Electronic Supporting Information for:

Tetrathiafulvalene-annulated [28]hexaphyrin(1.1.1.1.1.1): A multi-electron donor system subject to conformational control†

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General Experimental Sections

Instruments and materials.

^{1}H-NMR (400 MHz) and ^{19}F-NMR (282 MHz) spectra were recorded on a Bruker Avance II spectrometer and JEOL JNM-AL300 spectrometer, respectively. Chemical shifts (δ-scale) are reported in ppm relative to residual solvent and internal standard signals (CD_2Cl_2: 5.32 ppm and CD_3CN; 1.93 ppm for ^{1}H and $CFCl_3$: 0.0 ppm for ^{19}F). MALDI-TOF mass spectra were recorded on a BRUKER microflex 2 LRF20 spectrometer using dithranol (1,8,9-trihydroxyantharacene) as a matrix. Steady-state absorption spectra were acquired using a UV-vis-NIR spectrometer (Varian, Cary 5000). Elemental analysis was performed using a Thermo Finnigan Elemental Analyzer.

All chemicals and solvents were obtained from Aldrich chemicals in reagent grade purity and used without further purification unless otherwise noted. TTF-pyrrole(**2**) was prepared according to previously published procedures.[S1] 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 a JAIJEL-1H and -2H columns.

Electrochemical measurements.

Square wave voltammogram measurements were carried out using an electrochemical workstation (model 660B, CH Instruments) with a Pt working electrode (diameter 0.4 mm), a Pt wire counter electrode, and a Ag wire quasi-reference electrode in solvents that contained 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) under an Ar atmosphere. Ferrocene (Fc) was added as an internal reference for the Ag quasi-reference electrode. Potentials are reported versus the Fc/Fc^+ couple. Square wave voltammogram scanning was conducted with a pulse amplitude of 60 mV and a potential increment of 4 mV at a frequency of 25 Hz. The concentration of all the entities was maintained at 1.0 mM in CH_3CN and CH_2Cl_2.

EPR measurements.

The EPR measurements of photoexcited **1** were carried out with a JES-RE1XE X-band spectrometer (JEOL) to detect the transient radical species in a solution of 8 M) in frozen THF at 77K under irradiation with light from a high pressure mercury lamp (USH-1005D, Ushio). A quartz EPR tube containing a deaerated solution of **1** was irradiated in the cavity of the EPR spectrometer with the focused light of a 1000 W high-pressure Hg lamp through an aqueous filter. The *g* values were calibrated using an Mn^{2+} marker.

Femtosecond transient absorption measurements.

A dual-beam femtosecond time-resolved transient absorption spectrometer was used for this study. It consisted of a self-mode-lock femtosecond Ti:sapphire laser (Coherent, MIRA), a Ti:sapphire regenerative amplifier (Clark MXR, CPA-1000) pumped by a Q-switched Nd:YAG laser (ORC-1000), a pulse stretcher/compressor, an optical parametric generation (OPG) and optical parametric amplification (OPA) system, and an optical detection system. The amplified pulses were colour-tuned by the optical parametric amplification technique. The resulting laser pulses had a pulse width of approximately 150 fs and an average power of 5-30 mW at a 1 kHz repetition rate in the range of 550-700 nm. The pump beam was focused to a 1 mm diameter spot, and the laser fluence was adjusted to less than approximately 1.0 mJ cm^2 by the use of a variable neutral-density filter. The fundamental beam that remained in the OPG-OPA system was focused onto a flowing water cell to generate a white-light continuum, which was again split into two parts: One part of the white-light continuum was overlapped with the pump beam at the sample to probe the transient, whereas the other part of the beam was passed through the sample without overlapping the pump beam. The time delay between pump and probe beams was controlled by making the pump beam travel along a variable optical delay. The two white continuum beams were sent to a 15 cm focal-length spectrograph (Acton Research) through optical fibers and then detected by use of dual

512-channel photodiode arrays (Princeton Instruments). The intensity of the white light that reached each 512-channel photodiode array was processed to calculate the absorption difference spectrum at the desired time delay between the pump and probe pulses. To obtain the time-resolved transient-absorption difference signal at a specific wavelength, the monitoring wavelength was selected by using an interference filter. By chopping the pump pulses at 43 Hz, the modulated probe pulses as well as the reference pulses could be detected by using two separate photodiodes. The output current was amplified by using a homemade fast preamplifier, and then the resultant voltage signals of the probe pulses were gated and processed by using a boxcar averager. The resultant modulated signal was measure by a lock-in amplifier and then fed into a personal computer for further signal processing.

X-ray experimental for 1•1.7$CHCl_3$•1.7C_4H_8O:

Crystals of **1** were grown as black prisms by slow evaporation from chloroform and diethyl ether. The datum crystal was cut from a larger crystal and had approximate dimensions; 0.39 × 0.11 × 0.09 mm. The data were collected on a Rigaku AFC12 diffractometer with a Saturn 724+ CCD using a graphite monochromator with MoKa radiation (λ = 0.71073 Å). A total of 1372 frames of data were collected using ω-scans with a scan range of 0.5° and a counting time of 32 seconds per frame. The data were collected at 100 K using a Rigaku XStream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table S1. Data reduction were performed using the Rigaku Americas Corporation's Crystal Clear version 1.40.[S2] The structure was solved by direct methods using SIR97[S3] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.[S4] Structure analysis was aided by use of the programs PLATON98[S5] and WinGX.[S6] The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2 x U_{eq} of the attached atom (1.5 x U_{eq} for methyl hydrogen atoms).

The macrocycle resides around a crystallographic two-fold rotation axis at 1/2, y, 1/4. In the asymmetric unit, two of the pentafluorophenyl groups and one benzodithiol group were disordered. The disordered groups were modelled in essentially the same manner. For example, for a pentafluorophenyl group, the site occupancy factor for atoms of one component was assigned the variable x, while the site occupancy factors for the alternate component were set to (1-x). A common isotropic displacement parameter was refined for the F atoms and a second one for the C atoms. The geometry of the two components was restrained to be approximately equal throughout the refinement. In this way, the site occupancy factor for one component consisting of atoms, C23a, C24a, C25a, C26a, C27a, C28a, F1a, F2a, F3a, F4a and F5a refined to 52%. In the other disordered pentafluorophenyl group the site occupancy factor refined to 50%, as did the disordered benzodithiol group.

Two molecules of what appeared to be diethyl ether and chloroform were badly disordered. Attempts to model the disorder were unsatisfactory. The contributions to the scattering factors due to these solvent molecules were removed by use of the utility SQUEEZE[S7] in PLATON98. The electron count obtained using SQUEEZE indicated that slightly less than two molecules of each solvent were present in the crystal. The formula was adjusted to correspond to the SQUEEZE results. The function, $\Sigma w(|F_O|^2 - |F_C|^2)^2$, was minimized, where $w = 1/[(\sigma(F_O))^2 + (0.145{*}P)^2]$ and $P = (|F_O|^2 + 2|F_C|^2)/3$. $R_W(F^2)$ refined to 0.234, with $R(F)$ equal to 0.0800 and a goodness of fit, S, = 1.01. Definitions used for calculating $R(F)$, $R_W(F^2)$ and the goodness of fit, S, are given below.[S8] The data were checked for secondary extinction effects 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).[S9] All figures were generated using SHELXTL/PC.[S10] Further details of this structure (**1**) can be obtained from the Cambridge Crystallographic Data Centre by quoting reference number CCDC 946746.

Table S1. Crystallographic parameters for **1**.

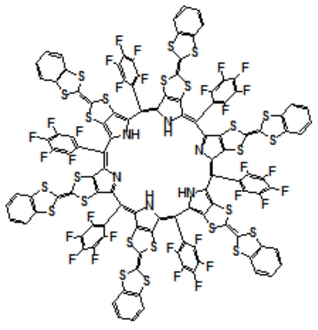
Empirical formula	$C_{122.5} H_{46.7} Cl_{5.1} F_{30} N_6 O_{1.7} S_{24}$	
Formula weight	3149.79	
Temperature	100(2) K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	*C2/c*	
Unit cell dimensions	a = 20.732(2) Å	α = 90°.
	b = 24.908(2) Å	β = 104.3(3)°.
	c = 28.820(3) Å	γ = 90°.
Volume	14422(9) $Å^3$	
Z,Z'	4,0	
Density (calculated)	1.451 Mg/m^3	
Absorption coefficient	0.538 mm^{-1}	
F(000)	6312	
Crystal size	0.39 x 0.11 x 0.09 mm	
Theta range for data collection	3.06 to 25.00°.	
Index ranges	$-24<=h<=23, 0<=k<=29, 0<=l<=34$	
Reflections collected	12694	
Independent reflections	12694 [*R*(int) = 0.0000]	
Completeness to theta = 25.00°	99.8%	
Absorption correction	Semi-empirical	
Max. and min. transmission	1.00 and 0.416	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12694 / 1542 / 1065	
Goodness-of-fit on F^2	0.985	
Final *R* indices [I > 2sigma(I)]	$R1$ = 0.0800, $wR2$ = 0.2103	
R indices (all data)	$R1$ = 0.1224, $wR2$ = 0.2338	
Largest diff. peak and hole	0.536 and -0.295 e.$Å^{-3}$	

DFT calculations

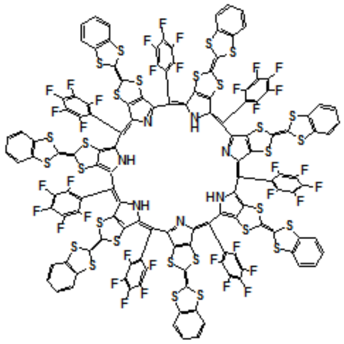
Quantum mechanical calculations were performed using the Gaussian 09 program suite.[S11] All calculations were carried out by the density functional theory (DFT) method with Becke's three-parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP)[S12] a basis set of 3-21G* was employed for all atoms. Ground state geometries were fully optimized and verified by using frequency calculations, where no imaginary frequency was found. To simulate the steady-state absorption spectra, the time-dependent (TD)-DFT calculations at the B3LYP/3-21G* levels were employed on the basis of the optimized structures. The solvation effect on the static electronic contribution was evaluated for by means of TD-DFT calculations using the polarizable continuum model (PCM) method implemented in the Gaussian program using the dielectric constants of toluene ($\varepsilon = 2.379$) and acetonitrile ($\varepsilon = 36.64$), respectively.

Synthetic Experimental for 1

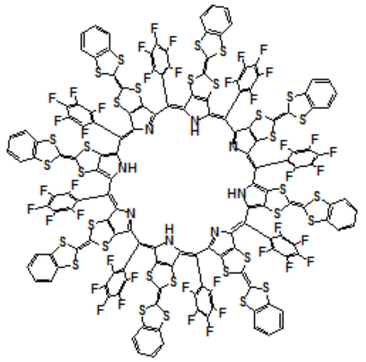
Benzo-TTF-pyrrole (**2**, 0.880 g, 3 mmol) and 2,3,4,5,6-pentafluorophenyl aldehyde (0.37 mL, 3 mmol) were dissolved in anhydrous CH_2Cl_2. The solution was degassed for 30 min by bubbling with argon before addition of a catalytic amount of $BF_3{\bullet}OEt_2$. Then the reaction mixture was stirred for 2 h at room temperature. Treatment with DDQ (1.49 g, 6.6 mmol) for 15 min, followed by neutralization with triethylamine, gave crude reaction mixture containing various higher order TTF-[n]phyrins (n = 6, 7, 8 and 9) as inferred from a MALDI-TOF mass spectrometric analysis below. Purification was effected by silica gel column chromatography followed by recycling GPC separation. This gave analytically pure hexaphyrin, **1**. Recrystallization from a $CHCl_3$–diethyl ether mixture generally afforded pure crystalline products. Yield: 6%; ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ [ppm] = 16.58 (s, 2H, NH), 13.64 (s, 2H, NH), 7.48 (d, J = 7.6 Hz, 2H, Ar-H), 7.34-7.15 (m, 20H, Ar-H), 6.82 (d, J = 7.8 Hz, 2H, Ar-H); ^{19}FNMR spectra (282 MHz, CD_2Cl_2, 298 K): δ [ppm] = -135.48, -136.82, -137.40, -137.98 (12F, *o*-F); -148.23, -149.66 (6F, *p*-F), -158.40, -158.92, -159.55 (12F, *m*-F). High resolution MALDI-TOF-MS: *m/z* calcd for $C_{114}H_{28}N_6S_{24}F_{30}$: 2817.5193; found: 2817.5187; elemental analysis calcd (%) for $C_{114}H_{28}N_6S_{24}F_{30}$: C 48.54, H 1.00, N 2.98, S 27.28; found: C 48.59, H 1.04, N 2.83, S 27.28.



Hexaphyrin (1)
Calculated mass:2817.52



Heptaphyrin
Calculated mass:3286.43



Octaphyrin
Calculated mass:3755.35

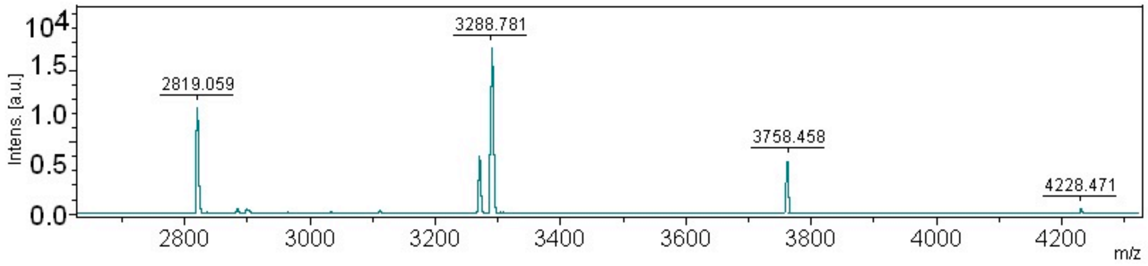
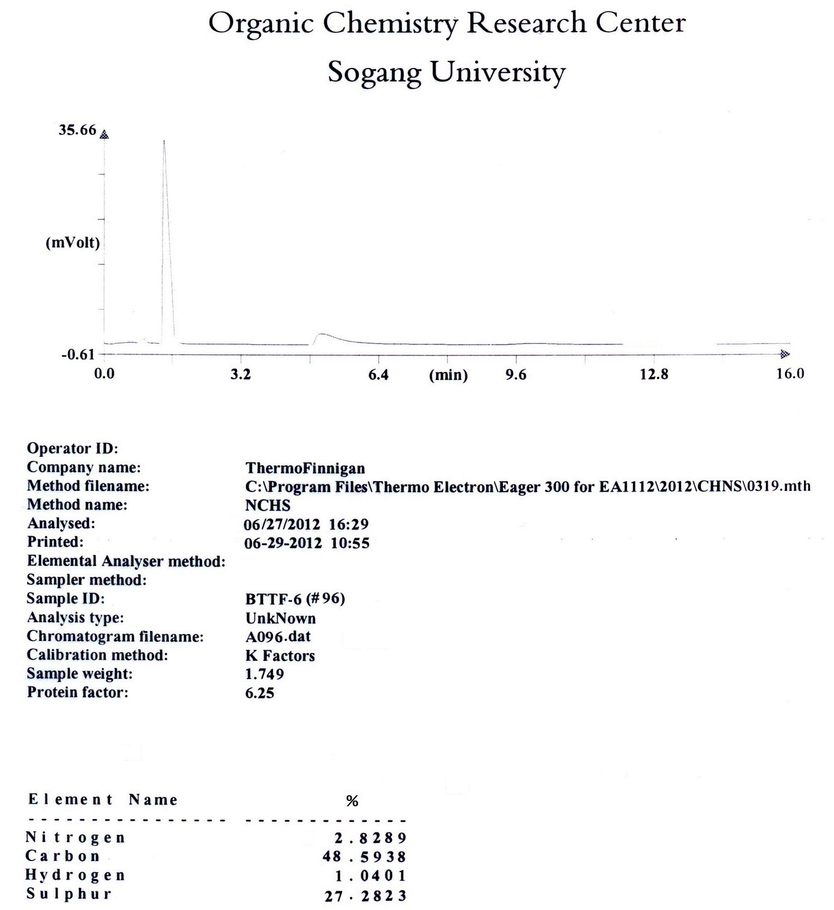


Fig. S1 MALDI-TOF mass spectrum of the reaction mixture yielding **1**.



Organic Chemistry Research Center
Sogang University

Operator ID:	
Company name:	ThermoFinnigan
Method filename:	C:\Program Files\Thermo Electron\Eager 300 for EA1112\2012\CHNS\0319.mth
Method name:	NCHS
Analysed:	06/27/2012 16:29
Printed:	06-29-2012 10:55
Elemental Analyser method:	
Sampler method:	
Sample ID:	BTTF-6 (#96)
Analysis type:	UnkNown
Chromatogram filename:	A096.dat
Calibration method:	K Factors
Sample weight:	1.749
Protein factor:	6.25

Element Name	%
Nitrogen	2.8289
Carbon	48.5938
Hydrogen	1.0401
Sulphur	27.2823

Fig. S2 Elemental analysis data for **1**.

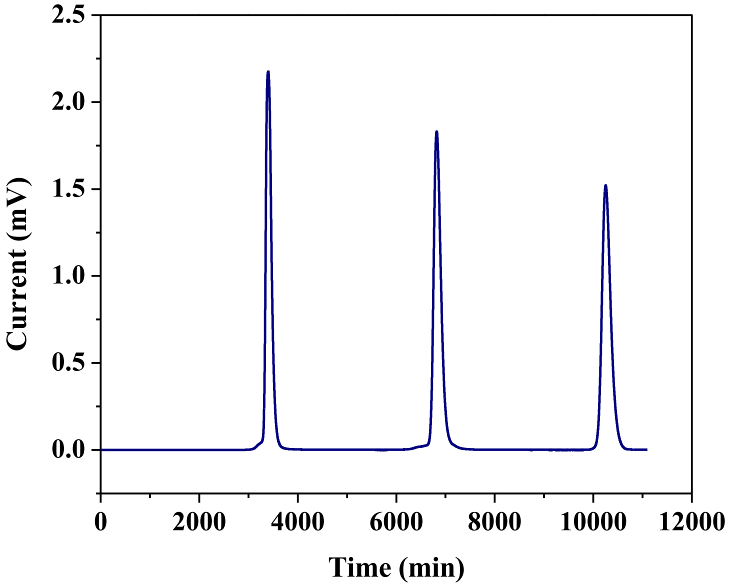


Fig. S3 Partial GPC trace for the target compound (**1**) of this study.

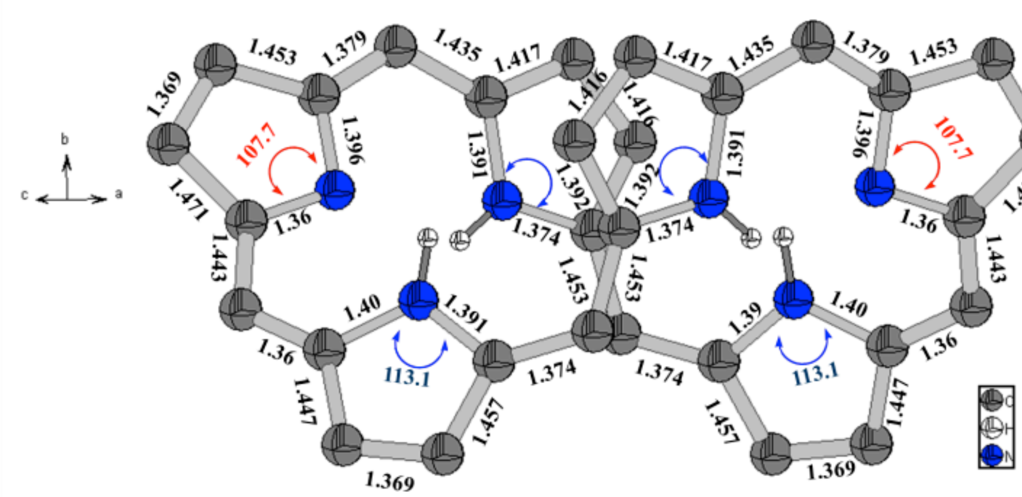


Fig. S4 Selected bond lengths and bond angles for **1**.

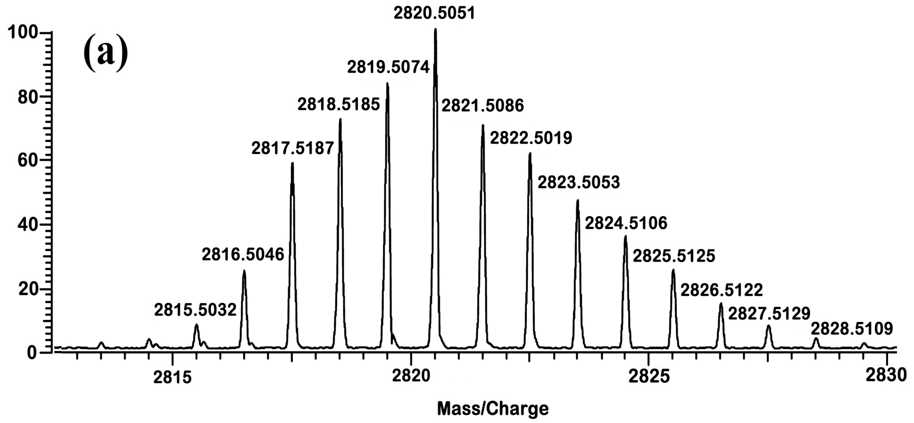


Fig. S5 High resolution MALDI-TOF mass spectrum of **1.**

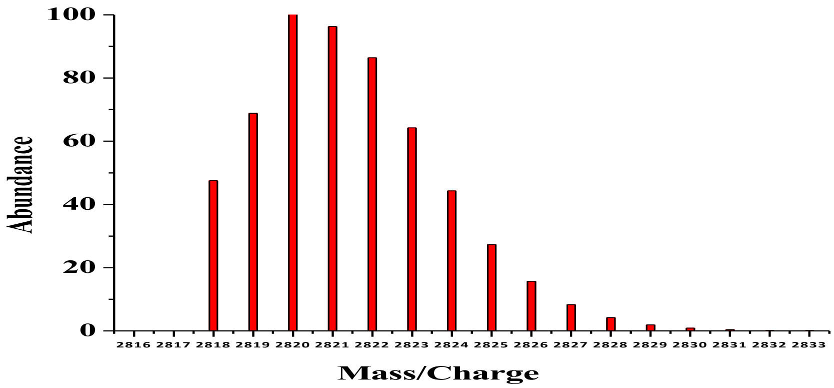


Fig. S6 Simulated mass spectrum of **1**.

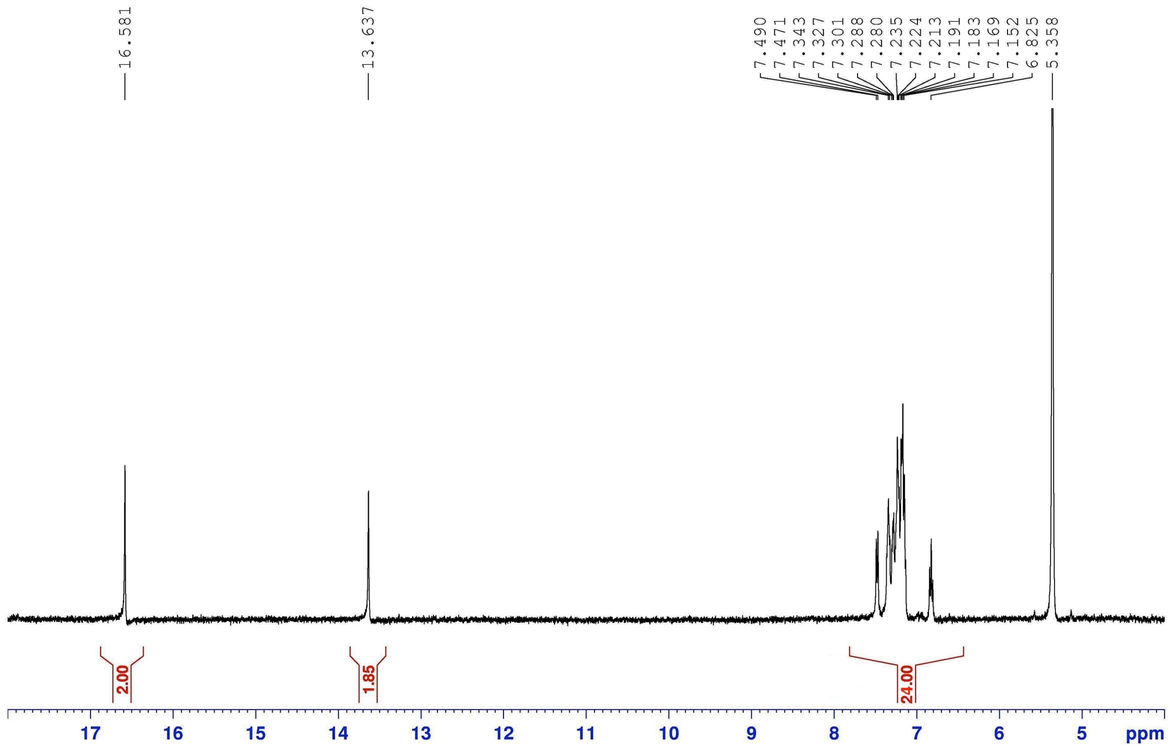


Fig. S7 ^{1}H NMR spectrum (500 MHz) of **1** recorded in CD_2Cl_2 at 298 K.

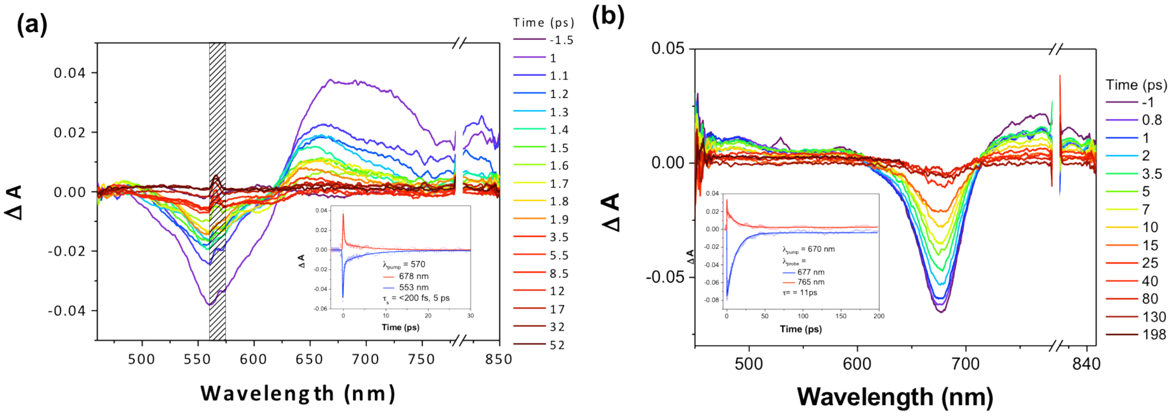


Fig. S8 Femtosecond transient absorption (TA) spectra of **1** recorded in (a) toluene and (b) benzonitrile, respectively. Inset shows the time profiles of the decay signals.

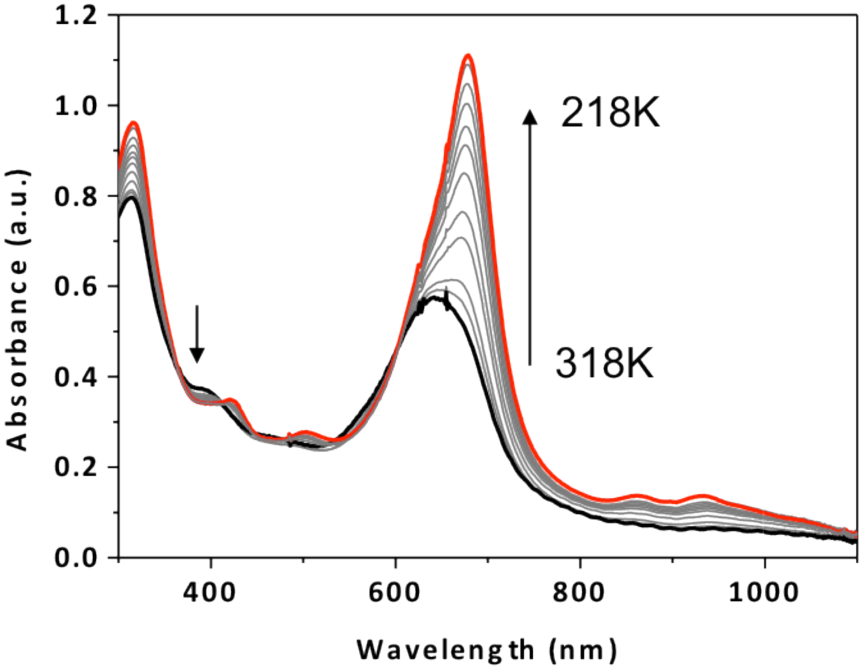


Fig. S9 UV-vis spectral changes for **1** observed in THF upon decreasing the temperature from 318 K to 218 K.

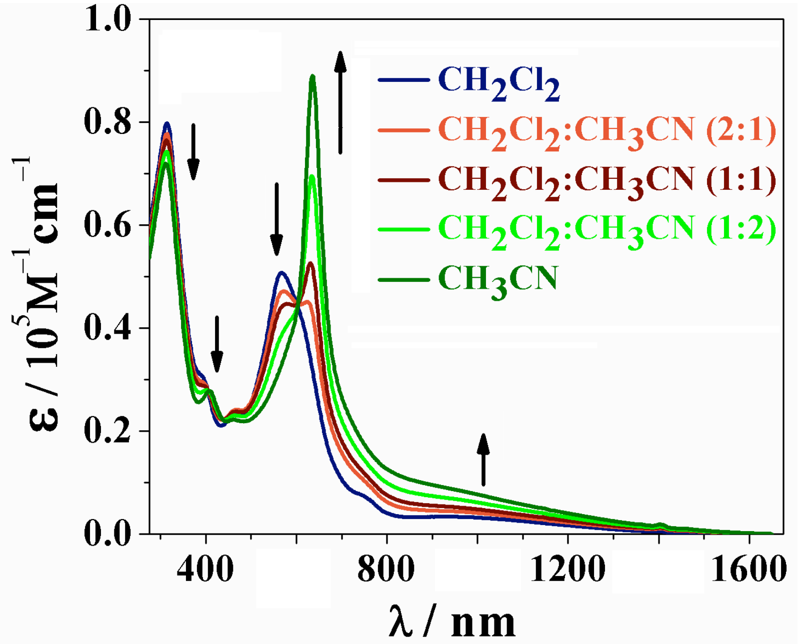


Fig. S10 UV-vis spectra of **1** recorded in pure CH_2Cl_2, pure CH_3CN and mixtures thereof.

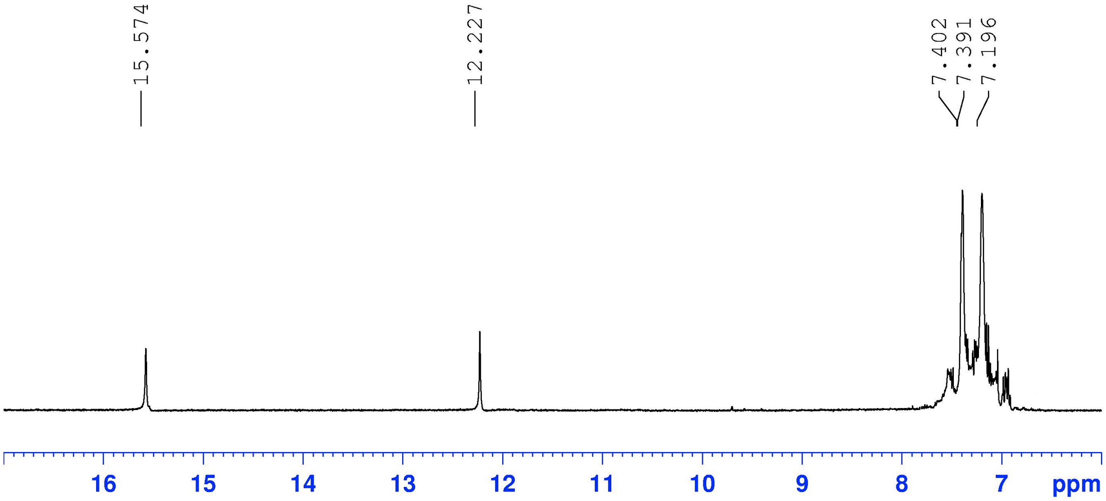


Fig. S11 ^{1}H NMR spectrum (400 MHz) of **1** recorded in THF-d_8 at 298K.

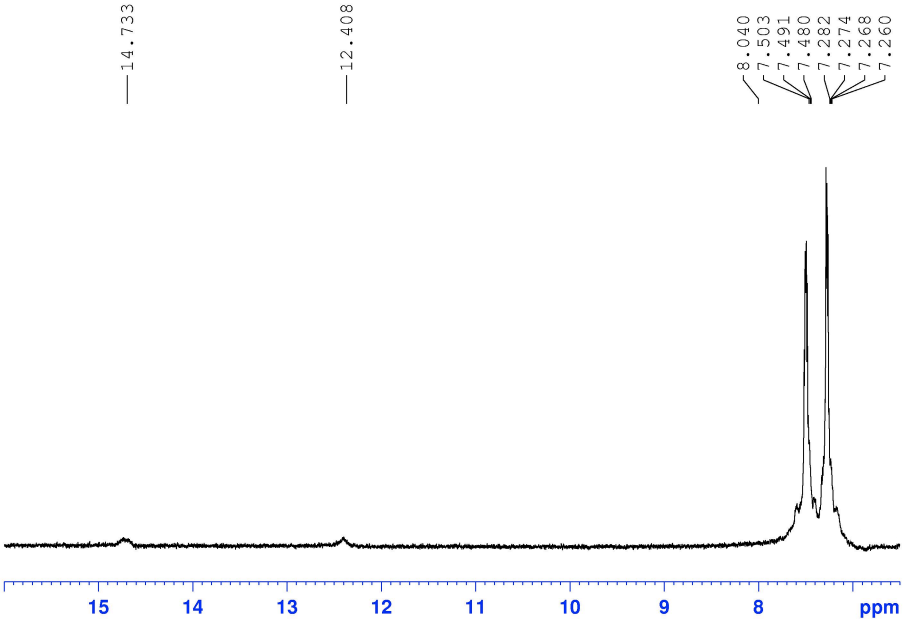


Fig. S12 ^{1}H NMR spectrum (400 MHz) of **1** recorded in acetone-d_6 at 298 K.

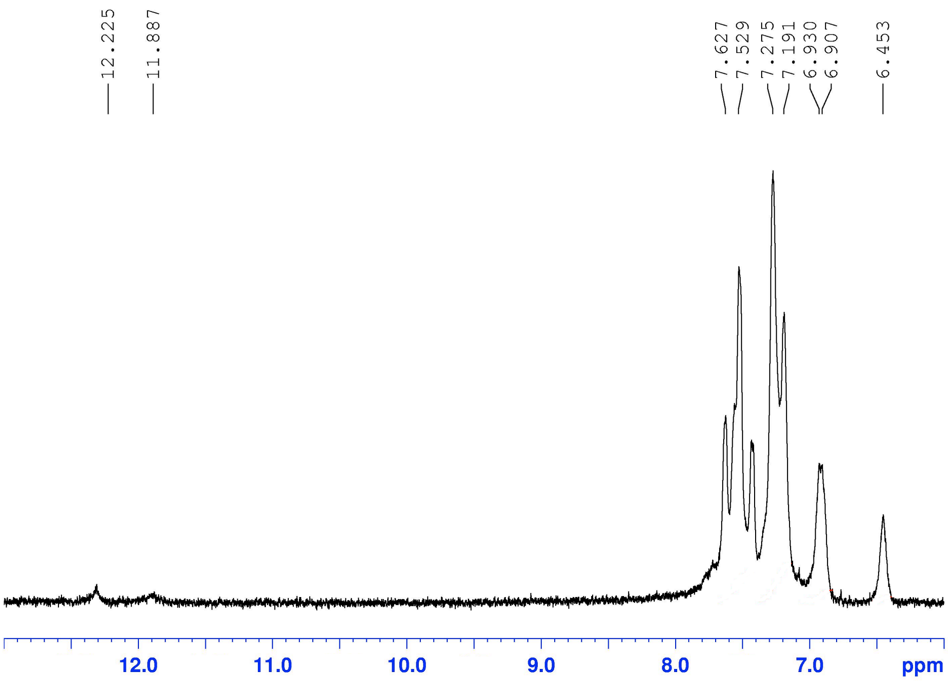


Fig. S13 ^{1}H NMR spectrum (400 MHz) of **1** recorded in DMSO-d_6 at 298 K.

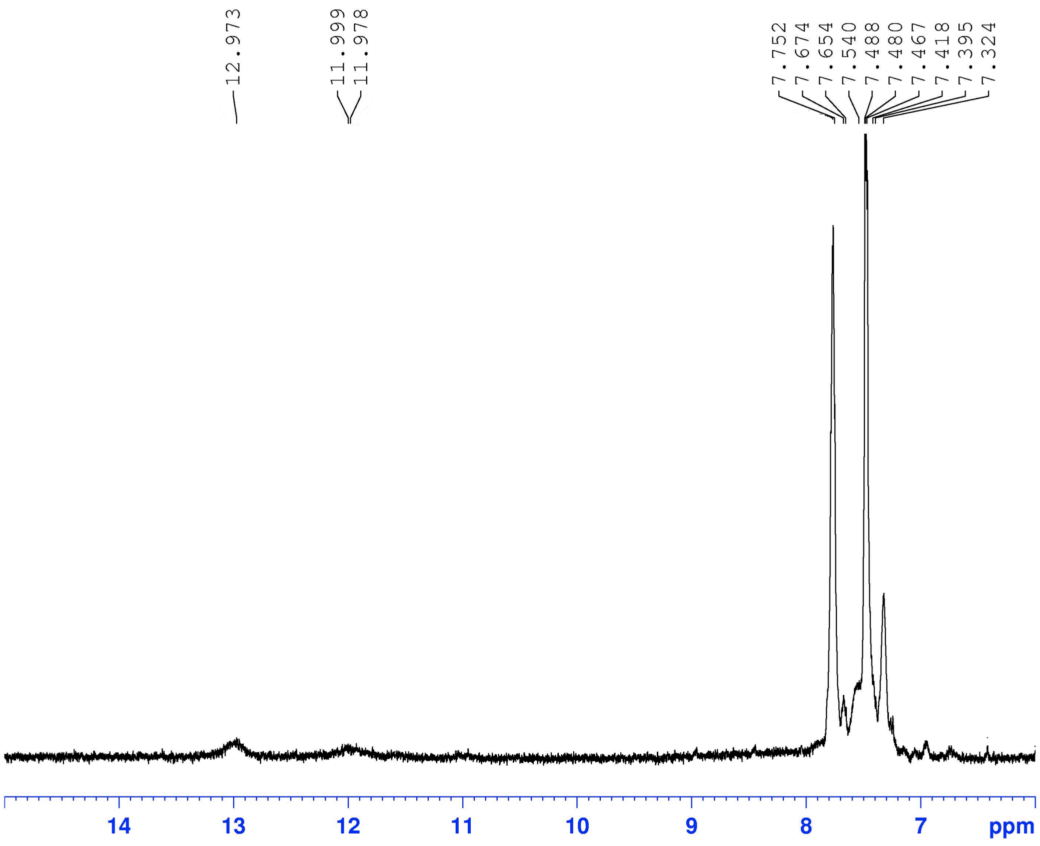


Fig. S14 ^{1}H NMR spectrum (400 MHz) of **1** recorded in *N,N*-dimethylformamide-d_7 at 298 K.

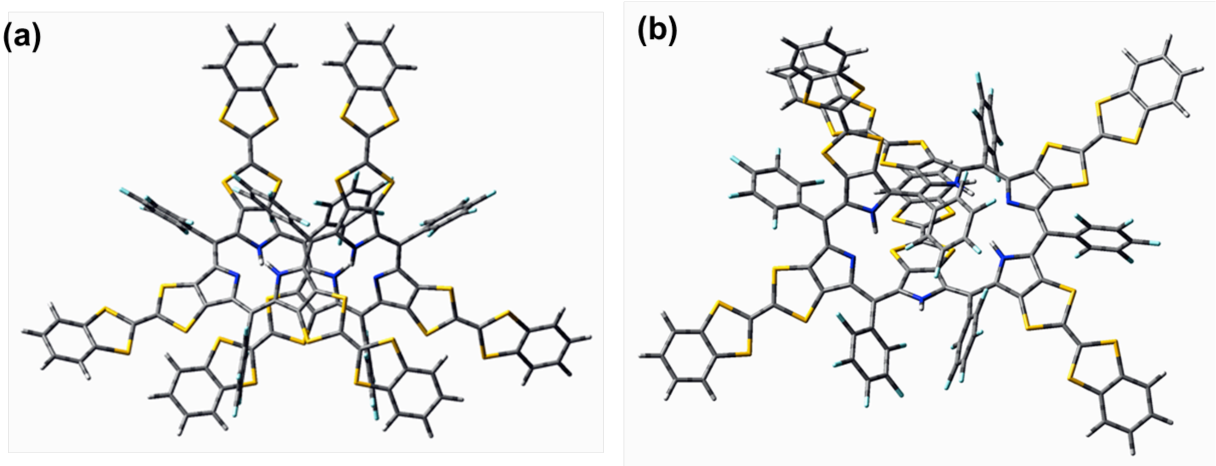


Fig. S15 Calculated optimized structures of (a) **1-H** and (b) **1-M** obtained at the B3LYP/3-21G* level.

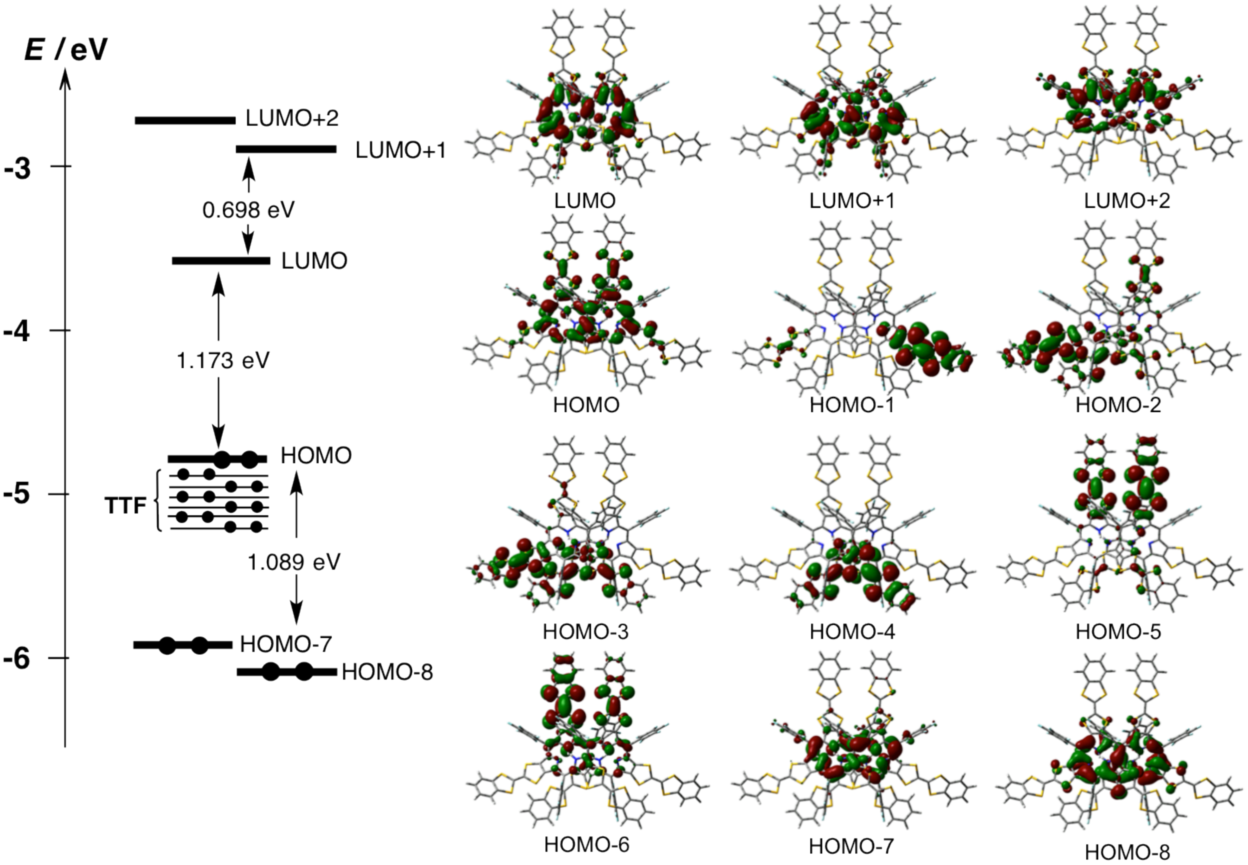


Fig. S16 Selected MO diagrams and energies for the figure-eight conformer, **1-H**. The relatively larger energy gap between the HOMO and HOMO-7 and LUMO and LUMO+1 pairs, respectively, is consistent with the weak 4n π-electron antiaromatic character proposed for **1-H**.

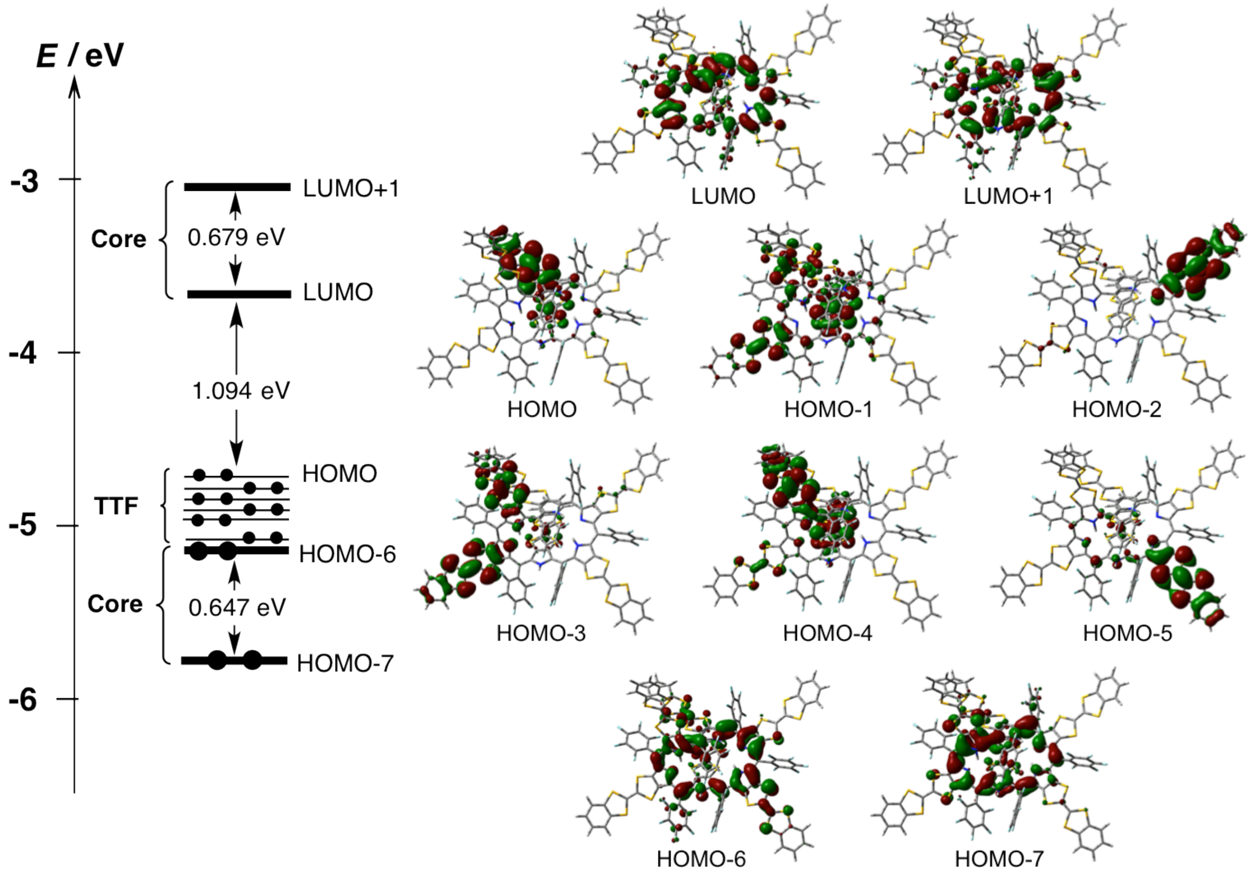


Fig. S17 Selected MO diagrams and energy of the twisted conformer, **1-M**. The trends associated with this energy diagram differ from those of **1-H** as shown above. The MOs in the present instance are dominated by the hexaphyrin electronic core.

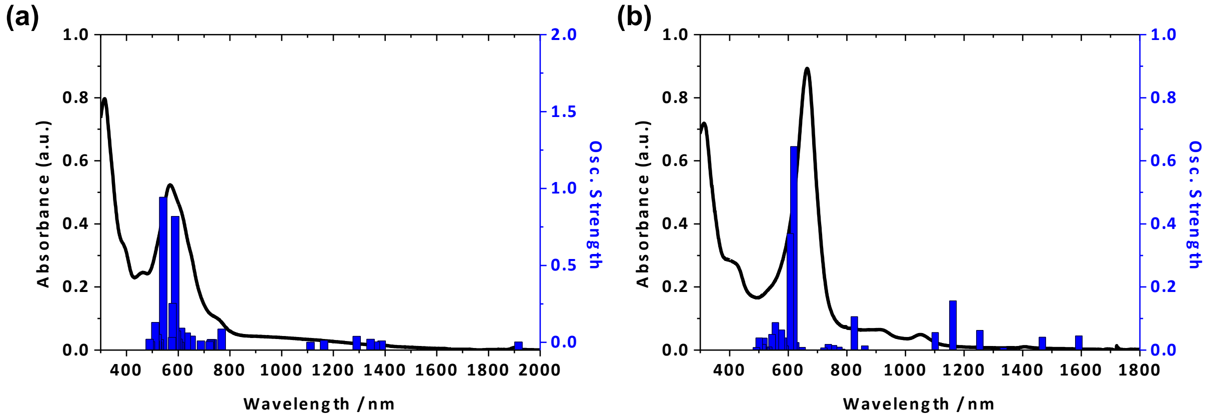


Fig. S18 TD-DFT simulated stick spectra (blue) and experimental spectra (black) of (a) **1-H** in toluene and (b) **1-M** in acetonitrile.

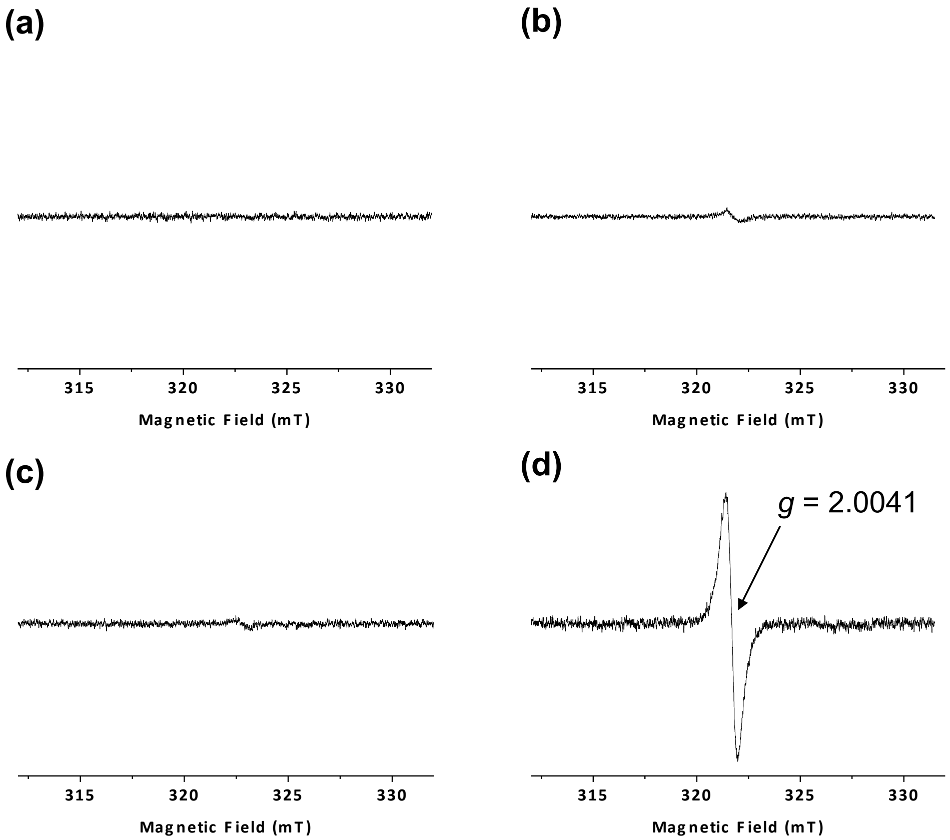


Fig. S19 EPR spectra of **1** recorded in (a) toluene at 298 K, (b) THF at 77 K in the dark, (c) toluene at 298 K under light irradiation by a high pressure Hg lamp, and (d) THF at 77 K under light irradiation by a high pressure Hg lamp.

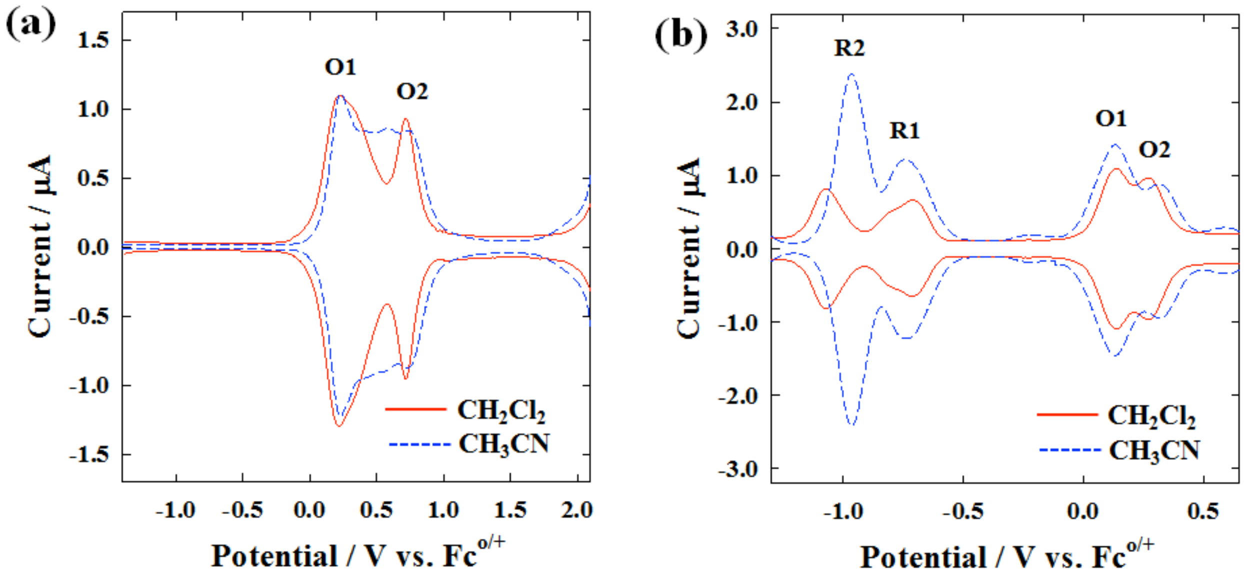


Fig. S20 Square wave voltammograms (SWVs) of **2** (a) and **3** (b) in CH_2Cl_2 and CH_3CN.

Table S2. Electrochemical data for **1-3**.

Compound	**Solvent**	**Potential[a] (electron count[b])**			
		***E*red 2**	***E*$_{Red}$ 1**	***E*$_{Ox}$ 1**	***E*$_{Ox}$ 2**
1	CH_2Cl_2	-1.04 (1 e^-)	-0.738 (1 e^-)	0.328 (6 e^-)	0.654 (12 e^-)
	CH_3CN	-1.04 (1 e^-)	-0.753 (1 e^-)	0.316 (1 e^-)	0.634 (1 e^-)
2	CH_2Cl_2			0.225 (1 e^-)	0.723 (1 e^-)
	CH_3CN			0.233 (1 e^-)	0.738 (1 e^-)
3	CH_2Cl_2	-1.07 (1 e^-)	-0.710 (1 e^-)	0.141 (1 e^-)	0.266 (1 e^-)
	CH_3CN	-0.966 (1 e^-)	-0.746 (1 e^-)	0.135 (1 e^-)	0.314 (1 e^-)

[a] Potential (V *vs*. Fc$^{0/+}$) measured by square wave voltammetry in the indicated solvent containing 0.1 M $TBAPF_6$. [b] Number of electrons estimated based on integration of current density observed in the square wave voltammograms.

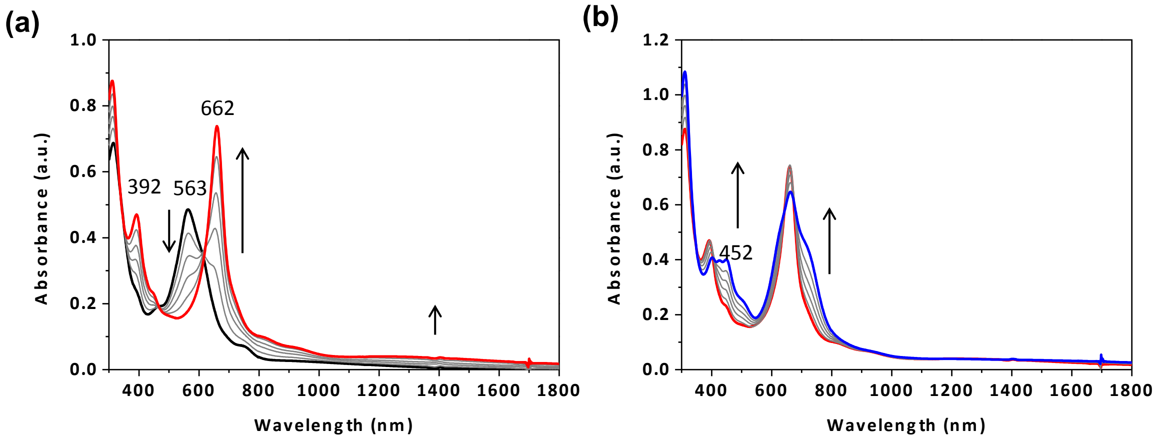


Fig. S21 UV-vis spectral titration of **1** in CH_2Cl_2 showing the changes in the optical spectrum seen upon the gradual addition of "*magic blue*" (tris(4-bromophenyl)aminium hexachloridoantimonate) from (a) 0 - 1 equiv and (b) 1 - 2 equiv.

Table S2. Energy and Cartesian coordinates for the figure eight conformer of **1-H**.

E = -17150.4074 Hartree

Row	Symbol	X	Y	Z
1	C	-0.1940610	-0.0417610	2.3108300
2	C	0.4475220	-1.2460310	2.6653370
3	C	-0.4639110	-2.3010430	2.4803410
4	C	-1.6692620	-1.7602000	1.9832620
5	C	-2.9050770	-2.3659970	1.6062010
6	C	-3.1500140	-3.7723140	2.0200530
7	C	-3.2683710	-4.7937310	1.0667510
8	C	-3.4781440	-6.1196220	1.4334920
9	C	-3.5903760	-6.4478140	2.7829590
10	C	-3.4848190	-5.4553390	3.7557620
11	C	-3.2627420	-4.1373990	3.3686450
12	F	-3.1647340	-3.2051810	4.3222570
13	F	-3.6001150	-5.7736150	5.0478060
14	F	-3.7976400	-7.7144080	3.1443200
15	F	-3.5681170	-7.0776660	0.5061970
16	F	-3.1602160	-4.5047700	-0.2341640
17	C	-3.8815220	-1.6821330	0.8842670
18	C	-5.2848820	-1.9923080	0.6952500
19	C	-5.8408110	-0.9228480	0.0375340
20	C	4.7264110	-0.0922620	0.1287100
21	C	4.7915460	1.1768420	0.8272570
22	C	6.0759380	1.9202950	0.8320100
23	C	6.8187330	2.1283990	2.0025700
24	C	8.0435380	2.7915160	1.9893240

25	C	8.5568590	3.2613560	0.7829910
26	C	7.8447240	3.0725000	-0.4004280
27	C	6.6229610	2.4102980	-0.3630230
28	F	6.3561670	1.6804590	3.1762650
29	F	8.7311030	2.9721210	3.1213180
30	F	9.7292520	3.8977370	0.7597740
31	F	8.3356060	3.5355920	-1.5536120
32	F	5.9514900	2.2532270	-1.5129190
33	C	3.6724720	1.6984190	1.4460140
34	C	3.4233920	3.0073370	2.0197340
35	C	2.1183510	3.0741400	2.4223430
36	C	1.4822890	1.7873760	2.1834730
37	C	1.7445640	-3.3975640	3.2581730
38	C	2.7654630	-4.2784490	3.3285750
39	C	5.1513190	-5.3212820	3.0479240
40	C	6.5182200	-5.5099730	2.8382590
41	H	7.2102900	-4.6830170	2.9665340
42	C	6.9820910	-6.7681750	2.4513880
43	H	8.0446150	-6.9167040	2.2835490
44	C	6.0881770	-7.8260060	2.2694150
45	H	6.4533070	-8.8010860	1.9607470
46	C	4.7199470	-7.6380320	2.4708550
47	H	4.0231600	-8.4563390	2.3161630
48	C	4.2538980	-6.3833200	2.8650770
49	C	-7.8255380	-2.4976800	0.5697000
50	C	-9.0602150	-2.9737310	0.8350490
51	C	-11.0675930	-4.1618770	2.0381950
52	C	-11.8559400	-4.9467180	2.8808730
53	H	-11.4168060	-5.7815510	3.4192860
54	C	-13.2107370	-4.6444580	3.0281070
55	H	-13.8256270	-5.2532200	3.6843340
56	C	-13.7720260	-3.5638030	2.3442170
57	H	-14.8252060	-3.3288520	2.4663250
58	C	-12.9849360	-2.7730330	1.5054630
59	H	-13.4187460	-1.9274060	0.9797770
60	C	-11.6313850	-3.0760310	1.3514640
61	C	3.0619150	5.4535340	2.7542780
62	S	4.6676630	7.6818120	2.5151270
63	S	1.8160380	7.8279540	3.3972870
64	C	3.1621300	6.7949300	2.8575070
65	C	3.9013170	9.2820620	2.4590280
66	C	4.5753060	10.4382500	2.0631740
67	H	5.6096900	10.3833260	1.7366800
68	C	3.9054190	11.6624430	2.0880460
69	H	4.4279310	12.5633410	1.7803700
70	C	2.5723360	11.7306400	2.4992360

71	H	2.0540300	12.6848250	2.5126570
72	C	1.8938020	10.5754340	2.8905780
73	H	0.8551830	10.6263290	3.2039940
74	C	2.5625620	9.3506530	2.8723480
75	C	0.2050180	1.3521970	2.4481610
76	C	-0.8351730	2.3034030	2.9467860
77	C	-0.9030050	2.6722650	4.2959280
78	C	-1.9034210	3.5119890	4.7809420
79	C	-2.8841490	3.9890950	3.9139060
80	C	-2.8596470	3.6260540	2.5687630
81	C	-1.8375760	2.8026200	2.1096120
82	F	0.0168470	2.2224610	5.1576860
83	F	-1.9332170	3.8557140	6.0718250
84	F	-3.8489390	4.7873490	4.3727430
85	F	-3.8049340	4.0690100	1.7345070
86	F	-1.8542830	2.4411400	0.8131680
87	S	0.0490880	-3.9034440	2.9712050
88	S	4.4541930	-3.7777340	3.5795750
89	S	2.5450990	-6.0386260	3.2014980
90	S	-6.3315320	-3.3353710	1.1084990
91	S	-7.5473950	-0.9994500	-0.3771760
92	S	-9.3483020	-4.4857240	1.7327100
93	S	-10.5485140	-2.1711890	0.2735440
94	S	4.4357990	4.4161020	2.2512770
95	S	1.5498990	4.5664800	3.1355500
96	C	0.1642560	-0.1115160	-2.3323110
97	C	-0.5077580	-1.3000930	-2.7036250
98	C	0.3763510	-2.3766280	-2.5244550
99	C	1.5957220	-1.8702150	-2.0179090
100	C	2.8191100	-2.4928250	-1.6361340
101	C	3.0405070	-3.9085340	-2.0289930
102	C	3.1512760	-4.9160350	-1.0603420
103	C	3.3363910	-6.2508960	-1.4068320
104	C	3.4316510	-6.6029460	-2.7515610
105	C	3.3338230	-5.6249220	-3.7394980
106	C	3.1365490	-4.2971630	-3.3723890
107	F	3.0456940	-3.3797740	-4.3405600
108	F	3.4330560	-5.9660280	-5.0270180
109	F	3.6150080	-7.8786560	-3.0934930
110	F	3.4181260	-7.1954990	-0.4649110
111	F	3.0587400	-4.6035160	0.2364440
112	C	3.8092560	-1.8074850	-0.9290290
113	C	5.2086130	-2.1287230	-0.7402350
114	C	5.7841570	-1.0459830	-0.1186880
115	C	-4.7670110	0.0090660	-0.2342520
116	C	-4.8162980	1.2483690	-0.9845860

117	C	-6.0884870	2.0073460	-1.0198570
118	C	-6.7907270	2.2424430	-2.2108090
119	C	-8.0041590	2.9253550	-2.2288750
120	C	-8.5498110	3.3873330	-1.0336460
121	C	-7.8806460	3.1690390	0.1693970
122	C	-6.6687480	2.4876800	0.1641000
123	F	-6.2982460	1.8014590	-3.3757960
124	F	-8.6512700	3.1313520	-3.3804630
125	F	-9.7121500	4.0426010	-1.0400820
126	F	-8.4033390	3.6218060	1.3130780
127	F	-6.0451800	2.2963510	1.3334480
128	C	-3.6837700	1.7279150	-1.6170670
129	C	-3.3822950	3.0175360	-2.2051790
130	C	-2.0545600	3.0471550	-2.5407190
131	C	-1.4659070	1.7586290	-2.2430000
132	C	-1.8607940	-3.4215310	-3.2822330
133	C	-2.9031490	-4.2781400	-3.3353040
134	C	-5.3094680	-5.2599410	-3.0148030
135	C	-6.6778150	-5.4134180	-2.7865940
136	H	-7.3512890	-4.5713720	-2.9157570
137	C	-7.1670000	-6.6558180	-2.3802230
138	H	-8.2306540	-6.7768570	-2.1981130
139	C	-6.2964810	-7.7328260	-2.1972080
140	H	-6.6810510	-8.6954890	-1.8735150
141	C	-4.9267070	-7.5800080	-2.4171680
142	H	-4.2479640	-8.4133670	-2.2624040
143	C	-4.4355330	-6.3412590	-2.8309900
144	C	7.7441630	-2.6623800	-0.6184750
145	C	8.9700480	-3.1627430	-0.8797890
146	C	10.9512400	-4.4163220	-2.0601810
147	C	11.7220900	-5.2384860	-2.8832440
148	H	11.2669710	-6.0829840	-3.3925290
149	C	13.0801150	-4.9611490	-3.0486250
150	H	13.6813930	-5.5990120	-3.6896550
151	C	13.6619900	-3.8683730	-2.4021980
152	H	14.7176590	-3.6530940	-2.5383180
153	C	12.8924290	-3.0403450	-1.5833900
154	H	13.3422540	-2.1853960	-1.0870540
155	C	11.5356530	-3.3181900	-1.4112710
156	C	-2.9370170	5.4125040	-3.0619320
157	S	-4.5015810	7.6812720	-2.9919200
158	S	-1.6143200	7.7298020	-3.7594780
159	C	-3.0033670	6.7495630	-3.2309950
160	C	-3.7006590	9.2655350	-2.9642450
161	C	-4.3626600	10.4506280	-2.6402500
162	H	-5.4102870	10.4312450	-2.3544680

163	C	-3.6635110	11.6578150	-2.6837610
164	H	-4.1764000	12.5812460	-2.4317820
165	C	-2.3137360	11.6806150	-3.0421160
166	H	-1.7729070	12.6218920	-3.0699380
167	C	-1.6473930	10.4965120	-3.3614520
168	H	-0.5959710	10.5123410	-3.6331010
169	C	-2.3451770	9.2884660	-3.3244750
170	C	-0.1742010	1.2950340	-2.4028010
171	C	0.9605800	2.2436050	-2.5393830
172	C	1.8891130	2.1359480	-3.5883830
173	C	3.0325520	2.9252010	-3.6513910
174	C	3.2804800	3.8614200	-2.6482940
175	C	2.3713090	4.0131670	-1.6047380
176	C	1.2379720	3.2072820	-1.5561950
177	F	1.6895040	1.2388070	-4.5603830
178	F	3.8931550	2.7924690	-4.6646540
179	F	4.3781590	4.6154820	-2.6948100
180	F	2.6073140	4.9053610	-0.6358540
181	F	0.4158800	3.3550260	-0.5067570
182	S	-0.1755930	-3.9667200	-3.0111630
183	S	-4.5821690	-3.7398170	-3.5730650
184	S	-2.7231960	-6.0417720	-3.1919440
185	S	6.2351670	-3.4973070	-1.1180440
186	S	7.4932230	-1.1331890	0.2854250
187	S	9.2297130	-4.7051200	-1.7334820
188	S	10.4738400	-2.3642670	-0.3550430
189	S	-4.3527620	4.4305640	-2.5582520
190	S	-1.4327710	4.4755250	-3.3395000
191	N	-3.6225230	-0.4563170	0.2867160
192	N	-1.4595790	-0.3906070	1.9124330
193	N	-2.5070810	0.9989750	-1.7387830
194	S	1.9795710	-1.6329440	3.4435120
195	N	3.5715060	-0.5609060	-0.3643860
196	N	2.4753590	1.0109340	1.6042510
197	N	1.4144510	-0.5014770	-1.9323010
198	S	-2.0563490	-1.6518950	-3.4649030
199	H	-2.3817670	0.1832270	-1.1436200
200	H	-2.1147320	0.1887910	1.3877670
201	H	2.3266740	0.1426460	1.0986240
202	H	2.1072940	0.0592510	-1.4346220

Table S3. Energy and Cartesian coordinates for the figure eight conformer of **1-M**.

E = -17150.4076 Hartree

Row	Symbol	X	Y	Z
1	C	-0.1940610	-0.0417610	2.3108300
2	C	0.4475220	-1.2460310	2.6653370
3	C	-0.4639110	-2.3010430	2.4803410
4	C	-1.6692620	-1.7602000	1.9832620
5	C	-2.9050770	-2.3659970	1.6062010
6	C	-3.1500140	-3.7723140	2.0200530
7	C	-3.2683710	-4.7937310	1.0667510
8	C	-3.4781440	-6.1196220	1.4334920
9	C	-3.5903760	-6.4478140	2.7829590
10	C	-3.4848190	-5.4553390	3.7557620
11	C	-3.2627420	-4.1373990	3.3686450
12	F	-3.1647340	-3.2051810	4.3222570
13	F	-3.6001150	-5.7736150	5.0478060
14	F	-3.7976400	-7.7144080	3.1443200
15	F	-3.5681170	-7.0776660	0.5061970
16	F	-3.1602160	-4.5047700	-0.2341640
17	C	-3.8815220	-1.6821330	0.8842670
18	C	-5.2848820	-1.9923080	0.6952500
19	C	-5.8408110	-0.9228480	0.0375340
20	C	4.7264110	-0.0922620	0.1287100
21	C	4.7915460	1.1768420	0.8272570
22	C	6.0759380	1.9202950	0.8320100
23	C	6.8187330	2.1283990	2.0025700
24	C	8.0435380	2.7915160	1.9893240
25	C	8.5568590	3.2613560	0.7829910
26	C	7.8447240	3.0725000	-0.4004280
27	C	6.6229610	2.4102980	-0.3630230
28	F	6.3561670	1.6804590	3.1762650
29	F	8.7311030	2.9721210	3.1213180
30	F	9.7292520	3.8977370	0.7597740
31	F	8.3356060	3.5355920	-1.5536120
32	F	5.9514900	2.2532270	-1.5129190
33	C	3.6724720	1.6984190	1.4460140
34	C	3.4233920	3.0073370	2.0197340
35	C	2.1183510	3.0741400	2.4223430
36	C	1.4822890	1.7873760	2.1834730
37	C	1.7445640	-3.3975640	3.2581730
38	C	2.7654630	-4.2784490	3.3285750
39	C	5.1513190	-5.3212820	3.0479240
40	C	6.5182200	-5.5099730	2.8382590
41	H	7.2102900	-4.6830170	2.9665340

42	C	6.9820910	-6.7681750	2.4513880
43	H	8.0446150	-6.9167040	2.2835490
44	C	6.0881770	-7.8260060	2.2694150
45	H	6.4533070	-8.8010860	1.9607470
46	C	4.7199470	-7.6380320	2.4708550
47	H	4.0231600	-8.4563390	2.3161630
48	C	4.2538980	-6.3833200	2.8650770
49	C	-7.8255380	-2.4976800	0.5697000
50	C	-9.0602150	-2.9737310	0.8350490
51	C	-11.0675930	-4.1618770	2.0381950
52	C	-11.8559400	-4.9467180	2.8808730
53	H	-11.4168060	-5.7815510	3.4192860
54	C	-13.2107370	-4.6444580	3.0281070
55	H	-13.8256270	-5.2532200	3.6843340
56	C	-13.7720260	-3.5638030	2.3442170
57	H	-14.8252060	-3.3288520	2.4663250
58	C	-12.9849360	-2.7730330	1.5054630
59	H	-13.4187460	-1.9274060	0.9797770
60	C	-11.6313850	-3.0760310	1.3514640
61	C	3.0619150	5.4535340	2.7542780
62	S	4.6676630	7.6818120	2.5151270
63	S	1.8160380	7.8279540	3.3972870
64	C	3.1621300	6.7949300	2.8575070
65	C	3.9013170	9.2820620	2.4590280
66	C	4.5753060	10.4382500	2.0631740
67	H	5.6096900	10.3833260	1.7366800
68	C	3.9054190	11.6624430	2.0880460
69	H	4.4279310	12.5633410	1.7803700
70	C	2.5723360	11.7306400	2.4992360
71	H	2.0540300	12.6848250	2.5126570
72	C	1.8938020	10.5754340	2.8905780
73	H	0.8551830	10.6263290	3.2039940
74	C	2.5625620	9.3506530	2.8723480
75	C	0.2050180	1.3521970	2.4481610
76	C	-0.8351730	2.3034030	2.9467860
77	C	-0.9030050	2.6722650	4.2959280
78	C	-1.9034210	3.5119890	4.7809420
79	C	-2.8841490	3.9890950	3.9139060
80	C	-2.8596470	3.6260540	2.5687630
81	C	-1.8375760	2.8026200	2.1096120
82	F	0.0168470	2.2224610	5.1576860
83	F	-1.9332170	3.8557140	6.0718250
84	F	-3.8489390	4.7873490	4.3727430
85	F	-3.8049340	4.0690100	1.7345070
86	F	-1.8542830	2.4411400	0.8131680
87	S	0.0490880	-3.9034440	2.9712050

88	S	4.4541930	-3.7777340	3.5795750
89	S	2.5450990	-6.0386260	3.2014980
90	S	-6.3315320	-3.3353710	1.1084990
91	S	-7.5473950	-0.9994500	-0.3771760
92	S	-9.3483020	-4.4857240	1.7327100
93	S	-10.5485140	-2.1711890	0.2735440
94	S	4.4357990	4.4161020	2.2512770
95	S	1.5498990	4.5664800	3.1355500
96	C	0.1642560	-0.1115160	-2.3323110
97	C	-0.5077580	-1.3000930	-2.7036250
98	C	0.3763510	-2.3766280	-2.5244550
99	C	1.5957220	-1.8702150	-2.0179090
100	C	2.8191100	-2.4928250	-1.6361340
101	C	3.0405070	-3.9085340	-2.0289930
102	C	3.1512760	-4.9160350	-1.0603420
103	C	3.3363910	-6.2508960	-1.4068320
104	C	3.4316510	-6.6029460	-2.7515610
105	C	3.3338230	-5.6249220	-3.7394980
106	C	3.1365490	-4.2971630	-3.3723890
107	F	3.0456940	-3.3797740	-4.3405600
108	F	3.4330560	-5.9660280	-5.0270180
109	F	3.6150080	-7.8786560	-3.0934930
110	F	3.4181260	-7.1954990	-0.4649110
111	F	3.0587400	-4.6035160	0.2364440
112	C	3.8092560	-1.8074850	-0.9290290
113	C	5.2086130	-2.1287230	-0.7402350
114	C	5.7841570	-1.0459830	-0.1186880
115	C	-4.7670110	0.0090660	-0.2342520
116	C	-4.8162980	1.2483690	-0.9845860
117	C	-6.0884870	2.0073460	-1.0198570
118	C	-6.7907270	2.2424430	-2.2108090
119	C	-8.0041590	2.9253550	-2.2288750
120	C	-8.5498110	3.3873330	-1.0336460
121	C	-7.8806460	3.1690390	0.1693970
122	C	-6.6687480	2.4876800	0.1641000
123	F	-6.2982460	1.8014590	-3.3757960
124	F	-8.6512700	3.1313520	-3.3804630
125	F	-9.7121500	4.0426010	-1.0400820
126	F	-8.4033390	3.6218060	1.3130780
127	F	-6.0451800	2.2963510	1.3334480
128	C	-3.6837700	1.7279150	-1.6170670
129	C	-3.3822950	3.0175360	-2.2051790
130	C	-2.0545600	3.0471550	-2.5407190
131	C	-1.4659070	1.7586290	-2.2430000
132	C	-1.8607940	-3.4215310	-3.2822330
133	C	-2.9031490	-4.2781400	-3.3353040

134	C	-5.3094680	-5.2599410	-3.0148030
135	C	-6.6778150	-5.4134180	-2.7865940
136	H	-7.3512890	-4.5713720	-2.9157570
137	C	-7.1670000	-6.6558180	-2.3802230
138	H	-8.2306540	-6.7768570	-2.1981130
139	C	-6.2964810	-7.7328260	-2.1972080
140	H	-6.6810510	-8.6954890	-1.8735150
141	C	-4.9267070	-7.5800080	-2.4171680
142	H	-4.2479640	-8.4133670	-2.2624040
143	C	-4.4355330	-6.3412590	-2.8309900
144	C	7.7441630	-2.6623800	-0.6184750
145	C	8.9700480	-3.1627430	-0.8797890
146	C	10.9512400	-4.4163220	-2.0601810
147	C	11.7220900	-5.2384860	-2.8832440
148	H	11.2669710	-6.0829840	-3.3925290
149	C	13.0801150	-4.9611490	-3.0486250
150	H	13.6813930	-5.5990120	-3.6896550
151	C	13.6619900	-3.8683730	-2.4021980
152	H	14.7176590	-3.6530940	-2.5383180
153	C	12.8924290	-3.0403450	-1.5833900
154	H	13.3422540	-2.1853960	-1.0870540
155	C	11.5356530	-3.3181900	-1.4112710
156	C	-2.9370170	5.4125040	-3.0619320
157	S	-4.5015810	7.6812720	-2.9919200
158	S	-1.6143200	7.7298020	-3.7594780
159	C	-3.0033670	6.7495630	-3.2309950
160	C	-3.7006590	9.2655350	-2.9642450
161	C	-4.3626600	10.4506280	-2.6402500
162	H	-5.4102870	10.4312450	-2.3544680
163	C	-3.6635110	11.6578150	-2.6837610
164	H	-4.1764000	12.5812460	-2.4317820
165	C	-2.3137360	11.6806150	-3.0421160
166	H	-1.7729070	12.6218920	-3.0699380
167	C	-1.6473930	10.4965120	-3.3614520
168	H	-0.5959710	10.5123410	-3.6331010
169	C	-2.3451770	9.2884660	-3.3244750
170	C	-0.1742010	1.2950340	-2.4028010
171	C	0.9605800	2.2436050	-2.5393830
172	C	1.8891130	2.1359480	-3.5883830
173	C	3.0325520	2.9252010	-3.6513910
174	C	3.2804800	3.8614200	-2.6482940
175	C	2.3713090	4.0131670	-1.6047380
176	C	1.2379720	3.2072820	-1.5561950
177	F	1.6895040	1.2388070	-4.5603830
178	F	3.8931550	2.7924690	-4.6646540
179	F	4.3781590	4.6154820	-2.6948100

180	F	2.6073140	4.9053610	-0.6358540
181	F	0.4158800	3.3550260	-0.5067570
182	S	-0.1755930	-3.9667200	-3.0111630
183	S	-4.5821690	-3.7398170	-3.5730650
184	S	-2.7231960	-6.0417720	-3.1919440
185	S	6.2351670	-3.4973070	-1.1180440
186	S	7.4932230	-1.1331890	0.2854250
187	S	9.2297130	-4.7051200	-1.7334820
188	S	10.4738400	-2.3642670	-0.3550430
189	S	-4.3527620	4.4305640	-2.5582520
190	S	-1.4327710	4.4755250	-3.3395000
191	N	-3.6225230	-0.4563170	0.2867160
192	N	-1.4595790	-0.3906070	1.9124330
193	N	-2.5070810	0.9989750	-1.7387830
194	S	1.9795710	-1.6329440	3.4435120
195	N	3.5715060	-0.5609060	-0.3643860
196	N	2.4753590	1.0109340	1.6042510
197	N	1.4144510	-0.5014770	-1.9323010
198	S	-2.0563490	-1.6518950	-3.4649030
199	H	-2.3817670	0.1832270	-1.1436200
200	H	-2.1147320	0.1887910	1.3877670
201	H	2.3266740	0.1426460	1.0986240
202	H	2.1072940	0.0592510	-1.4346220

References:

1) J. S. Park, F. L. Derf, C. M. Bejger, V. M. Lynch, J. L. Sessler, K. A. Nielsen, C. Johnsen and J. O. Jeppesen, *Chem. Eur. J.,* 2010, **16**, 848.

2) DENZO-SMN. (1997). Z. Otwinowski and W. Minor, Methods in Enzymology, **276**: Macromolecular Crystallography, part A, 307 – 326, C. W. Carter, Jr. and R. M. Sweets, Editors, Academic Press.

3) SIR97. A program for crystal structure solution. A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Cryst*. 1999, **32**, 115-119.

4) G. M. Sheldrick (1994). SHELXL97. Program for the Refinement of Crystal Structures. University of Gottingen, Germany.

5) A. L. Spek (1998). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands.

6) WinGX 1.64. An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. L. J. Farrugia, *J. Appl. Cryst.* 1999, **32**. 837-838.

7) P. v. d. Sluis and A. L. Spek, SQUEEZE. *Acta Cryst.* 1990, **A46**, 194-201.

8) $R_W(F^2) = \{\Sigma w(|F_O|^2 - |F_c|^2)^2/\Sigma w(|F_O|)^4\}^{1/2}$ 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.

9) 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.

10) G. M. Sheldrick(1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

11) 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 and D. J. Fox Gaussian, Inc., Wallingford CT, 2009.

12) (*a*) A. D. Becke, *Phys. Rev. A,* 1988, **38**, 3098; (*b*) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B,* 1988, **37**, 785.