Electronic Supporting Information for

Synthesis and anion binding studies of *o*-phenylenevinylene-bridged tetrapyrrolic macrocycle as an expanded analogue of calix[4]pyrrole†

Sudip Kumar Ghosh,[a] Masatoshi Ishida,[a,b] Jiazhu Li,[a] Won-Young Cha,[a] Vincent M. Lynch,[c] Dongho Kim,*[a] and Jonathan L. Sessler*[a,c]

[a] *Department of Chemistry, Yonsei University, Seoul 120-749, Korea*
[b] *Education Center for Global Leaders in Molecular Systems for Devices, Kyushu University, Fukuoka, 819-0395, Japan*
[c] *Department of Chemistry, 105 E. 24th Street-Stop A5300, The University of Texas at Austin, Austin, Texas 78712-1224, United States.*

*E-mail addresses: sessler@cm.utexas.edu (J.L.S); dongho@yonsei.ac.kr (D.K)

Table of Contents

I. General Experimental Section

II. Synthesis

III. Supporting Tables and Figures

IV. X-ray Experimental

V. References

General Experimental Section

Instruments and Materials

^{1}H NMR (400 MHz) spectra were recorded on a Bruker Advance II spectrometer. Chemical shifts (δ-scale) are reported in parts per million (ppm) relative to residual solvent and internal standard signals (chloroform-*d*: 7.24 ppm, tetrahydrofuran-d_8: 3.58, 1.73 ppm, dimethyl sulfoxide-d_6: 2.50 ppm, CD_2Cl_2: 5.32 ppm). Peak multiplicities are abbreviated as: s, singlet; brs, broad singlet; d, doublet; t, triplet; m, multiplet. Proton decoupled ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Advance II spectrometer using TMS as the internal standard. ^{19}F NMR (282 MHz) spectra were recorded on a JEOL JNM-AL300 spectrometer ($CFCl_3$: 0.0 ppm). MALDI-TOF mass spectra were recorded on a BRUKER microflex 2 LRF20 spectrometer using dithranol (1,8,9-trihydroxyantharacene) as the matrix. High-resolution mass spectra (HR-MS) were recorded on a JEOL JMS-700 FAB mass spectrometer with *m*-nitrobenzyl alcohol (NBA) as the matrix. Steady-state absorption spectra were acquired using a UV-vis-NIR spectrometer (Varian, Cary 5000). The absolution florescence quantum yield was recorded on Hamamatsu C9920-02G with an integration sphere. Pyrrole was distilled under normal atmospheric pressure from CaH_2. All other chemicals and solvents were purchased from commercial sources and were used as such, unless otherwise mentioned. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel 60 pre-coated on glass plates. Column chromatography was carried out using silica gel 60 (200 mesh, Merck). Preparative HPLC (GPC) analyses were performed on a JAI LC-908 instrument using JAIJEL-1H and -2H columns. Preparative TLC was performed on Merck silica gel 60 (thickness: 1 mm) pre-coated on glass plates. All titrations (UV-vis and fluorescence) were performed using HPLC grade solvents purchased from Aldrich. Tetraethyl(1,2-phenylenebis(methylene))bis(phosphonate)[1] and 1-((2-(trimethylsilyl)ethoxy)methyl)-1H-pyrrole-2,5-dicarbaldehyde[2] were synthesized using previously reported procedures.

DFT calculations

Theoretical calculations were performed using the Gaussian 09 program suite.[3] All calculations were carried out by the density functional theory (DFT) method with Becke's three-parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP)[4] with a basis set of 6-31G* was employed for all atoms.

Syntheses

Synthesis of macrocycles, **3a-c**

In a suspension of sodium hydride (240 mg, 10 mmol) in anhydrous tetrahydrofuran (300 mL) was

added a solution of tetraethyl(1,2-phenylenebis(methylene))bis(phosphonate) (757.6 mg, 2 mmol) in tetrahydrofuran (100 mL); this was followed by the addition of a solution of 1-((2-(trimethylsilyl)ethoxy)methyl)-1H-pyrrole-2,5-dicarbaldehyde (507.1 mg, 2 mmol) in tetrahydrofuran (100 mL). The mixture was cautiously heated on oil-bath at 50°C until the evolution of hydrogen ceased. Then, the mixture was heated at reflux for 36 h under nitrogen. After this time, the reaction mixture was concentrated under reduced pressure and water (300 mL) was added. The crude products from the mixture were extracted into dichloromethane (3×200 mL). The organic phases were combined, washed with water, and dried over anhydrous Na_2SO_4. The volatiles were evaporated off using a rotary evaporator to afford a brown oil. Purification was effected by silica gel column chromatography followed by preparative TLC (silica gel, hexane/ethyl acetate (4:1)). After evaporation of the eluent, the first fraction provided trimer **3a** as a yellow solid (65 mg, 10%), while the second gave tetramer **3b** as an orange solid (116 mg, 18%). The pentamer, **3c**, was obtained as a yellow solid from the third fraction, albeit only in small quantities. This latter product proved to be unstable under normal laboratory conditions and was thus only characterized by mass spectrometry.

3a: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.46 (m, 6H, *o*-phenyl), 7.27 (m, 6H, *o*-phenyl), 7.19 (d, J = 16.0 Hz, 6H, *trans*-alkene-H), 6.89 (d, J = 16.0 Hz, 6H, *trans*-alkene-H), 6.49 (brs, 6H, pyrrole-H), 5.30 (s, 6H, N-$\underline{CH_2}$-O), 3.47 (t, J = 8.0 Hz, 6H, O-$\underline{CH_2}CH_2$-Si), 0.77 (t, J = 8.0 Hz, 6H, O-$CH_2\underline{CH_2}$-Si), -0.13 (s, 27H, Si($\underline{CH_3}$)$_3$); UV-vis (THF) λ_{max} [nm] (ε): 376 (8.5 x 10^4); MALDI-TOF MS calcd. for $C_{60}H_{75}N_3O_3Si_3$ 969.51; found 970.44 $[M+H]^+$, HR-MS calcd. for $C_{60}H_{75}N_3O_3Si_3$ 969.5116; found 969.5118.

3b: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.57 (dd, J = 5.4, 3.5 Hz, 8H, *o*-phenyl), 7.36 (d, J = 15.7 Hz, 8H, *trans*-alkene-H), 7.27 (dd, J = 6.0, 2.7 Hz, 8H, *o*-phenyl), 7.00 (d, J = 15.6 Hz, 8H, *trans*-alkene-H), 6.65 (brs, 8H, pyrrole-H), 5.43 (s, 8H, N-$\underline{CH_2}$-O), 3.66 (t, J = 8.0 Hz, 8H, O-$\underline{CH_2}CH_2$-Si), 0.99 (t, J = 8.0 Hz, 8H, O-$CH_2\underline{CH_2}$-Si), 0.02 (s, 36H, Si($\underline{CH_3}$)$_3$); UV-vis (THF) λ_{max}[nm](ε): 395 (8.6 x 10^4); MALDI-TOF MS calcd. for $C_{80}H_{100}N_4O_4Si_4$ 1292.68; found 1294.93 $[M+2H]^+$, HR-MS; calcd. for $C_{80}H_{100}N_4O_4Si_4$ 1292.6822; found 1292.6813.

3c: MALDI-TOF MS calcd. for $C_{100}H_{125}N_5O_5Si_5$ 1615.85; found 1618.28 $[M+2H]^+$, HR-MS calcd. for $C_{100}H_{125}N_5O_5Si_5$ 1615.8527; found 1616.8553 $[M+H]^+$.

Synthesis of **2**

To a solution of 650 mg of **3b** (0.502 mmol, 1.0 equiv.) in 20 mL of tetrahydrofuran was added 12.1 mL of 1M TBAF solution in tetrahydrofuran (12.1 mmol, 24 equiv.) and 0.4 mL of ethylenediamine (6.05 mmol, 12 equiv.). The mixture was heated at 50 °C under N_2 for 72 h. The reaction mixture was cooled

and diluted with 200 mL of water. The resulting material was extracted into dichloromethane (3 × 200 mL). The organic phases were combined, washed with water and dried over Na_2SO_4 and finally evaporated in a rotary evaporator to afford a brown solid. The crude solid obtained in this way was recrystallized from tetrahydrofuran and acetonitrile. Further purification was effected by chromatography on preparative TLC plates eluting using hexanes / ethyl acetate (4:1) as the eluent. Yield: 295 mg (75%). ^{1}H NMR (400 MHz, THF-d_8) δ (ppm) 10.66 (s, 4H, NH), 7.54 (d, J = 3.2 Hz, 8H, *o*-phenyl), 7.23 (d, J = 16.2 Hz, 8H, *trans*-alkene-H), 7.16 – 7.15 (m, 8H, *m*-phenyl), 6.91 (d, J = 16.1 Hz, 8H, *trans*-alkene-H), 6.25 (d, J = 2.2 Hz, 8H, pyrrole-H); ^{13}C NMR (100 MHz, THF-d_8) δ (ppm) 136.57, 134.49, 127.79, 125.41, 121.79, 121.53, 112.79. UV-vis (THF) λ_{max}[nm](ε): 366 (7.6 x 10^4), 400 (6.1 x 10^4), 414 (6.2 x 10^4); MALDI-TOF MS calcd. for $C_{56}H_{44}N_4$ 772.36; found 773.95 $[M+H]^+$, HR-MS calcd. for $C_{56}H_{44}N_4$ 772.3566; found 772.

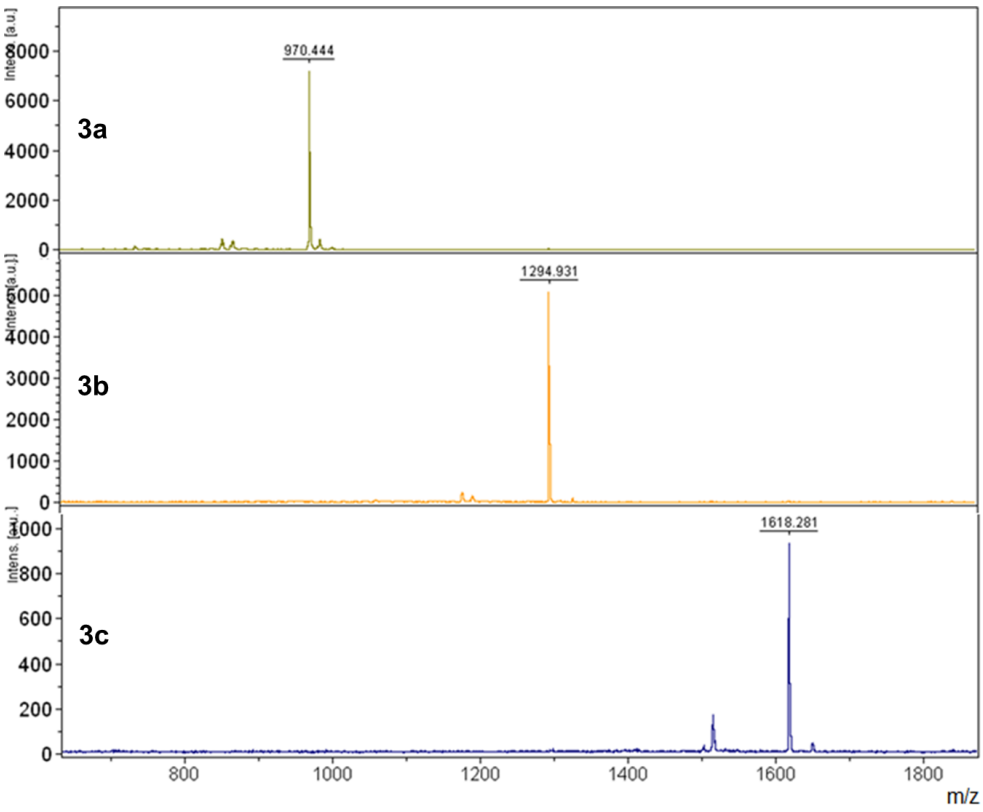

Fig. S1 MALDI-TOF mass spectra of **3a-c**.

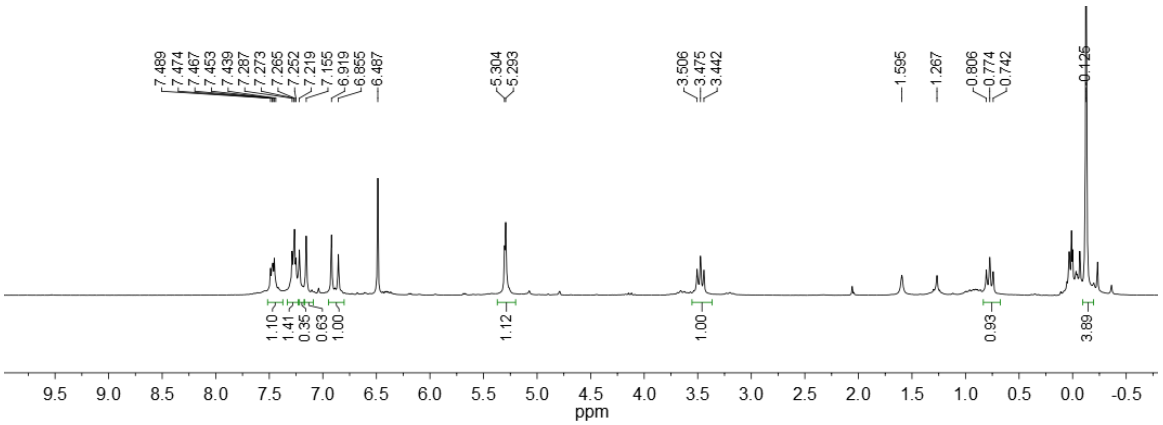

Fig. S2 ^{1}H NMR spectrum (400 MHz) of **3a** in $CDCl_3$ at 298 K.

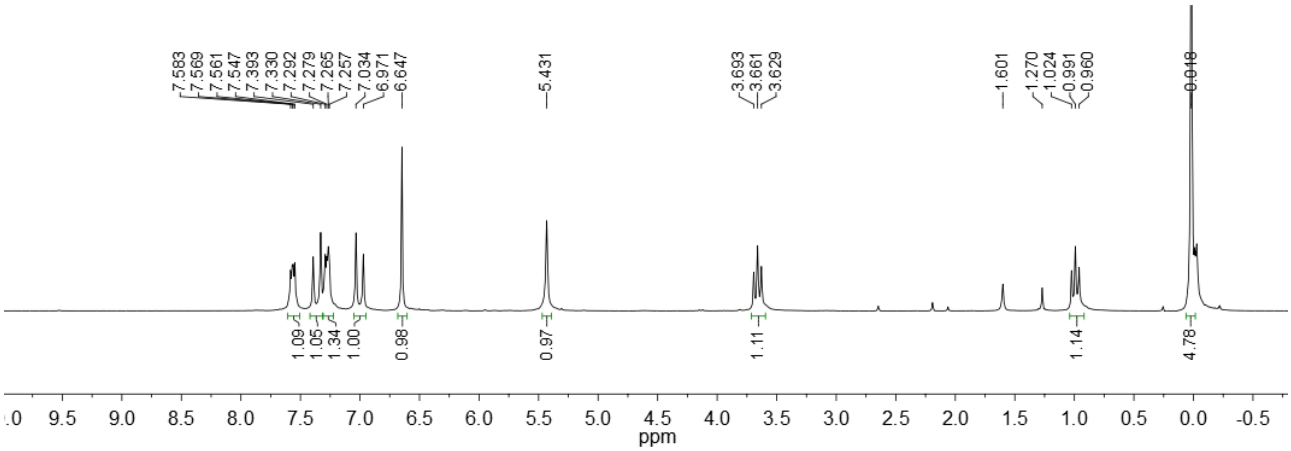

Fig. S3 ^{1}H NMR spectrum (400 MHz) of **3b** in $CDCl_3$ at 298 K.

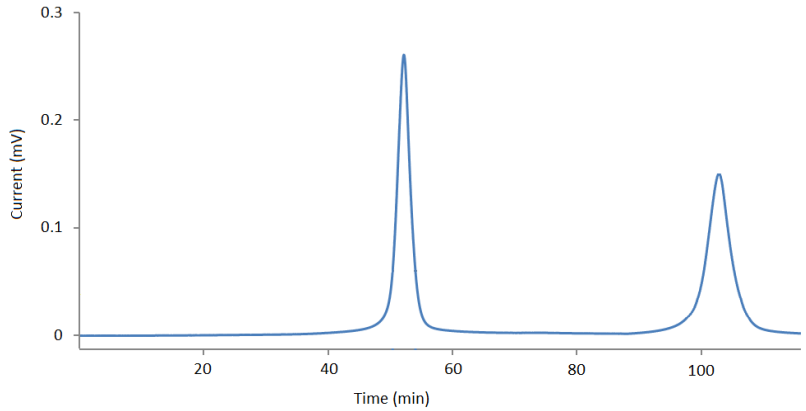

Fig. S4 HPLC trace of **2** ($CHCl_3$ used as mobile phase). Note that the chromatogram shown is the product of two cycles through a recycling instrument. Noteworthy is the absence of any detectable signals between the two peaks corresponding to the two passes of **2** through the instrument.

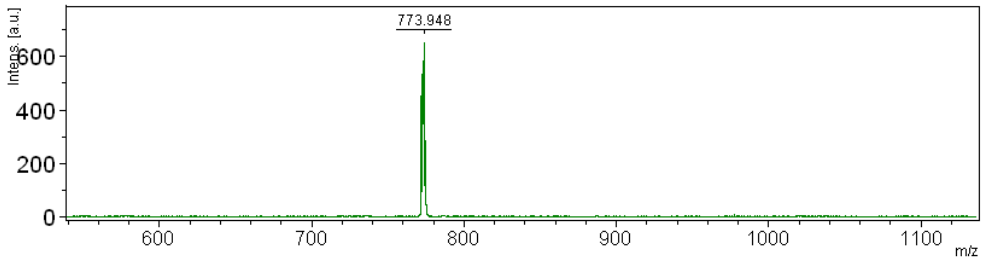

Fig. S5 MALDI-TOF mass spectrum of **2**.

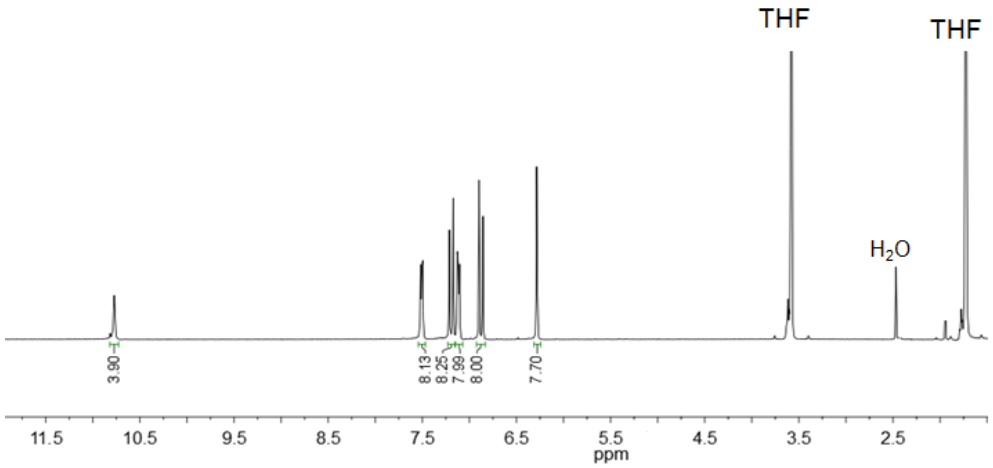

Fig. S6 ^{1}H NMR spectrum of **2** in THF-d_8 at 298 K.

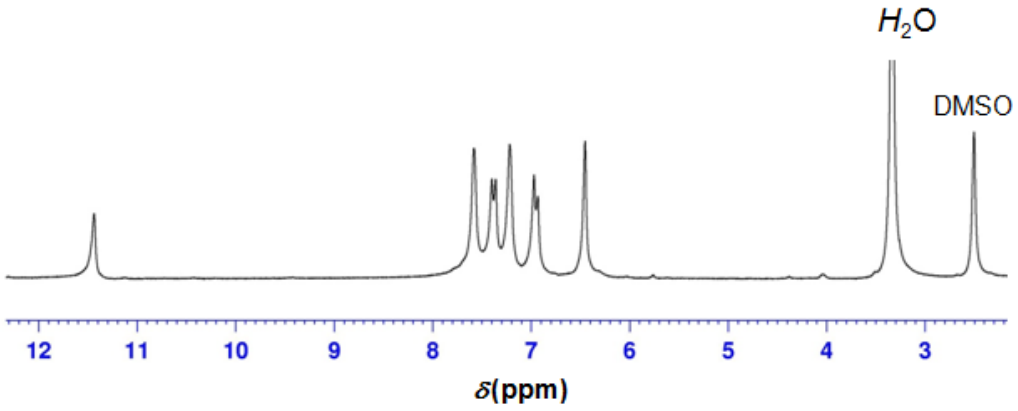

Fig. S7 ^{1}H NMR spectrum of **2** in DMSO-d_6 at 298 K.

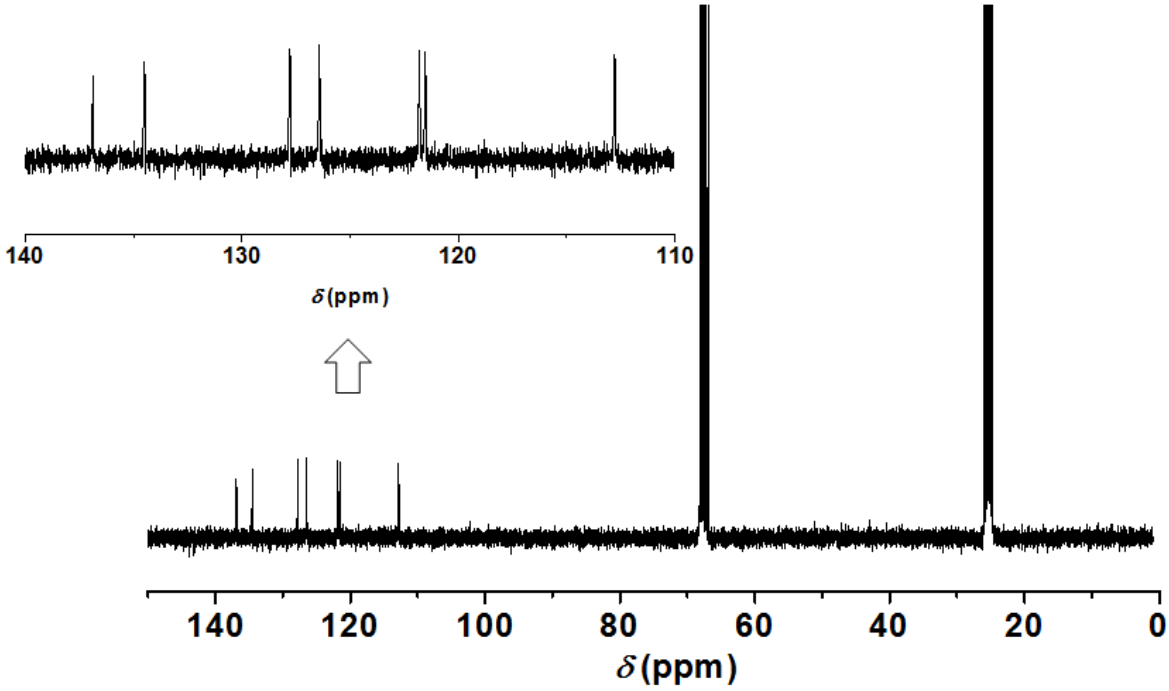

Fig. S8 ^{13}C NMR spectrum (100 MHz) of **2** in THF-d_8 at 298 K.

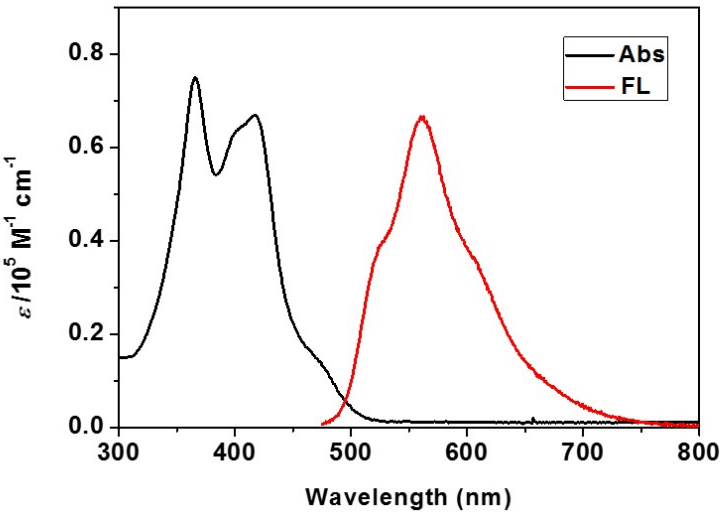

Fig. S9 UV-vis absorption and emission spectra at 298 K recorded in THF. The excitation was effected at 417 nm. The absolute fluorescence quantum yield was estimated to be 67%.

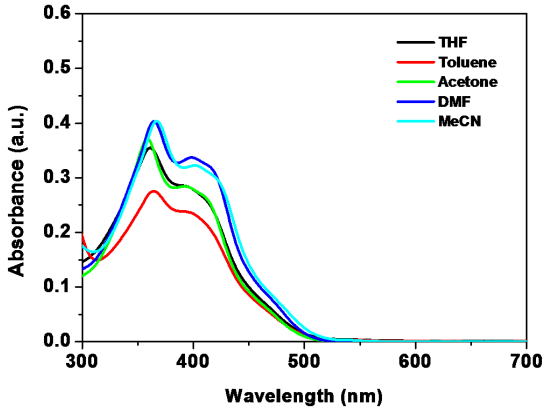

Fig. S10 UV-vis spectra of **2** observed in different solvents at 298 K; [**2**] = 5 μM.

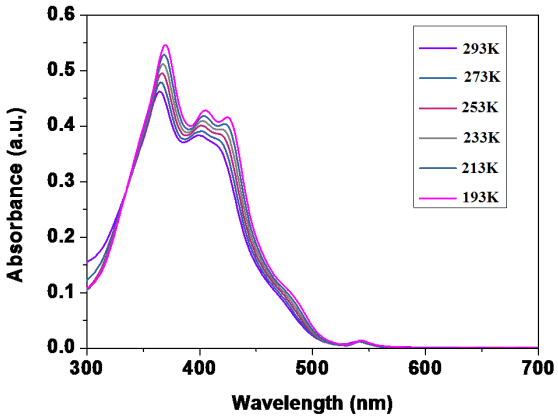

Fig. S11 UV-vis spectral change of **2** observed in THF upon decreasing the temperature from 293 K to 193 K. [**2**] = 6 μM.

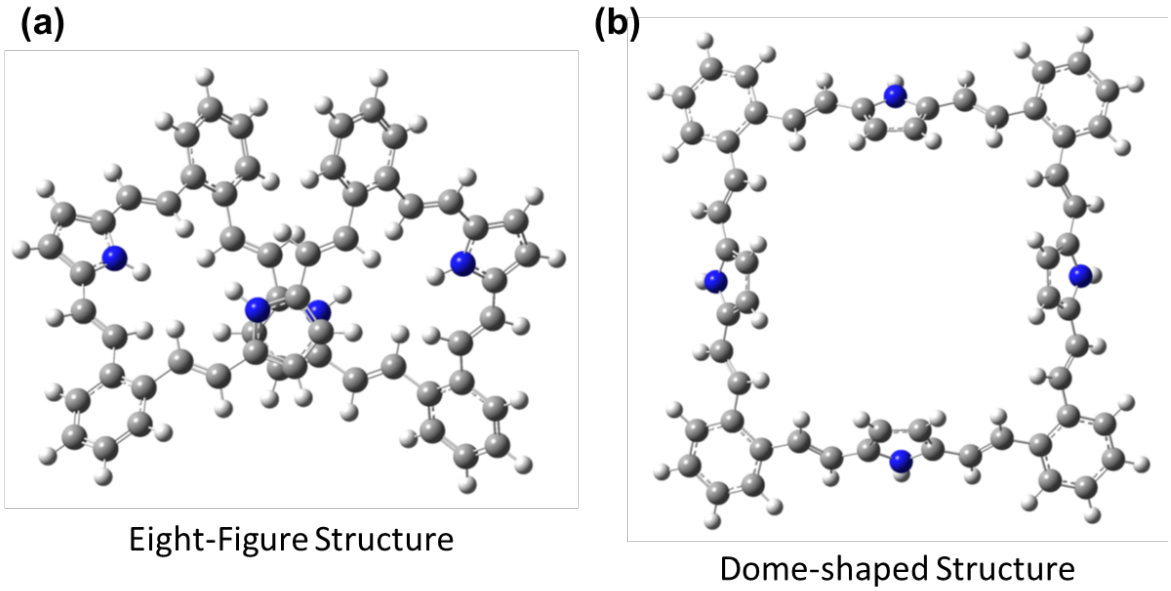

Fig. S12. DFT optimized structures for **2** with (a) eight-figure conformation and (b) dome-shaped confor mation obtained at B3LYP/6-31G(d) level calculations.

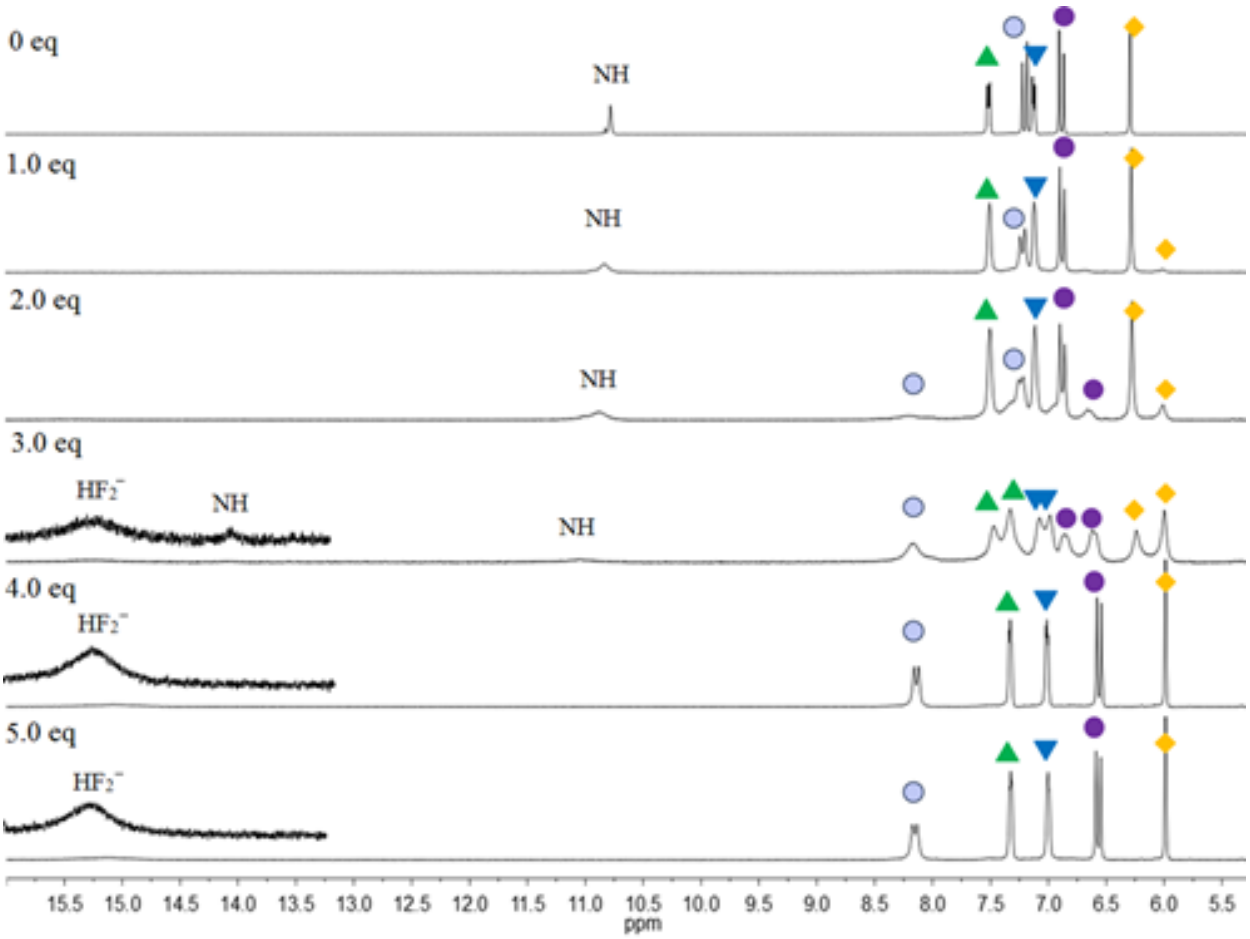

Fig. S13 ^{1}H NMR spectral changes seen upon the addition of fluoride (as its tetrabutylammonium salt) to **2** in THF-d_8 at 298 K.

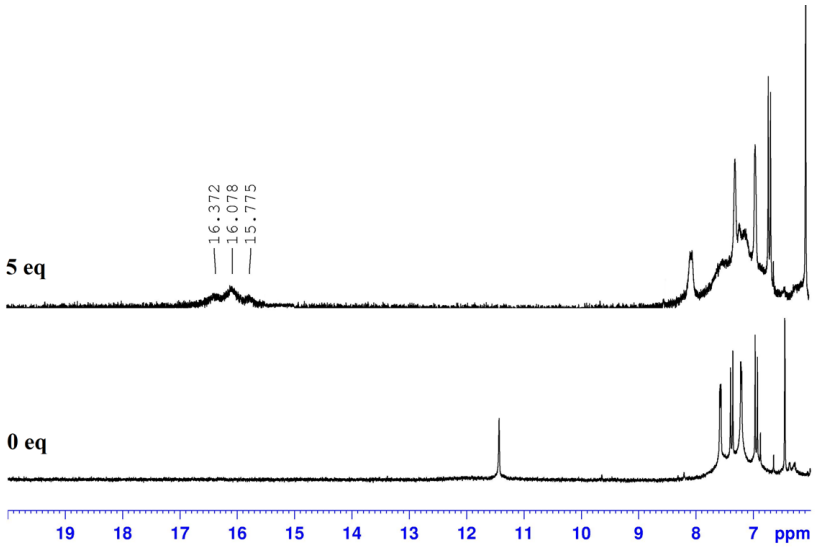

Fig. S14 ^{1}H NMR spectra of **2** in DMSO-d_6 recorded before and after the addition of 5 equiv. of TBAF at 298 K.

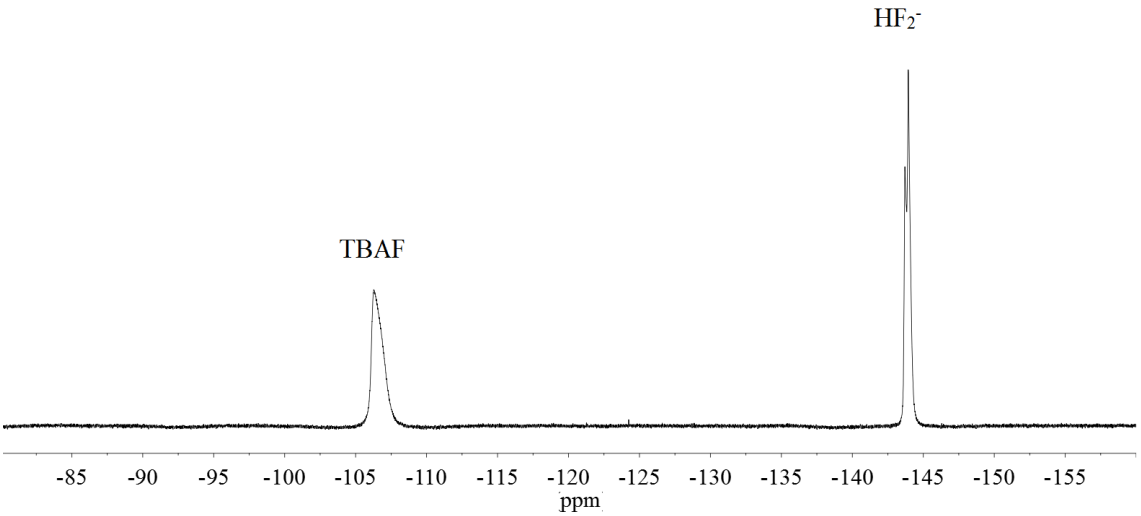

Fig. S15 ^{19}F NMR spectrum of **2** in DMSO-d_6 recorded upon the addition of 5 equivalents of TBAF at 298 K.

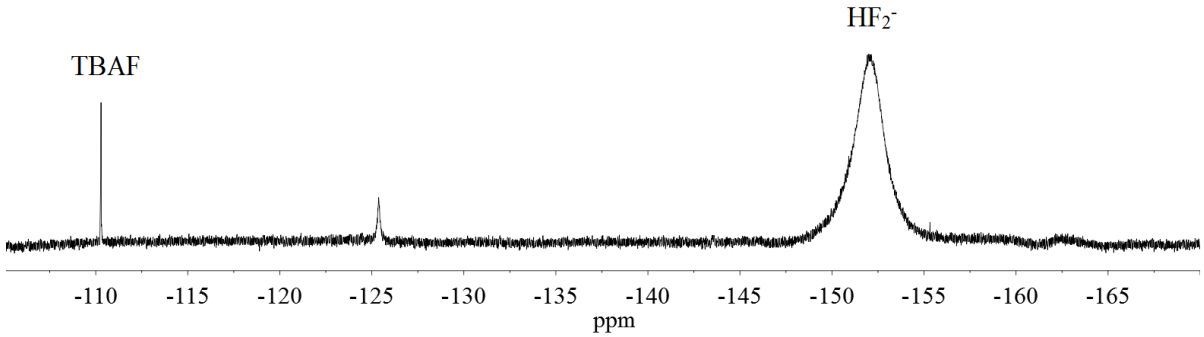

Fig. S16 ^{19}F NMR spectrum of **2** in THF-d_8 recorded upon the addition of 4 equivalents of TBAF at 298 K.

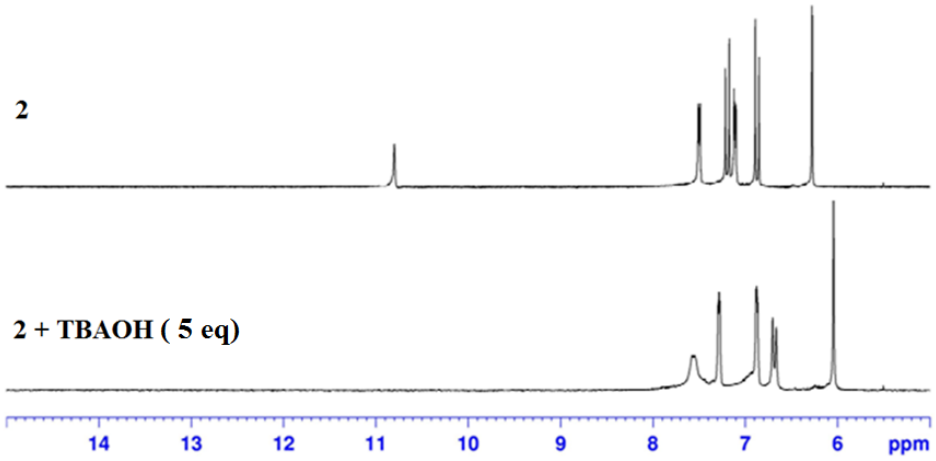

Fig. S17 ^{1}H NMR spectral changes of **2** after the addition of excess tetrabutylammonium hydroxide (TBAOH) in THF-d_8 at 298 K.

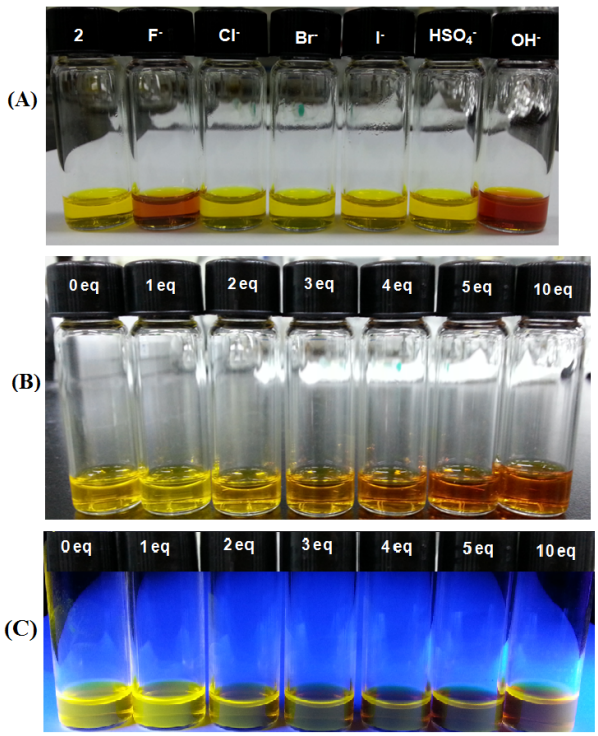

Fig. S18 Colour changes (A) seen upon the addition of various tetrabutylammonium salts (10 equivalents) to a solution of **2** (1 mM) in THF and (B) seen upon the addition of increasing quantities of TBAF to a THF solution of **2** (1 mM) (C) observed upon exposing the solutions in (B) to 365 nm UV-light.

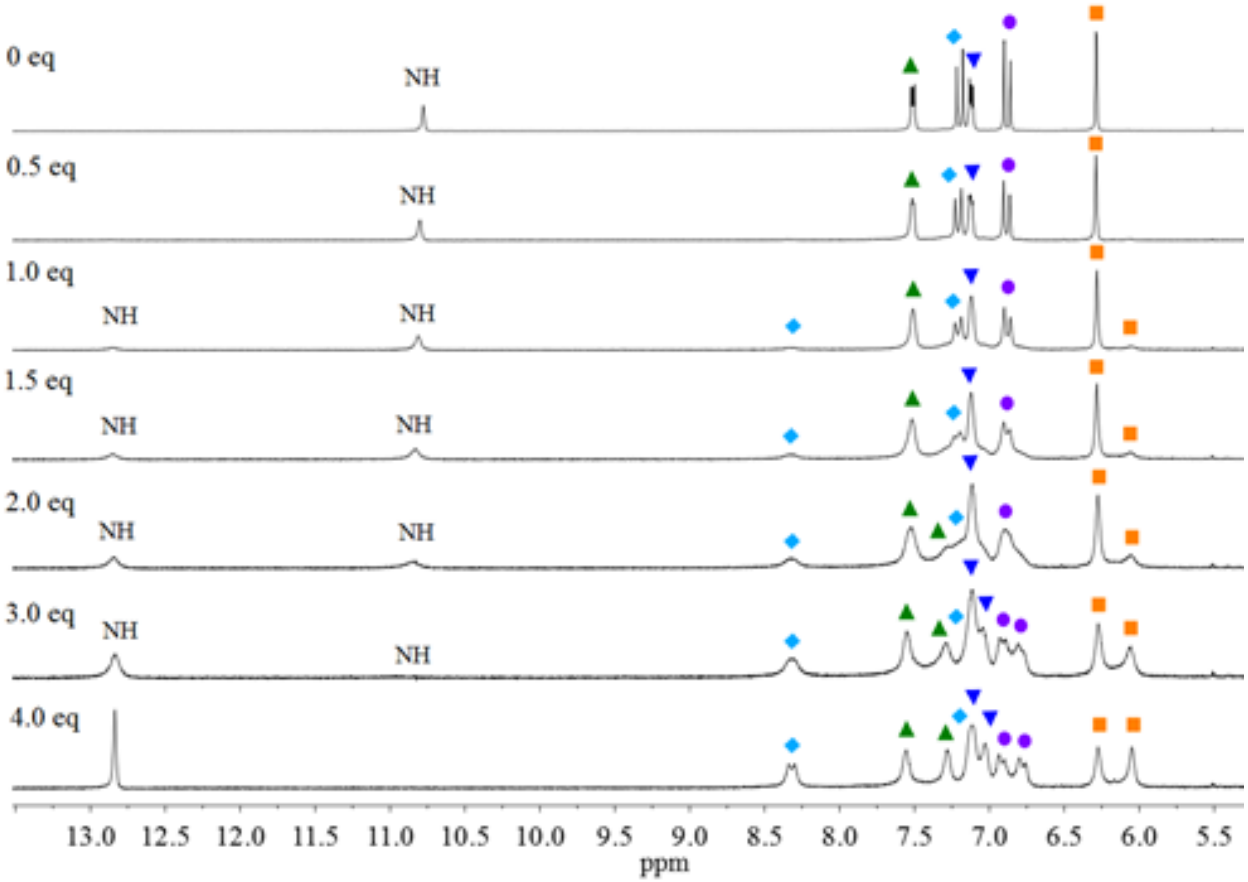

Fig. S19 ^{1}H NMR spectral changes of **2** seen upon the addition of chloride (as its tetrabutylammonium salt) in THF-d_8 at 298 K.

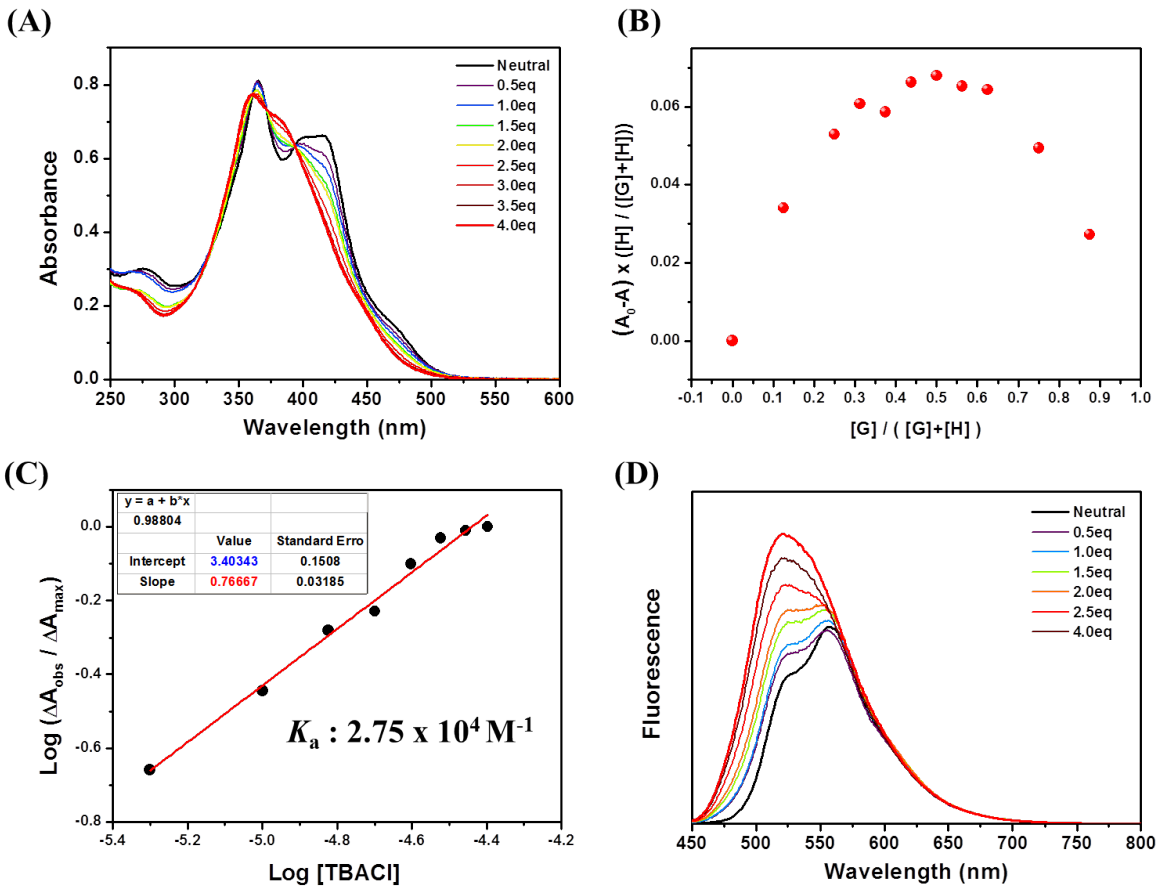

Fig. S20 (A) UV-vis spectra recorded upon the titration of a 10^{-5} M solution of **2** in THF with TBACl (B) Job's plot showing features consistent with a 1:1 binding stoichiometry between **2** and chloride (C) Titration plot of the 10^{-5} M solution of **2** in THF with TBACl, showing a linear relation (D) Emission spectra.

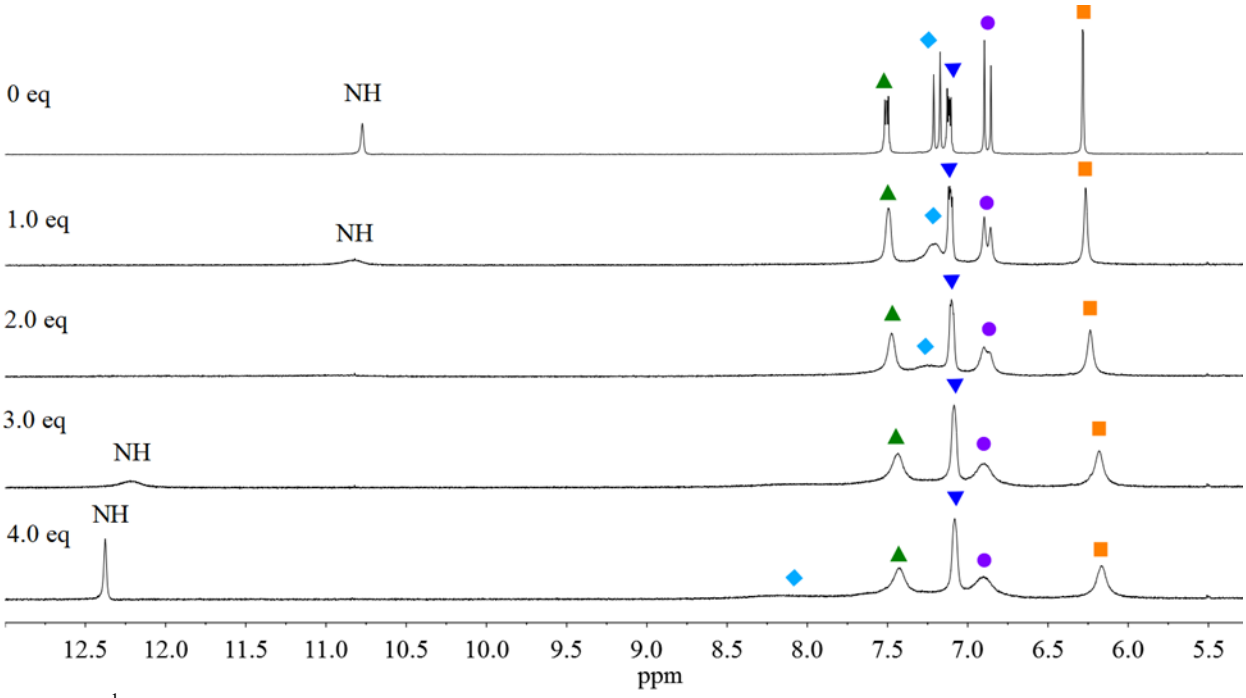

Fig. S21 ^{1}H NMR spectral changes of **2** seen upon the addition of bromide (as its tetrabutylammonium salt) in THF-d_8 at 298 K.

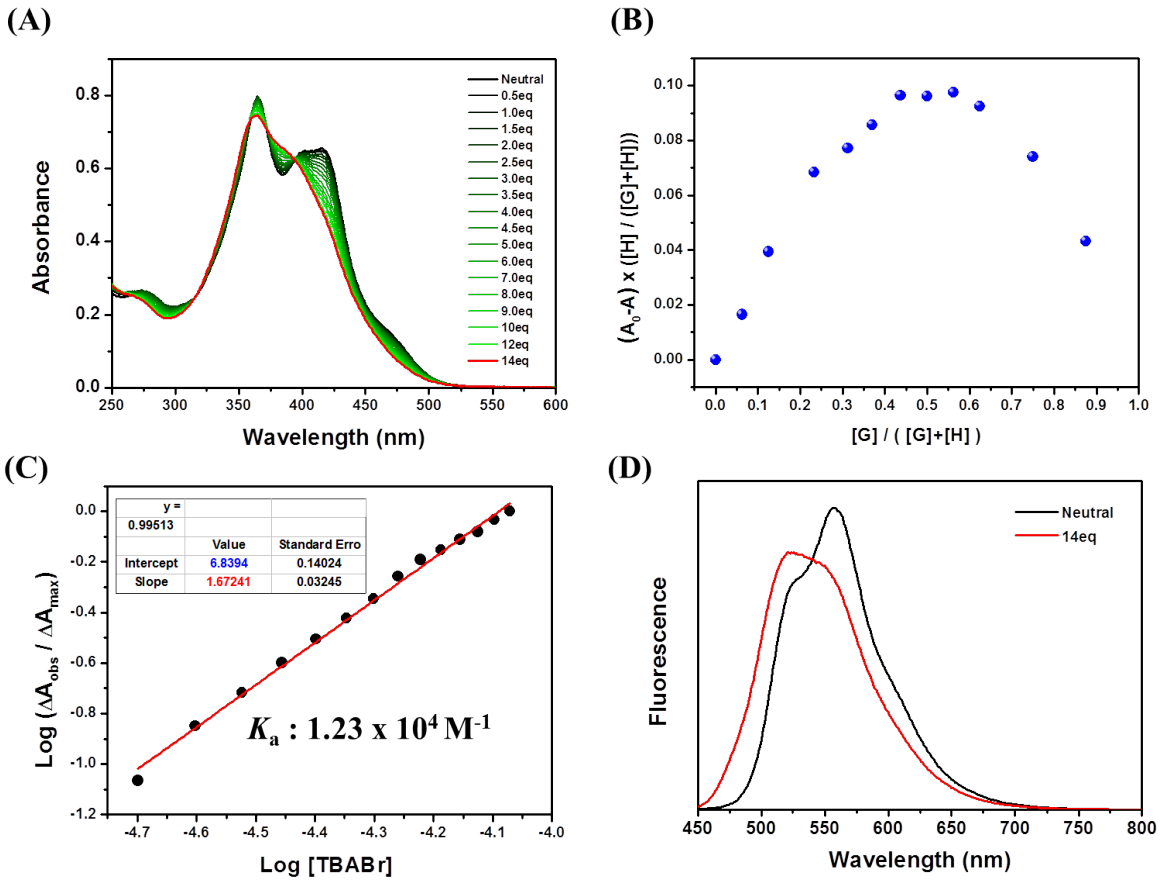

Fig. S22 (A) UV-vis spectra recorded upon the titration of a 10^{-5} M solution of **2** in THF with TBABr (B)

Job's plot showing features consistent with a 1:1 binding stoichiometry between **2** and bromide (C) Titration plot of the 10^{-5} M solution of **2** in THF with TBABr, showing a linear relation (D) Emission spectra.

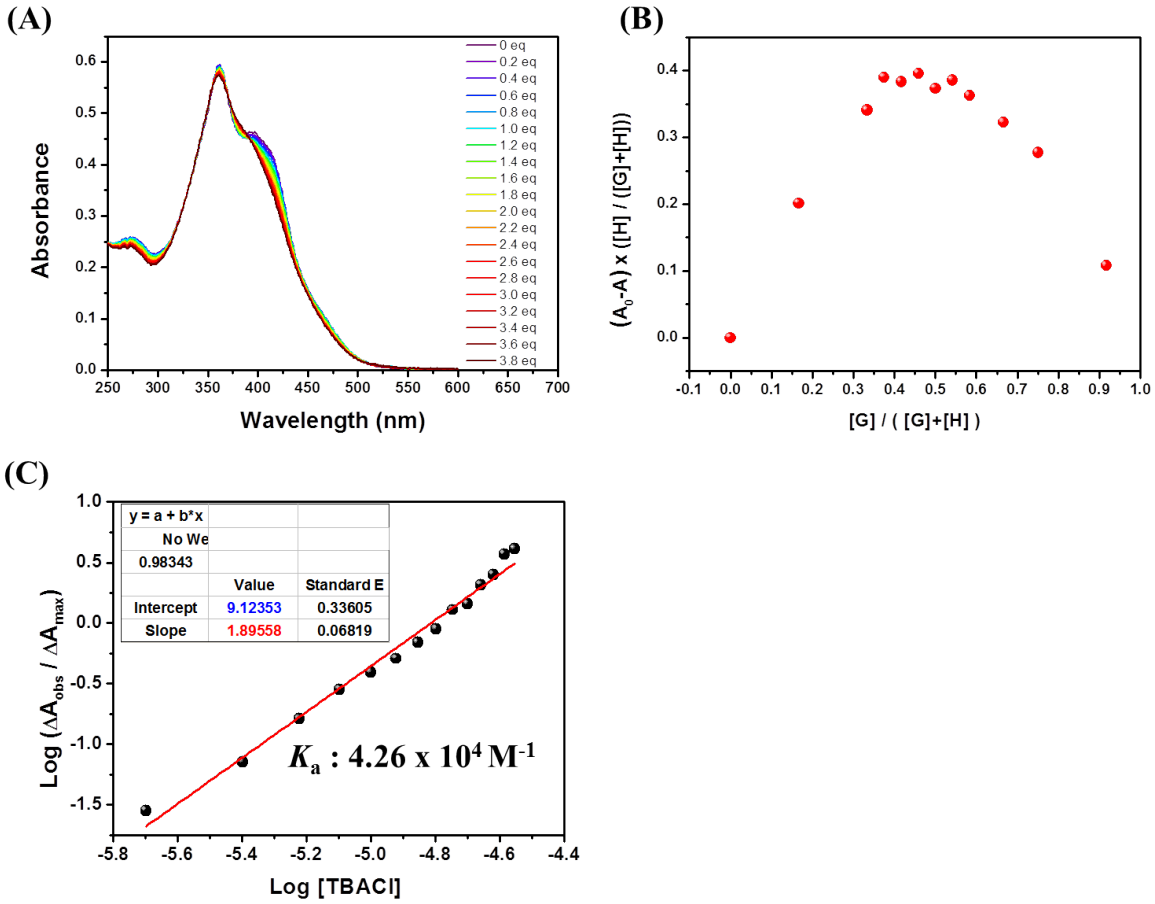

Fig. S23 (A) UV-vis spectra recorded for titration of a 10^{-5} M solution of **2** in CH_2Cl_2 with TBACl (B) Job's plot showing features that are interpreted in terms of what is predominantly a 1:1 binding stoichiometry between **2** and the chloride anion (C) Log-log plot corresponding to the titration of a 10^{-5} M solution of **2** in CH_2Cl_2 with TBACl. The near linear relation is taken as further support for the predominant 1:1 binding stoichiometry.

X-ray Experimental for $C_{56}H_{44}N_4$ – 4 C_2H_3N -2 C_4H_8O: Crystals grew as brown blocks by slow evaporation from acetonitrile and THF. The data crystal had approximate dimensions; 0.10 x 0.04 x 0.04 mm. The data were collected at -173 °C on a diffractometer using a Bruker AXS Apex II detector and a graphite monochromator with CuKα radiation (λ = 1.54178Å). A total of 998 frames of data were collected using ω- and ϕ-scans. Details of crystal data, data collection and structure refinement are listed in Table S1. Data reduction were performed using SAINT V8.27B.[5] The structure was solved by direct methods using XS[6] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2013.[7] Structure analysis was aided by use of the programs PLATON98[8] and WinGX.[9]

A molecule of acetonitrile was badly disordered. Attempts to model the disorder were unsatisfactory. The contributions to the scattering factors due to the solvent molecule were removed by use of the utility SQUEEZE[10] in PLATON98. The two molecules of THF were disordered. The disorder was modeled in the same manner for both molecules. The site occupancy for one component of a disordered THF molecule consisting of atoms, O1, C57, C58, C59 and C60, was assigned to the variable x. The site occupancy for the alternate component consisting of atoms, O1a, C57a, C58a, C59a and C60a, was assigned to 1-x. A common isotropic displacement parameter was refined for all atoms in the molecule while refining x. After several cycles of refinement, the hydrogen atoms were added in ideal positions and the variable x was refined again. In this way the site occupancy for the major component of the disordered molecule, O1, C57, C58, C59 and C60 refined to 59(2)%. The second THF molecule refined to 73(2)% for the major component. The non-H atoms of the first molecule were refined anisotropically. For the second disordered THF molecule, only the atoms of the major component were refined anisotropically. In both molecules, the displacement parameters were restrained to be approximately isotropic in the final refinement model.

The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.15*P)^2]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.366, with R(F) equal to 0.122 and a goodness of fit, S, = 1.69. Definitions used for calculating R(F),$Rw(F^2)$ and the goodness of fit, S, are given below.[11] The data were checked for secondary extinction but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[12] All figures were generated using SHELXTL/PC.[13] Further details of the crystal structure may be obtained from the Cambridge Crystallographic Data Centre by making reference to CCDC no. 983010.

Table 1. Crystal data and structure refinement for **2**.

Empirical formula	C72 H72 N8 O2	
Formula weight	1081.37	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 16.3594(12) Å	α= 90°.
	b = 16.2083(13) Å	β= 90.182(4)°.
	c = 24.658(2) Å	γ = 90°.
Volume	6538.2(9) $Å^3$	
Z	4	
Density (calculated)	1.099 Mg/m^3	
Absorption coefficient	0.521 mm^{-1}	
F(000)	2304	
Crystal size	0.10 x 0.04 x 0.04 mm	
Theta range for data collection	2.701 to 64.991°.	
Index ranges	-19<=h<=19, -19<=k<=19, -23<=l<=28	
Reflections collected	61513	
Independent reflections	11009 [R(int) = 0.0549]	
Completeness to theta = 67.679°	92.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7538 and 0.6755	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11009 / 322 / 779	
Goodness-of-fit on F^2	1.690	
Final R indices [I > 2sigma(I)]	R1 = 0.1225, $_wR2$ = 0.3419	
R indices (all data)	R1 = 0.1582, $_wR2$ = 0.3655	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.732 and -0.493 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N1	4351(2)	4459(2)	1352(2)	54(1)
N2	3259(2)	7510(2)	2654(2)	55(1)
N3	-272(2)	5613(2)	1553(2)	67(1)
N4	-991(3)	9224(3)	1462(2)	81(1)
C1	142(3)	9992(3)	1004(3)	84(2)
C2	-696(3)	9861(3)	1157(3)	82(2)
C3	-1359(3)	10341(4)	1014(3)	97(2)
C4	-2058(4)	9956(4)	1224(3)	109(2)
C5	-1835(3)	9279(4)	1499(3)	90(2)
C6	-2363(3)	8680(4)	1749(3)	107(2)
C7	-2134(3)	8008(4)	2014(3)	94(2)
C8	-2716(3)	7412(4)	2272(3)	90(2)
C9	-2490(3)	6579(3)	2328(3)	85(2)
C10	-1740(3)	6268(3)	2088(3)	82(2)
C11	-1287(3)	5644(3)	2280(2)	74(1)
C12	-567(3)	5306(3)	2023(2)	65(1)
C13	-107(3)	4634(3)	2160(2)	68(1)
C14	467(3)	4525(3)	1746(2)	68(1)
C15	732(3)	5328(3)	856(2)	63(1)
C16	338(3)	5143(3)	1373(2)	63(1)
C17	1393(3)	4964(3)	656(2)	62(1)
C18	1737(3)	5125(3)	120(2)	60(1)
C19	1229(3)	5383(3)	-310(2)	64(1)
C20	1528(3)	5510(3)	-826(2)	68(1)
C21	2351(3)	5363(3)	-931(2)	68(1)
C22	2855(3)	5121(3)	-510(2)	64(1)
C23	2578(3)	5008(2)	18(2)	55(1)
C24	3145(3)	4803(3)	458(2)	56(1)
C25	3903(3)	4509(3)	393(2)	61(1)
C26	4485(3)	4323(3)	821(2)	60(1)
C27	5244(3)	3955(3)	768(2)	71(1)

C28	5563(3)	3856(3)	1283(2)	70(1)
C29	5013(2)	4175(3)	1659(2)	58(1)
C30	5065(2)	4226(2)	2229(2)	54(1)
C31	4566(2)	4630(2)	2560(2)	55(1)
C32	4598(2)	4611(2)	3151(2)	53(1)
C33	4867(2)	3894(3)	3414(2)	58(1)
C34	4867(3)	3830(3)	3965(2)	69(1)
C35	4604(3)	4484(3)	4283(2)	72(1)
C36	4340(3)	5211(3)	4027(2)	67(1)
C37	4320(2)	5284(3)	3471(2)	57(1)
C38	3463(2)	6550(2)	3427(2)	58(1)
C39	3996(2)	6029(2)	3207(2)	56(1)
C40	3074(2)	7239(2)	3165(2)	55(1)
C41	2424(2)	7720(3)	3346(2)	61(1)
C42	2222(2)	8274(3)	2935(2)	58(1)
C43	2740(2)	8135(2)	2496(2)	54(1)
C44	2799(2)	8522(3)	1982(2)	58(1)
C45	2231(2)	9017(3)	1761(2)	61(1)
C46	2314(3)	9462(3)	1247(2)	65(1)
C47	1624(3)	9708(3)	944(2)	72(1)
C48	785(3)	9532(3)	1126(2)	72(1)
C49	3089(3)	9672(3)	1055(2)	78(1)
C50	3192(4)	10083(4)	572(3)	95(2)
C51	2529(4)	10294(4)	263(3)	101(2)
C52	1744(4)	10121(4)	458(3)	94(2)
C53	-3452(3)	7672(4)	2493(3)	92(2)
C54	-3973(4)	7131(4)	2733(3)	98(2)
C55	-3778(3)	6320(5)	2795(3)	98(2)
C56	-3028(3)	6037(4)	2590(3)	96(2)
O1	-917(14)	6898(15)	854(11)	134(3)
C57	-499(10)	7496(12)	561(11)	140(3)
C58	-1110(12)	7987(10)	283(9)	147(3)
C59	-1795(10)	7300(10)	157(7)	149(3)
C60	-1726(11)	6906(12)	657(10)	137(3)
O1A	-860(20)	6980(20)	879(15)	134(3)
C57A	-252(14)	7439(17)	615(15)	139(3)

C58A	-657(15)	8031(14)	269(12)	147(3)
C59A	-1614(13)	7812(14)	311(11)	145(3)
C60A	-1528(16)	7020(16)	521(14)	140(3)
O2	2612(7)	8075(6)	-292(4)	150(2)
C61	3324(8)	7753(9)	-73(6)	140(2)
C62	3091(9)	7252(10)	431(6)	137(2)
C63	2198(8)	7383(7)	482(5)	123(2)
C64	1887(8)	7750(8)	28(6)	139(2)
O2A	2468(16)	7794(17)	-271(9)	148
C61A	3100(20)	7220(20)	-286(10)	140
C62A	3457(19)	7140(20)	288(12)	131
C63A	2740(20)	7430(20)	610(10)	136
C64A	2360(20)	8044(19)	320(12)	143
N5	2860(3)	5255(4)	1840(2)	101(2)
C65	2348(4)	5494(7)	2101(3)	139(4)
C66	1747(4)	6006(8)	2368(5)	193(6)
N6	4409(3)	6824(3)	1811(2)	84(1)
C67	4942(3)	6577(3)	1584(2)	72(1)
C68	5668(4)	6280(4)	1302(3)	98(2)
N7	77(3)	7840(3)	2024(3)	102(2)
C69	152(4)	7492(4)	2435(3)	116(3)
C70	206(7)	7078(7)	2964(4)	166(4)

Table S3. Bond lengths [Å] and angles [°] for **2.**

N1-C26	1.347(6)	C13-C14	1.401(7)
N1-C29	1.396(5)	C13-H13	0.95
N1-H1N	0.88	C14-C16	1.377(7)
N2-C40	1.370(6)	C14-H14	0.95
N2-C43	1.378(5)	C15-C17	1.328(7)
N2-H2N	0.88	C15-C16	1.461(7)
N3-C16	1.331(6)	C15-H15	0.95
N3-C12	1.352(7)	C17-C18	1.464(7)
N3-H3N	0.88	C17-H17	0.95
N4-C2	1.367(7)	C18-C23	1.413(6)
N4-C5	1.387(6)	C18-C19	1.406(6)
N4-H4N	0.88	C19-C20	1.381(7)
C1-C48	1.323(7)	C19-H19	0.95
C1-C2	1.438(7)	C20-C21	1.393(7)
C1-H1A	0.95	C20-H20	0.95
C2-C3	1.381(7)	C21-C22	1.381(7)
C3-C4	1.402(9)	C21-H21	0.95
C3-H3A	0.95	C22-C23	1.391(7)
C4-C5	1.341(8)	C22-H22	0.95
C4-H4A	0.95	C23-C24	1.463(6)
C5-C6	1.438(8)	C24-C25	1.339(6)
C6-C7	1.324(8)	C24-H24	0.95
C6-H6	0.95	C25-C26	1.451(6)
C7-C8	1.499(8)	C25-H25	0.95
C7-H7	0.95	C26-C27	1.384(6)
C8-C53	1.389(9)	C27-C28	1.380(7)
C8-C9	1.407(8)	C27-H1	0.95
C9-C56	1.402(8)	C28-C29	1.393(7)
C9-C10	1.454(8)	C28-H28	0.95
C10-C11	1.338(7)	C29-C30	1.411(6)
C10-H10	0.95	C30-C31	1.328(6)
C11-C12	1.447(7)	C30-H30	0.95
C11-H11	0.95	C31-C32	1.460(6)
C12-C13	1.365(7)	C31-H31	0.95

C32-C33	1.401(6)	C52-H52	0.95
C32-C37	1.422(6)	C53-C54	1.359(9)
C33-C34	1.362(7)	C53-H53	0.95
C33-H33	0.95	C54-C55	1.361(9)
C34-C35	1.388(7)	C54-H54	0.95
C34-H34	0.95	C55-C56	1.406(9)
C35-C36	1.404(7)	C55-H55	0.95
C35-H35	0.95	C56-H56	0.95
C36-C37	1.378(7)	O1-C60	1.407(11)
C36-H36	0.95	O1-C57	1.391(12)
C37-C39	1.470(6)	C57-C58	1.448(15)
C38-C39	1.331(6)	C57-H57A	0.99
C38-C40	1.437(6)	C57-H57B	0.99
C38-H38	0.95	C58-C59	1.609(17)
C39-H39	0.95	C58-H58A	0.99
C40-C41	1.394(6)	C58-H58B	0.99
C41-C42	1.394(6)	C59-C60	1.394(18)
C41-H41	0.95	C59-H59A	0.99
C42-C43	1.396(6)	C59-H59B	0.99
C42-H42	0.95	C60-H60A	0.99
C43-C44	1.417(7)	C60-H60B	0.99
C44-C45	1.342(6)	O1A-C60A	1.410(13)
C44-H44	0.95	O1A-C57A	1.395(13)
C45-C46	1.465(7)	C57A-C58A	1.444(15)
C45-H45	0.95	C57A-H57C	0.99
C46-C49	1.397(7)	C57A-H57D	0.99
C46-C47	1.410(6)	C58A-C59A	1.609(18)
C47-C52	1.387(8)	C58A-H58C	0.99
C47-C48	1.474(7)	C58A-H58D	0.99
C48-H48	0.95	C59A-C60A	1.391(19)
C49-C50	1.376(8)	C59A-H59C	0.99
C49-H49	0.95	C59A-H59D	0.99
C50-C51	1.366(8)	C60A-H60C	0.99
C50-H50	0.95	C60A-H60D	0.99
C51-C52	1.403(8)	O2-C61	1.385(13)
C51-H51	0.95	O2-C64	1.519(15)

C61-C62	1.533(16)	C63A-H63C	0.99
C61-H61A	0.99	C63A-H63D	0.99
C61-H61B	0.99	C64A-H64C	0.99
C62-C63	1.482(17)	C64A-H64D	0.99
C62-H62A	0.99	N5-C65	1.128(7)
C62-H62B	0.99	C65-C66	1.446(9)
C63-C64	1.365(16)	C66-H66A	0.98
C63-H63A	0.99	C66-H66B	0.98
C63-H63B	0.99	C66-H66C	0.98
C64-H64A	0.99	N6-C67	1.114(6)
C64-H64B	0.99	C67-C68	1.459(7)
O2A-C61A	1.391(15)	C68-H68A	0.98
O2A-C64A	1.523(17)	C68-H68B	0.98
C61A-C62A	1.535(18)	C68-H68C	0.98
C61A-H61C	0.99	N7-C69	1.167(7)
C61A-H61D	0.99	C69-C70	1.468(8)
C62A-C63A	1.490(19)	C70-H70A	0.98
C62A-H62C	0.99	C70-H70B	0.98
C62A-H62D	0.99	C70-H70C	0.98
C63A-C64A	1.375(18)		

C26-N1-C29	110.1(4)	N4-C2-C3	106.7(5)
C26-N1-H1N	124.9	N4-C2-C1	126.5(4)
C29-N1-H1N	124.9	C3-C2-C1	126.8(5)
C40-N2-C43	111.0(3)	C2-C3-C4	107.2(5)
C40-N2-H2N	124.5	C2-C3-H3A	126.4
C43-N2-H2N	124.5	C4-C3-H3A	126.4
C16-N3-C12	110.3(4)	C5-C4-C3	109.4(5)
C16-N3-H3N	124.9	C5-C4-H4A	125.3
C12-N3-H3N	124.9	C3-C4-H4A	125.3
C2-N4-C5	110.0(4)	C4-C5-N4	106.7(5)
C2-N4-H4N	125.0	C4-C5-C6	127.4(5)
C5-N4-H4N	125.0	N4-C5-C6	125.7(5)
C48-C1-C2	128.0(5)	C7-C6-C5	126.7(5)
C48-C1-H1A	116.0	C7-C6-H6	116.7
C2-C1-H1A	116.0	C5-C6-H6	116.7

C6-C7-C8	124.1(5)	C20-C19-C18	121.9(4)
C6-C7-H7	117.9	C20-C19-H19	119.1
C8-C7-H7	117.9	C18-C19-H19	119.1
C53-C8-C9	118.7(5)	C19-C20-C21	119.5(4)
C53-C8-C7	121.6(5)	C19-C20-H20	120.3
C9-C8-C7	119.5(5)	C21-C20-H20	120.3
C56-C9-C8	118.8(5)	C22-C21-C20	118.9(5)
C56-C9-C10	120.1(5)	C22-C21-H21	120.5
C8-C9-C10	121.0(5)	C20-C21-H21	120.5
C11-C10-C9	125.8(6)	C21-C22-C23	123.1(5)
C11-C10-H10	117.1	C21-C22-H22	118.5
C9-C10-H10	117.1	C23-C22-H22	118.5
C10-C11-C12	125.5(5)	C22-C23-C18	118.0(4)
C10-C11-H11	117.2	C22-C23-C24	121.1(4)
C12-C11-H11	117.2	C18-C23-C24	120.9(4)
N3-C12-C13	107.9(4)	C25-C24-C23	125.3(4)
N3-C12-C11	122.0(4)	C25-C24-H24	117.4
C13-C12-C11	130.0(5)	C23-C24-H24	117.4
C12-C13-C14	106.9(5)	C24-C25-C26	126.4(5)
C12-C13-H13	126.5	C24-C25-H25	116.8
C14-C13-H13	126.5	C26-C25-H25	116.8
C16-C14-C13	107.0(4)	N1-C26-C27	108.1(4)
C16-C14-H14	126.5	N1-C26-C25	124.4(4)
C13-C14-H14	126.5	C27-C26-C25	127.4(5)
C17-C15-C16	126.5(4)	C28-C27-C26	107.5(4)
C17-C15-H15	116.7	C28-C27-H1	126.3
C16-C15-H15	116.7	C26-C27-H1	126.3
N3-C16-C14	107.9(4)	C27-C28-C29	109.0(4)
N3-C16-C15	120.5(4)	C27-C28-H28	125.5
C14-C16-C15	131.7(4)	C29-C28-H28	125.5
C15-C17-C18	124.9(4)	N1-C29-C28	105.3(4)
C15-C17-H17	117.5	N1-C29-C30	124.3(4)
C18-C17-H17	117.5	C28-C29-C30	130.4(4)
C23-C18-C19	118.7(4)	C31-C30-C29	127.2(4)
C23-C18-C17	121.0(4)	C31-C30-H30	116.4
C19-C18-C17	120.3(4)	C29-C30-H30	116.4

C30-C31-C32	125.6(4)	N2-C43-C42	106.0(4)
C30-C31-H31	117.2	N2-C43-C44	122.3(4)
C32-C31-H31	117.2	C42-C43-C44	131.7(4)
C33-C32-C37	118.7(4)	C45-C44-C43	125.3(4)
C33-C32-C31	119.4(4)	C45-C44-H44	117.4
C37-C32-C31	121.8(4)	C43-C44-H44	117.4
C34-C33-C32	121.6(4)	C44-C45-C46	125.4(4)
C34-C33-H33	119.2	C44-C45-H45	117.3
C32-C33-H33	119.2	C46-C45-H45	117.3
C33-C34-C35	120.4(4)	C49-C46-C47	118.5(5)
C33-C34-H34	119.8	C49-C46-C45	120.0(4)
C35-C34-H34	119.8	C47-C46-C45	121.4(4)
C34-C35-C36	118.8(5)	C52-C47-C46	118.7(5)
C34-C35-H35	120.6	C52-C47-C48	119.4(4)
C36-C35-H35	120.6	C46-C47-C48	122.0(5)
C37-C36-C35	121.8(5)	C1-C48-C47	124.2(5)
C37-C36-H36	119.1	C1-C48-H48	117.9
C35-C36-H36	119.1	C47-C48-H48	117.9
C36-C37-C32	118.6(4)	C50-C49-C46	121.7(5)
C36-C37-C39	121.3(4)	C50-C49-H49	119.2
C32-C37-C39	120.0(4)	C46-C49-H49	119.2
C39-C38-C40	126.8(5)	C49-C50-C51	120.4(5)
C39-C38-H38	116.6	C49-C50-H50	119.8
C40-C38-H38	116.6	C51-C50-H50	119.8
C38-C39-C37	125.2(4)	C50-C51-C52	119.0(6)
C38-C39-H39	117.4	C50-C51-H51	120.5
C37-C39-H39	117.4	C52-C51-H51	120.5
N2-C40-C41	106.7(4)	C47-C52-C51	121.7(5)
N2-C40-C38	124.3(4)	C47-C52-H52	119.2
C41-C40-C38	128.9(4)	C51-C52-H52	119.2
C40-C41-C42	107.9(4)	C54-C53-C8	121.4(6)
C40-C41-H41	126.1	C54-C53-H53	119.3
C42-C41-H41	126.1	C8-C53-H53	119.3
C43-C42-C41	108.5(4)	C55-C54-C53	121.6(6)
C43-C42-H42	125.8	C55-C54-H54	119.2
C41-C42-H42	125.8	C53-C54-H54	119.2

C54-C55-C56	118.6(6)	C58A-C57A-H57D	110.2
C54-C55-H55	120.7	H57C-C57A-H57D	108.5
C56-C55-H55	120.7	C57A-C58A-C59A	105.1(12)
C9-C56-C55	120.7(6)	C57A-C58A-H58C	110.7
C9-C56-H56	119.6	C59A-C58A-H58C	110.7
C55-C56-H56	119.6	C57A-C58A-H58D	110.7
C60-O1-C57	106.2(8)	C59A-C58A-H58D	110.7
O1-C57-C58	106.7(11)	H58C-C58A-H58D	108.8
O1-C57-H57A	110.4	C60A-C59A-C58A	97.4(12)
C58-C57-H57A	110.4	C60A-C59A-H59C	112.3
O1-C57-H57B	110.4	C58A-C59A-H59C	112.3
C58-C57-H57B	110.4	C60A-C59A-H59D	112.3
H57A-C57-H57B	108.6	C58A-C59A-H59D	112.3
C57-C58-C59	101.0(11)	H59C-C59A-H59D	109.9
C57-C58-H58A	111.6	O1A-C60A-C59A	110.5(17)
C59-C58-H58A	111.6	O1A-C60A-H60C	109.5
C57-C58-H58B	111.6	C59A-C60A-H60C	109.5
C59-C58-H58B	111.6	O1A-C60A-H60D	109.5
H58A-C58-H58B	109.4	C59A-C60A-H60D	109.5
C60-C59-C58	95.2(11)	H60C-C60A-H60D	108.1
C60-C59-H59A	112.7	C61-O2-C64	109.0(9)
C58-C59-H59A	112.7	O2-C61-C62	107.7(11)
C60-C59-H59B	112.7	O2-C61-H61A	110.2
C58-C59-H59B	112.7	C62-C61-H61A	110.2
H59A-C59-H59B	110.2	O2-C61-H61B	110.2
O1-C60-C59	112.5(14)	C62-C61-H61B	110.2
O1-C60-H60A	109.1	H61A-C61-H61B	108.5
C59-C60-H60A	109.1	C63-C62-C61	104.0(10)
O1-C60-H60B	109.1	C63-C62-H62A	111.0
C59-C60-H60B	109.1	C61-C62-H62A	111.0
H60A-C60-H60B	107.8	C63-C62-H62B	111.0
C60A-O1A-C57A	103.8(12)	C61-C62-H62B	111.0
O1A-C57A-C58A	107.6(13)	H62A-C62-H62B	109.0
O1A-C57A-H57C	110.2	C64-C63-C62	111.0(12)
C58A-C57A-H57C	110.2	C64-C63-H63A	109.4
O1A-C57A-H57D	110.2	C62-C63-H63A	109.4

C64-C63-H63B	109.4	C63A-C64A-O2A	104.5(14)
C62-C63-H63B	109.4	C63A-C64A-H64C	110.8
H63A-C63-H63B	108.0	O2A-C64A-H64C	110.8
C63-C64-O2	106.7(11)	C63A-C64A-H64D	110.9
C63-C64-H64A	110.4	O2A-C64A-H64D	110.8
O2-C64-H64A	110.4	H64C-C64A-H64D	108.9
C63-C64-H64B	110.4	N5-C65-C66	164.7(13)
O2-C64-H64B	110.4	C65-C66-H66A	109.5
H64A-C64-H64B	108.6	C65-C66-H66B	109.5
C61A-O2A-C64A	107.0(12)	H66A-C66-H66B	109.5
O2A-C61A-C62A	108.2(14)	C65-C66-H66C	109.5
O2A-C61A-H61C	110.1	H66A-C66-H66C	109.5
C62A-C61A-H61C	110.1	H66B-C66-H66C	109.5
O2A-C61A-H61D	110.1	N6-C67-C68	177.1(6)
C62A-C61A-H61D	110.1	C67-C68-H68A	109.5
H61C-C61A-H61D	108.4	C67-C68-H68B	109.5
C63A-C62A-C61A	99.6(14)	H68A-C68-H68B	109.5
C63A-C62A-H62C	111.8	C67-C68-H68C	109.5
C61A-C62A-H62C	111.9	H68A-C68-H68C	109.5
C63A-C62A-H62D	111.8	H68B-C68-H68C	109.5
C61A-C62A-H62D	111.8	N7-C69-C70	176.8(9)
H62C-C62A-H62D	109.6	C69-C70-H70A	109.5
C64A-C63A-C62A	107.9(16)	C69-C70-H70B	109.5
C64A-C63A-H63C	110.1	H70A-C70-H70B	109.5
C62A-C63A-H63C	110.1	C69-C70-H70C	109.5
C64A-C63A-H63D	110.1	H70A-C70-H70C	109.5
C62A-C63A-H63D	110.1	H70B-C70-H70C	109.5
H63C-C63A-H63D	108.4		

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N1	41(2)	60(2)	62(2)	4(2)	-2(1)	5(1)
N2	44(2)	56(2)	64(2)	-7(2)	-3(1)	4(1)
N3	50(2)	60(2)	92(3)	12(2)	5(2)	-3(2)
N4	62(2)	73(2)	109(4)	30(2)	5(2)	13(2)
C1	54(3)	75(3)	124(5)	35(3)	-9(3)	-2(2)
C2	58(3)	74(3)	113(5)	27(3)	-5(3)	10(2)
C3	63(3)	90(4)	138(6)	43(4)	0(3)	17(3)
C4	62(3)	102(4)	164(7)	51(4)	17(4)	28(3)
C5	56(3)	86(3)	129(5)	27(3)	17(3)	15(2)
C6	59(3)	90(4)	173(7)	36(4)	16(3)	16(3)
C7	55(3)	86(4)	142(6)	19(4)	6(3)	14(2)
C8	60(3)	83(3)	126(5)	28(3)	-2(3)	6(2)
C9	55(3)	81(3)	119(5)	15(3)	4(3)	1(2)
C10	60(3)	78(3)	110(4)	14(3)	1(3)	-4(2)
C11	61(3)	62(3)	100(4)	7(2)	12(2)	-3(2)
C12	51(2)	58(2)	86(3)	7(2)	7(2)	-1(2)
C13	58(3)	65(2)	81(3)	2(2)	11(2)	-3(2)
C14	52(2)	67(3)	84(3)	-2(2)	-2(2)	6(2)
C15	47(2)	66(2)	77(3)	6(2)	-14(2)	0(2)
C16	48(2)	62(2)	79(3)	8(2)	-7(2)	-6(2)
C17	50(2)	69(3)	68(3)	6(2)	-8(2)	-7(2)
C18	54(2)	61(2)	65(3)	3(2)	-4(2)	-13(2)
C19	53(2)	68(3)	71(3)	7(2)	-8(2)	-10(2)
C20	66(3)	71(3)	67(3)	9(2)	-14(2)	-14(2)
C21	77(3)	72(3)	56(3)	8(2)	-4(2)	-6(2)
C22	59(2)	68(3)	67(3)	1(2)	2(2)	-2(2)
C23	56(2)	54(2)	56(3)	4(2)	-4(2)	-6(2)
C24	53(2)	60(2)	56(3)	7(2)	-2(2)	-2(2)
C25	57(2)	65(2)	62(3)	3(2)	2(2)	2(2)
C26	50(2)	67(2)	64(3)	3(2)	-1(2)	6(2)
C27	61(3)	84(3)	69(3)	4(2)	8(2)	13(2)

C28	47(2)	77(3)	88(4)	5(2)	6(2)	14(2)
C29	39(2)	62(2)	73(3)	10(2)	-3(2)	3(2)
C30	38(2)	58(2)	66(3)	7(2)	-5(2)	3(2)
C31	42(2)	53(2)	70(3)	4(2)	-11(2)	-1(2)
C32	35(2)	59(2)	66(3)	2(2)	-9(2)	-3(2)
C33	44(2)	60(2)	70(3)	2(2)	-12(2)	-1(2)
C34	58(3)	70(3)	80(3)	12(2)	-9(2)	2(2)
C35	62(3)	84(3)	68(3)	5(2)	-9(2)	4(2)
C36	56(2)	77(3)	68(3)	-6(2)	-8(2)	8(2)
C37	42(2)	61(2)	67(3)	-1(2)	-10(2)	-2(2)
C38	52(2)	58(2)	65(3)	-6(2)	-10(2)	1(2)
C39	45(2)	59(2)	64(3)	-2(2)	-7(2)	-3(2)
C40	45(2)	53(2)	67(3)	-10(2)	-7(2)	-1(2)
C41	50(2)	68(3)	64(3)	-8(2)	-3(2)	6(2)
C42	48(2)	61(2)	66(3)	-11(2)	-7(2)	7(2)
C43	43(2)	51(2)	70(3)	-10(2)	-8(2)	3(2)
C44	47(2)	57(2)	68(3)	-8(2)	-3(2)	2(2)
C45	45(2)	63(2)	75(3)	-12(2)	-3(2)	1(2)
C46	51(2)	61(2)	83(3)	6(2)	-4(2)	2(2)
C47	55(3)	73(3)	88(4)	16(3)	-2(2)	0(2)
C48	50(2)	76(3)	90(4)	21(3)	-2(2)	6(2)
C49	57(3)	85(3)	94(4)	14(3)	-2(2)	5(2)
C50	60(3)	115(4)	111(5)	37(4)	13(3)	1(3)
C51	77(4)	112(4)	114(5)	55(4)	4(3)	3(3)
C52	67(3)	109(4)	107(5)	44(4)	-4(3)	4(3)
C53	56(3)	91(4)	128(5)	14(3)	-3(3)	5(3)
C54	63(3)	114(5)	117(5)	15(4)	-2(3)	15(3)
C55	52(3)	117(5)	126(5)	13(4)	9(3)	0(3)
C56	59(3)	91(4)	137(6)	16(4)	7(3)	-3(3)
O1	122(5)	96(5)	183(5)	52(4)	-53(4)	-14(4)
C57	137(6)	103(4)	181(6)	49(4)	-49(5)	-16(5)
C58	142(7)	113(5)	187(6)	43(5)	-54(6)	-16(6)
C59	150(7)	107(5)	190(7)	39(5)	-56(6)	-16(5)
C60	128(6)	96(5)	187(6)	38(5)	-56(5)	-18(5)
O1A	124(6)	96(5)	182(6)	49(5)	-53(5)	-18(5)
C57A	134(7)	102(5)	180(6)	49(5)	-47(6)	-19(5)

C58A	141(7)	114(6)	186(7)	43(6)	-48(7)	-18(6)
C59A	141(7)	108(5)	187(6)	41(5)	-50(6)	-21(5)
C60A	136(6)	102(5)	183(6)	44(5)	-54(5)	-16(5)
O2	160(4)	136(4)	155(4)	9(4)	5(4)	-7(4)
C61	145(4)	137(4)	137(4)	-1(4)	0(4)	8(4)
C62	142(4)	130(4)	140(4)	-4(4)	4(4)	-4(4)
C63	139(5)	107(4)	122(5)	-7(4)	-14(4)	-10(4)
C64	152(5)	129(5)	135(5)	-1(4)	5(5)	-5(4)
N5	70(3)	145(5)	88(4)	-27(3)	-24(3)	46(3)
C65	62(4)	239(11)	116(6)	-47(7)	-33(4)	-22(5)
C66	72(5)	229(11)	277(14)	-134(11)	-25(6)	-38(6)
N6	81(3)	81(3)	89(3)	-2(2)	12(2)	15(2)
C67	78(3)	58(2)	81(3)	-4(2)	14(3)	-1(2)
C68	86(4)	97(4)	113(5)	-9(4)	30(3)	0(3)
N7	90(3)	67(3)	150(5)	0(3)	-15(3)	8(2)
C69	92(5)	88(4)	167(8)	13(5)	-20(5)	17(3)
C70	146(8)	178(9)	174(10)	32(8)	-36(7)	-1(7)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **2**.

	x	y	z	U(eq)
H1N	3911	4692	1487	65
H2N	3657	7310	2452	65
H3N	-456	6058	1389	81
H4N	-691	8836	1612	97
H1A	247	10467	790	101
H3A	-1345	10840	811	117
H4A	-2603	10145	1177	131
H6	-2934	8777	1721	129
H7	-1565	7896	2043	113
H10	-1554	6530	1767	99
H11	-1453	5402	2613	89
H13	-166	4304	2476	82
H14	870	4103	1727	81
H15	492	5751	642	76
H17	1662	4569	879	75
H19	665	5471	-242	77
H20	1175	5697	-1107	82
H21	2562	5428	-1287	82
H22	3417	5028	-584	77
H24	2960	4886	818	67
H25	4077	4412	31	74
H1	5499	3799	438	85
H28	6076	3611	1367	85
H30	5506	3939	2395	65
H31	4152	4960	2397	66
H33	5053	3441	3204	70
H34	5048	3335	4133	83
H35	4602	4440	4668	86
H36	4172	5665	4244	80
H38	3324	6456	3795	70
H39	4182	6149	2851	67

H41	2165	7678	3689	73
H42	1802	8678	2951	70
H44	3280	8422	1777	69
H45	1734	9085	1955	73
H48	700	9058	1345	86
H49	3557	9526	1263	94
H50	3726	10222	453	114
H51	2600	10554	-79	121
H52	1281	10291	253	113
H53	-3595	8239	2476	110
H54	-4485	7324	2861	118
H55	-4141	5953	2973	118
H56	-2883	5473	2630	115
H57A	-127	7234	296	168
H57B	-170	7847	808	168
H58A	-891	8232	-54	177
H58B	-1325	8430	519	177
H59A	-2343	7542	96	179
H59B	-1646	6937	-151	179
H60A	-2080	7191	923	165
H60B	-1923	6331	621	165
H57C	99	7070	397	166
H57D	96	7728	884	166
H58C	-465	7977	-110	177
H58D	-552	8601	395	177
H59C	-1907	8185	563	174
H59D	-1888	7814	-48	174
H60C	-2032	6863	716	168
H60D	-1447	6624	220	168
H61A	3703	8205	28	168
H61B	3600	7395	-341	168
H62A	3219	6661	380	165
H62B	3383	7457	756	165
H63A	1924	6846	539	147
H63B	2087	7735	801	147
H64A	1517	8209	128	167

H64B	1575	7346	-191	167
H61C	3528	7404	-542	168
H61D	2889	6679	-410	168
H62C	3606	6565	375	157
H62D	3940	7503	340	157
H63C	2361	6967	674	163
H63D	2927	7644	965	163
H64C	2616	8586	392	172
H64D	1772	8075	415	172
H66A	1587	6458	2126	289
H66B	1982	6234	2702	289
H66C	1266	5674	2456	289
H68A	5720	6568	954	148
H68B	5618	5686	1237	148
H68C	6154	6388	1525	148
H70A	437	6525	2916	248
H70B	-341	7034	3122	248
H70C	559	7399	3207	248

Table S6. Torsion angles [°] for **2**.

C5-N4-C2-C3	1.9(8)
C5-N4-C2-C1	-176.7(7)
C48-C1-C2-N4	-0.1(12)
C48-C1-C2-C3	-178.4(7)
N4-C2-C3-C4	-2.2(9)
C1-C2-C3-C4	176.4(7)
C2-C3-C4-C5	1.8(10)
C3-C4-C5-N4	-0.6(9)
C3-C4-C5-C6	-175.8(8)
C2-N4-C5-C4	-0.8(8)
C2-N4-C5-C6	174.5(7)
C4-C5-C6-C7	179.0(9)
N4-C5-C6-C7	4.7(14)
C5-C6-C7-C8	179.2(8)
C6-C7-C8-C53	-32.6(12)
C6-C7-C8-C9	151.9(8)
C53-C8-C9-C56	1.9(10)
C7-C8-C9-C56	177.4(6)
C53-C8-C9-C10	177.8(6)
C7-C8-C9-C10	-6.6(10)
C56-C9-C10-C11	-33.9(10)
C8-C9-C10-C11	150.2(6)
C9-C10-C11-C12	176.3(5)
C16-N3-C12-C13	2.5(5)
C16-N3-C12-C11	-173.4(4)
C10-C11-C12-N3	1.0(8)
C10-C11-C12-C13	-173.8(5)
N3-C12-C13-C14	-1.7(6)
C11-C12-C13-C14	173.6(5)
C12-C13-C14-C16	0.5(6)
C12-N3-C16-C14	-2.2(5)
C12-N3-C16-C15	177.2(4)
C13-C14-C16-N3	1.0(5)
C13-C14-C16-C15	-178.2(5)
C17-C15-C16-N3	172.8(4)
C17-C15-C16-C14	-8.0(8)

C16-C15-C17-C18	175.4(4)
C15-C17-C18-C23	152.9(4)
C15-C17-C18-C19	-28.6(7)
C23-C18-C19-C20	1.0(7)
C17-C18-C19-C20	-177.5(4)
C18-C19-C20-C21	1.5(7)
C19-C20-C21-C22	-2.4(7)
C20-C21-C22-C23	0.7(7)
C21-C22-C23-C18	1.8(7)
C21-C22-C23-C24	-176.0(4)
C19-C18-C23-C22	-2.6(6)
C17-C18-C23-C22	175.9(4)
C19-C18-C23-C24	175.2(4)
C17-C18-C23-C24	-6.3(6)
C22-C23-C24-C25	-17.5(7)
C18-C23-C24-C25	164.8(4)
C23-C24-C25-C26	178.1(4)
C29-N1-C26-C27	-0.7(5)
C29-N1-C26-C25	177.0(4)
C24-C25-C26-N1	-3.1(7)
C24-C25-C26-C27	174.2(5)
N1-C26-C27-C28	1.1(6)
C25-C26-C27-C28	-176.5(5)
C26-C27-C28-C29	-1.1(6)
C26-N1-C29-C28	0.0(5)
C26-N1-C29-C30	179.9(4)
C27-C28-C29-N1	0.6(5)
C27-C28-C29-C30	-179.2(5)
N1-C29-C30-C31	-9.1(7)
C28-C29-C30-C31	170.8(5)
C29-C30-C31-C32	174.4(4)
C30-C31-C32-C33	-31.7(6)
C30-C31-C32-C37	152.0(4)
C37-C32-C33-C34	0.0(6)
C31-C32-C33-C34	-176.5(4)
C32-C33-C34-C35	-0.5(7)

C33-C34-C35-C36	-0.2(7)
C34-C35-C36-C37	1.4(7)
C35-C36-C37-C32	-1.9(6)
C35-C36-C37-C39	176.2(4)
C33-C32-C37-C36	1.2(6)
C31-C32-C37-C36	177.6(4)
C33-C32-C37-C39	-176.9(3)
C31-C32-C37-C39	-0.6(6)
C40-C38-C39-C37	-173.7(4)
C36-C37-C39-C38	-24.1(6)
C32-C37-C39-C38	153.9(4)
C43-N2-C40-C41	-1.3(4)
C43-N2-C40-C38	174.9(3)
C39-C38-C40-N2	-6.4(6)
C39-C38-C40-C41	168.9(4)
N2-C40-C41-C42	0.5(4)
C38-C40-C41-C42	-175.5(4)
C40-C41-C42-C43	0.5(5)
C40-N2-C43-C42	1.5(4)
C40-N2-C43-C44	-179.7(3)
C41-C42-C43-N2	-1.2(4)
C41-C42-C43-C44	-179.7(4)
N2-C43-C44-C45	166.7(4)
C42-C43-C44-C45	-14.9(7)
C43-C44-C45-C46	175.6(4)
C44-C45-C46-C49	-26.0(7)
C44-C45-C46-C47	155.8(5)
C49-C46-C47-C52	2.3(8)
C45-C46-C47-C52	-179.5(5)
C49-C46-C47-C48	-178.3(5)
C45-C46-C47-C48	0.0(8)
C2-C1-C48-C47	179.0(6)
C52-C47-C48-C1	-29.0(10)
C46-C47-C48-C1	151.5(6)
C47-C46-C49-C50	-2.2(9)
C45-C46-C49-C50	179.4(6)

C46-C49-C50-C51	-0.5(11)
C49-C50-C51-C52	3.1(12)
C46-C47-C52-C51	0.4(10)
C48-C47-C52-C51	-179.1(6)
C50-C51-C52-C47	-3.1(12)
C9-C8-C53-C54	-3.6(11)
C7-C8-C53-C54	-179.1(6)
C8-C53-C54-C55	3.7(11)
C53-C54-C55-C56	-1.9(11)
C8-C9-C56-C55	-0.2(11)
C10-C9-C56-C55	-176.2(6)
C54-C55-C56-C9	0.1(11)
C60-O1-C57-C58	13(3)
O1-C57-C58-C59	-34(2)
C57-C58-C59-C60	41(2)
C57-O1-C60-C59	17(3)
C58-C59-C60-O1	-36(3)
C60A-O1A-C57A-C58A	27(4)
O1A-C57A-C58A-C59A	-5(3)
C57A-C58A-C59A-C60A	-18(3)
C57A-O1A-C60A-C59A	-42(4)
C58A-C59A-C60A-O1A	36(3)
C64-O2-C61-C62	-4.2(16)
O2-C61-C62-C63	-3.8(16)
C61-C62-C63-C64	11.4(16)
C62-C63-C64-O2	-14.0(15)
C61-O2-C64-C63	11.4(15)
C64A-O2A-C61A-C62A	-5(4)
O2A-C61A-C62A-C63A	23(3)
C61A-C62A-C63A-C64A	-36(3)
C62A-C63A-C64A-O2A	34(3)
C61A-O2A-C64A-C63A	-18(4)

Table S7. Hydrogen bonds for **2** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

N1-H1N...N5	0.88	2.13	3.012(6)	178
N2-H2N...N6	0.88	2.16	3.018(6)	166
N3-H3N...O1	0.88	2.04	2.901(12)	166
N3-H3N...O1A	0.88	2.06	2.933(18)	170
N4-H4N...N7	0.88	2.28	3.161(7)	178

References:

1) J. M. Muchowski and D. R. Solas, *J. Org. Chem.*, 1984, **49**, 203.
2) (a) A. Winter, C. Friebe, M. D. Hager and U. S. Schubert, *Eur. J. Org. Chem.*, 2009, 801; (b) C. N. Robinson and R. C. Lewis, *J. Heterocycl. Chem.*, 1973, **10**, 395.
3) Gaussian 09, Revision A.1, M. J. Frisch; G. W. Trucks; H. B. Schlegel; G. E. Scuseria; M. A. Robb; J. R. Cheeseman; G. Scalmani; V. Barone; B. Mennucci; G. A. Petersson; H. Nakatsuji; M. Caricato; X. Li; H. P. Hratchian; A. F. Izmaylov; J. Bloino; G. Zheng; J. L. Sonnenberg; M. Hada; M. Ehara; K. Toyota; R. Fukuda; J. Hasegawa; M. Ishida; T. Nakajima; Y. Honda; O. Kitao; H. Nakai; T. Vreven; J. A. Montgomery, Jr.; J. E. Peralta; F. Ogliaro; M. Bearpark; J. J. Heyd; E. Brothers; K. N. Kudin; V. N. Staroverov; R. Kobayashi; J. Normand; K. Raghavachari; A. Rendell; J. C. Burant; S. S. Iyengar; J. Tomasi; M. Cossi; N. Rega; N. J. Millam; M. Klene; J. E. Knox; J. B. Cross; V. Bakken; C. Adamo; J. Jaramillo; R. Gomperts; R. E. Stratmann; O. Yazyev; A. J. Austin; R. Cammi; C. Pomelli; J. W. Ochterski; R. L. Martin; K. Morokuma; V. G. Zakrzewski; G. A. Voth; P. Salvador; J. J. Dannenberg; S. Dapprich; A. D. Daniels; Ö. Farkas; J. B. Foresman; J. V. Ortiz; J. Cioslowski; D. J. Fox Gaussian, Inc., Wallingford CT, **2009**.
4) (a) Becke, A. D. *Phys. Rev. A*, 1988, ***38*****,** 3098; (b) C. Lee, W. Yang and R. G. Parr *Phys. Rev. B,* 1988, **37**, 785.
5) *SAINT V8.27B* Bruker AXS Inc, (2012), Madison, WI.
6) *XS*. Program for the Solution of Crystal Structures. Sheldrick, G. M., *Acta Cryst*., 2008, **A64**, 112-122.
7) *SHELXL-2013*. Program for the Refinement of Crystal Structures. Sheldrick, G. M. *Acta Cryst.,* 2008, **A64**, 112-122.
8) *PLATON*, A Multipurpose Crystallographic Tool. Spek, A. L. (1998). Utrecht University, The Netherlands.
9) *WinGX 1.64*. An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. *J. Appl. Cryst*. 1999, **32**. 837-838.
10) *SQUEEZE*. Sluis, P. v. d. and Spek, A. L. *Acta Cryst*., 1990, **A46**, 194-201.
11) $R_W(F^2) = \{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|)^4\}^{1/2}$ where w is the weight given each reflection.
$R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|\}$ for reflections with $F_o > 4(\sigma(F_o))$.
$S = [\Sigma w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.
12) *International Tables for X-ray Crystallography* (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
13) *SHELXTL/PC* (Version 5.03). Sheldrick, G. M. (1994). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.