(7)	4.4(6)
C12	20.1(8)	22.8(8)	21.8(8)	2.0(6)	1.4(6)	3.8(6)
C13	26.0(9)	22.8(8)	25.6(9)	2.8(7)	2.6(7)	9.8(7)
C14	33.1(10)	19.6(8)	20.2(8)	-1.1(6)	4.4(7)	4.5(7)
C15	24.9(9)	27.1(9)	22.9(9)	-3.1(7)	0.2(7)	2.5(7)
C16	20.2(8)	26.7(8)	20.3(8)	-0.5(6)	2.2(6)	6.9(7)
C17	21.6(8)	15.7(7)	19.9(8)	-0.6(6)	3.0(6)	2.0(6)
C18	14.3(7)	19.3(7)	18.7(8)	0.2(6)	1.5(6)	4.0(6)
C19	16.4(8)	19.3(7)	17.8(8)	3.7(6)	2.3(6)	4.4(6)
C20	13.3(7)	17.4(7)	19.8(8)	0.6(6)	0.9(6)	3.2(6)
C21	21.1(8)	17.2(7)	22.3(8)	3.5(6)	3.2(6)	4.8(6)
C22	22.2(9)	17.6(7)	26.2(9)	-2.1(6)	0.6(7)	4.4(6)
C23	21.1(8)	25.8(8)	18.8(8)	-4.8(6)	-0.6(6)	4.5(7)
C24	19.8(8)	23.7(8)	18.5(8)	2.8(6)	1.3(6)	4.8(6)
C25	13.0(7)	19.1(7)	19.1(8)	-0.4(6)	1.6(6)	2.7(6)
C26	20.2(8)	18.6(7)	20.6(8)	4.7(6)	1.4(6)	4.1(6)
C27	19.7(8)	14.7(7)	23.7(8)	0.9(6)	2.9(6)	3.1(6)

Table 4 Bond Lengths for **2-NP**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
O1	C1	1.204(2)	C12	C13	1.377(2)
O2	C1	1.3524(19)	C13	C14	1.388(3)
O2	C17	1.4475(19)	C14	C15	1.381(3)
N1	C11	1.4889(19)	C15	C16	1.378(2)
N1	C12	1.347(2)	C17	C18	1.502(2)

N1	C16	1.347(2)	C18	C19	1.373(2)
C1	C2	1.505(2)	C18	C27	1.416(2)
C2	C3	1.530(2)	C19	C20	1.420(2)
C3	C4	1.525(2)	C20	C21	1.424(2)
C4	C5	1.530(2)	C20	C25	1.415(2)
C5	C6	1.524(2)	C21	C22	1.368(2)
C6	C7	1.524(2)	C22	C23	1.411(2)
C7	C8	1.530(2)	C23	C24	1.371(2)
C8	C9	1.526(2)	C24	C25	1.425(2)
C9	C10	1.526(2)	C25	C26	1.422(2)
C10	C11	1.519(2)	C26	C27	1.367(2)

Table 5 Bond Angles for **2-NP**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C1	O2	C17	114.36(12)	C16	C15	C14	119.50(16)
C12	N1	C11	118.97(14)	N1	C16	C15	120.24(16)
C16	N1	C11	119.81(14)	O2	C17	C18	109.82(13)
C16	N1	C12	121.17(14)	C19	C18	C17	119.34(15)
O1	C1	O2	122.67(14)	C19	C18	C27	119.73(14)
O1	C1	C2	125.36(14)	C27	C18	C17	120.80(14)
O2	C1	C2	111.95(14)	C18	C19	C20	121.14(15)
C1	C2	C3	112.34(14)	C19	C20	C21	121.94(15)
C4	C3	C2	114.17(14)	C25	C20	C19	118.85(14)
C3	C4	C5	111.79(14)	C25	C20	C21	119.20(14)
C6	C5	C4	114.27(14)	C22	C21	C20	120.27(16)
C5	C6	C7	111.67(14)	C21	C22	C23	120.69(15)
C6	C7	C8	114.37(14)	C24	C23	C22	120.32(15)
C9	C8	C7	110.98(14)	C23	C24	C25	120.45(16)
C8	C9	C10	115.30(14)	C20	C25	C24	119.04(14)

C11	C10	C9	108.19(14)	C20	C25	C26	119.00(14)
N1	C11	C10	113.49(14)	C26	C25	C24	121.96(15)
N1	C12	C13	120.45(16)	C27	C26	C25	120.82(15)
C12	C13	C14	119.20(16)	C26	C27	C18	120.43(14)
C15	C14	C13	119.42(16)				

Table 6 Hydrogen Bonds for **2-NP**.

D	**H**	**A**	**d(D-H)/Å**	**d(H-A)/Å**	**d(D-A)/Å**	**D-H-A/°**
O3	H3WA	Br1	0.759(18)	2.584(19)	3.3419(15)	176(2)
O3	H3WB	Br1[1]	0.776(18)	2.536(18)	3.3118(15)	177(2)

[1]1-X,1-Y,-Z

Table 7 Torsion Angles for **2-NP**.

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
O1	C1	C2	C3	20.4(2)	C16	N1	C12	C13	-1.1(3)
O2	C1	C2	C3	-161.42(13)	C17	O2	C1	O1	2.6(2)
O2	C17	C18	C19	149.24(14)	C17	O2	C1	C2	-175.67(13)
O2	C17	C18	C27	-35.0(2)	C17	C18	C19	C20	177.20(14)
N1	C12	C13	C14	0.4(3)	C17	C18	C27	C26	-177.08(15)
C1	O2	C17	C18	166.50(13)	C18	C19	C20	C21	179.71(15)
C1	C2	C3	C4	-159.15(14)	C18	C19	C20	C25	-0.1(2)
C2	C3	C4	C5	174.34(14)	C19	C18	C27	C26	-1.3(2)
C3	C4	C5	C6	-172.60(14)	C19	C20	C21	C22	-177.86(16)
C4	C5	C6	C7	177.19(14)	C19	C20	C25	C24	178.02(14)
C5	C6	C7	C8	-177.81(14)	C19	C20	C25	C26	-1.2(2)
C6	C7	C8	C9	179.51(14)	C20	C21	C22	C23	-0.8(3)
C7	C8	C9	C10	-178.65(14)	C20	C25	C26	C27	1.2(2)
C8	C9	C10	C11	177.70(15)	C21	C20	C25	C24	-1.8(2)
C9	C10	C11	N1	174.09(14)	C21	C20	C25	C26	178.99(15)

C11	N1	C12	C13	176.36(16)	C21	C22	C23	C24	-0.5(3)
C11	N1	C16	C15	-176.70(16)	C22	C23	C24	C25	0.6(3)
C12	N1	C11	C10	74.04(19)	C23	C24	C25	C20	0.6(2)
C12	N1	C16	C15	0.8(3)	C23	C24	C25	C26	179.69(16)
C12	C13	C14	C15	0.7(3)	C24	C25	C26	C27	-177.92(15)
C13	C14	C15	C16	-1.0(3)	C25	C20	C21	C22	2.0(2)
C14	C15	C16	N1	0.3(3)	C25	C26	C27	C18	0.0(2)
C16	N1	C11	C10	-108.45(18)	C27	C18	C19	C20	1.4(2)

Table 8 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **2-NP**.

Atom	***x***	***y***	***z***	**U(eq)**
H3WA	3470(30)	5100(30)	502(12)	41(7)
H3WB	3310(30)	5950(30)	46(10)	35(7)
H2A	7549	7053	4848	23
H2B	9389	6368	4973	23
H3A	7479	6941	6043	24
H3B	9586	6883	6057	24
H4A	8089	9563	5543	23
H4B	10209	9516	5633	23
H5A	8098	9498	6703	24
H5B	10256	9683	6756	24
H6A	8408	12168	6257	25
H6B	10571	12355	6348	25
H7A	10535	12295	7478	24
H7B	8369	12039	7396	24
H8A	10771	15023	7102	25
H8B	8599	14767	7014	25
H9A	10730	14777	8227	25

H9B	8562	14478	8144	25
H10A	10927	17573	7948	26
H10B	8750	17281	7834	26
H11A	8527	16757	8923	26
H11B	10669	16847	9048	26
H12	7573	19373	8582	26
H13	7885	22166	8914	29
H14	10581	23552	9521	29
H15	12926	22117	9763	31
H16	12518	19317	9426	27
H17A	4899	2135	4651	23
H17B	6651	1371	4863	23
H19	5828	-1042	4147	21
H21	5424	-3594	3406	24
H22	5278	-4769	2373	27
H23	5411	-3094	1482	27
H24	5660	-245	1628	25
H26	5905	2287	2371	24
H27	6172	3484	3403	23

Crystal Data for $C_{27}H_{36}BrNO_3$ (M =502.48): triclinic, space group P-1 (no. 2), a = 7.5480(11) Å, b = 8.2091(12) Å, c = 20.886(3) Å, α = 92.198(3)°, β = 95.579(3)°, γ = 101.425(3)°, V = 1260.3(3) Å^3, Z = 2, T = 100(2) K, μ(MoKα) = 1.658 mm^{-1}, *Dcalc* = 1.324 g/mm^3, 22971 reflections measured ($3.92 \leq 2\Theta \leq 55.58$), 5920 unique ($R_{int}$ = 0.0319) which were used in all calculations. The final R_1 was 0.0314 (>2sigma(I)) and wR_2 was 0.0800 (all data).