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Electronic Supplementary Information

A "Reverse Interruptor": Novel Molecular Design of a Fluorescent Photochromic DTE-Based Bipyridine

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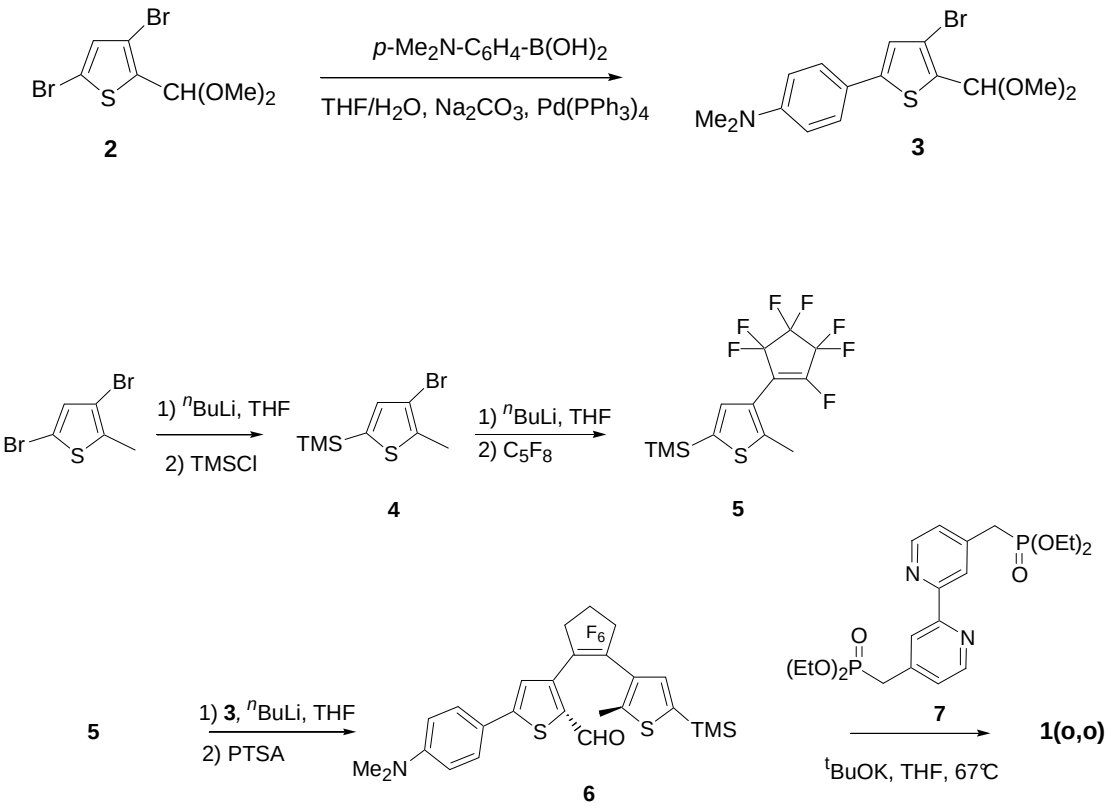
General Procedure. All manipulations were performed using Schlenk techniques under an Ar atmosphere. All solvents were dried and purified by standard procedures. NMR spectra were recorded on Bruker DPX-200, AV 300 or AV 500 MHz spectrometers. ^{1}H and ^{13}C chemical shifts are given versus tetramethylsilane $SiMe_4$ (δ = 0 ppm) and were determined by reference to residual ^{1}H and ^{13}C solvent signals. Assigments of carbon atoms were based on HMBC, HMQC and COSY experiments. High resolution mass spectra (HRMS) were performed on a MS/MS ZABSpec TOF at the CRMPO (Centre de Mesures Physiques de l'Ouest) in Rennes. Elemental analyses were performed by Muriel Escadeillas at the CRMPO. UV/vis absorption spectra were recorded using a UVIKON 9413 or Biotek Instruments XS spectrophotometer using quartz cuvettes of 1 cm pathlength. 4,4'-bis(diethylphosphonomethyl)-[2,2']-bipyridine[1] was synthesized using published procedure. Compound **2** was prepared following a reported procedure.[2] Compound **4** was obtained by using the procedure previously described.[3]

Steady-state luminescence spectra were measured using a Jobin Yvon FluoroMax-2 or Tau-3 spectrofluorimeter, fitted with a red-sensitive Hamamatsu R928 photomultiplier tube. The spectra shown are corrected for the wavelength dependence of the detector, and the quoted emission maxima refer to the values after correction. Luminescence quantum yields were determined using the method of continuous dilution, using $[Ru(bpy)_3]Cl_2$ (ϕ = 0.028 in air-equilibrated aqueous solution) or coumarin 540A (ϕ = 0.38 in ethanol) as standards and

correcting for the refractive index. Lifetimes were obtained either by excitation at 355 nm with the third harmonic of a Q-switched Nd:YAG laser and detection of emitted light using an R928 PMT, or by TCSPC following excitation at 405 nm using a laser diode in an Edinburgh Instruments Mini-Tau system.

Spectroscopic grade solvents were used for all optical measurements. Photoisomerization experiments and kinetics were performed by using a Hamamatsu UV Spot Light Source (Xe-Hg lamp) as an excitation light source equipped with interferential filters (17.2 $mW.cm^{-2}$ at 313 nm, 8.1 $mW.cm^{-2}$ at 436 nm, and 25.2 $mW.cm^{-2}$ at 588 nm) and an optical fiber while simultaneous probing was performed with a continuous Xe lamp (450 W) and a CCD camera coupled with a spectrometer (Princeton Instruments).



Scheme S1

4-(4-bromo-5-(dimethoxymethyl)thiophen-2-yl)-*N*,*N*-dimethylbenzenamine, 3.

To a mixture of THF/H_2O (15 mL, 15 mL) containing **2** (1g, 3.1 mmol) and *p*-dimethylaminophenylboronic acid (305 mg, 1.85 mmol) were added Na_2CO_3 (3 g, 28 mmol) and $Pd(PPh_3)_4$ (64 mg, 0.055 mmol). The reaction mixture was refluxed for 16 h. The residue was extracted with $CHCl_3$ (2 x 30 mL). The combined organic phases were dried over

$MgSO_4$, filtered and evaporated *in vacuo*. Chromatography was performed on silica gel. (pentane / CH_2Cl_2, 30:70) and afforded **3** as an orange powder (370 mg, 55%).^{1}H NMR (200 MHz, $CDCl_3$): 7.45 (d, ^3J = 9 Hz, 2H, C_6H_4), 7.02 (s, 1H, thio), 6.72 (d, ^3J = 8.8 Hz, 2H, C_6H_4), 5.63 (s, 1H, CH), 3.44 (s, 6H, OMe), 3.01 (s, 6H, NMe_2). HRMS: *m/z* 355.0238 $[M]^+$ calcd for $C_{15}H_{18}NO_2{}^{79}BrS$ 355.0241. Compound **3** was fully characterized as its unprotected aldehyde: ^{1}H NMR(200 MHz, $CDCl_3$): 9.90 (s, 1H, CHO), 7.54 (d, ^3J = 8.78 Hz, 2H, C_6H_4), 7.20 (s, 1H, Thio), 6.73 (d, ^3J = 8.78 Hz, 2H, C_6H_4), 3.06 (s, 3H, CH_3). ^{13}C[^{1}H] NMR (75 MHz, CD_2Cl_2): 182.4, 155.0, 151.3, 132.8, 129.9, 127.3, 124.7, 121.6, 112.2, 40.3, 30.3. Anal. Calcd. for $C_{13}H_{12}BrNOS$. 2 C_5H_{12}: C, 51.80; H, 4.47; N, 4.31; S, 9.88. Found: C, 51.80; H, 4.27; N, 4.28;. S, 9.97.

(4-bromo-5-methylthiophen-2-yl)trimethylsilane, 4. To a THF (50 mL) solution of *n*BuLi (1.35 M in hexane, 3.14 mL, 4.24 mmol), 3,5-dibromo-2-methylthiophene (1.1 g, 4.3 mmol) was added dropwise. After stirring for 1 h at -80°C, trimethylsilylchloride (0.56 mL, 4.45 mmol) was added dropwise and the temperature was allowed to naturally rise to room temperature. After hydrolysis (40 mL), the THF was removed under reduced pressure, and the residue was extracted with diethylether (50 mL). The combined organic phases were dried over $MgSO_4$, filtered and evaporated *in vacuo*. Chromatography of the residue was performed on silica gel (pentane), and afforded **4** as a colorless oil (0.97 g, 90%).^{1}H NMR (200 MHz, $CDCl_3$): 7.04 (s, 1H, thio), 2.45 (s, 3H, Me), 0.32 (s, 9H, TMS).

Trimethyl(5-methyl-4-(perfluorocyclopentenyl)thiophen-2-yl)silane, 5. To a Schlenk tube containing a THF (75 mL) solution of **4** (2.62 g, 10.51 mmol), ^{n}BuLi (1.27 M in hexane, 8.69 mL, 11.05 mmol) was added at -78°C. After 1h of stirring, the reaction medium was transferred to a THF (15 mL) solution of C_5F_8 (4.23 mL, 31 mmol). The reaction mixture was stirred for 1 hour at -78°C, then allowed to warm up to room temperature. After stirring for an additional 16 h, the mixture was hydrolyzed (200 mL of water), the THF was removed under reduced pressure, and the residue was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic phases were dried over $MgSO_4$, filtered and evaporated *in vacuo*. Chromatography was performed with silica gel (pentane), and afforded **5** as a yellow oil (2.3 g, 60%). ^{1}H NMR (200 MHz, $CDCl_3$): 7.17 (s, 1H, thio), 2.50 (d, $^6J_{H\text{-}F}$= 3 Hz, 3H, Me), 0.33 (s, 9H, TMS). ^{13}C[^{1}H] NMR (75 MHz, CD_2Cl_2): 149.2, 139.9, 139.2, 134.4, 133.8, 14.8, 0.0. HRMS: *m/z* 362.0378 $[M]^+$ calcd for $C_{13}H_{13}F_7SSi$ 362.0395; 347.0170 $[M\text{-}CH_3]^+$ calcd for. $C_{12}H_{10}F_7SSi$ 347.01607.

5-(4-(dimethylamino)phenyl)-3-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-(trimethylsilyl) thiophen-3-yl)cyclopent-1-enyl)thiophene-2-carbaldehyde, 6. To a solution of **3** (192 mg,

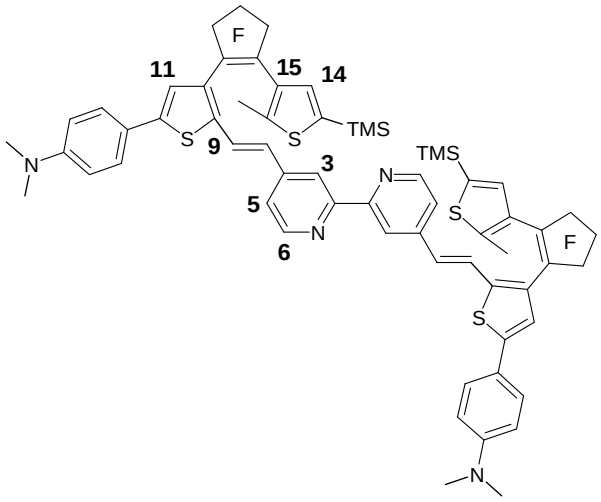
0.5 mmol) in 15 mL of THF, which was cooled to -78°C, was added dropwise *n*BuLi (2.16 M in hexane, 0.25 mL, 0.54 mmol). After stirring at -78°C for 1 h, a solution of **5** (196 mg, 0.54 mmol) in 10 mL of THF was added to the reaction mixture. After stirring at -78°C for 1 h and at room temperature for 16 h, the reaction mixture was hydrolyzed with water (25 mL), and the solvent was removed *in vacuo*. The residue was extracted with CH_2Cl_2 (2 x 30 mL) and then dried over $MgSO_4$. After evaporation of the solvent, the residual orange oil was dissolved in 20 mL of THF, then PTSA (*para*-toluenesulfonic acid) (20 mg, 0.1 mmol) and a few drops of water were added. After stirring at 40°C for 16 h, the solvent was removed and the oil was purified by column chromatography (SiO_2, pentane-CH_2Cl_2 1:1) to give a red powder (179 mg, 60%). ^{1}H NMR (500 MHz, $CDCl_3$): 9.40 (s, 1H, CHO), 7.55 (d, ^3J = 8.9 Hz, 2H, C_6H_4), 7.28 (s, 1H, thio), 7.10 (s, 1H, thio), 6.74 (d, ^3J = 8.9 Hz, 2H, C_6H_4), 3.07 (s, 6H, NMe_2), 2.08 (s, 3H, Me); 0.30 (s, 9H, TMS). ^{13}C[^{1}H] NMR (125 MHz, $CDCl_3$): 180.5, 155.6, 151.5, 147.4, 140.1, 137.2, 135.7, 133.7, 127.5, 124.7, 121.7, 119.7, 112.1, 40.2, 30.3, 14.4, -0.3. Anal. Calcd. for $C_{26}H_{25}F_6N_1S_2Si$. 0.5 CH_2Cl_2: C, 54.46; H, 4.44; N, 2.33. Found: C, 54.80; H, 4.70; N, 2.30. HRMS: *m/z* 573.1069 $[M]^+$ calcd for $C_{26}H_{25}F_6N_1S_2Si$ 573.1051.

Preparation of 1(o,o). To a THF solution of **6** (350 mg, 0.64 mmol) and **7** (126 mg, 0.28 mmol) was added *tert*-BuOK (77 mg, 0.70 mmol). After refluxing overnight, the reaction mixture was hydrolyzed with water and the organic phase washed with a saturated solution of Na_2CO_3, and dried over $MgSO_4$ and evaporated in vacuo. The residue was recrystallized from a CH_2Cl_2/pentane mixture at -20°C to give **1(o,o)** as a red powder (180 mg, 50%). ^{1}H NMR (500 MHz, $CDCl_3$): 8.63 (d, ^3J = 5.1 Hz, 1H, Py^6), 8.26 (s, 1H, Py^3), 7.53 (d, ^3J = 8.9 Hz, 2H, C_6H_4), 7.25 (s, 1H, thio), 7.23 (s, 1H, thio), 7.17 (dd, ^3J = 5.1 Hz and ^4J = 1.6 Hz, 1H, Py^5), 6.94 (d, ^3J = 15.9 Hz, 1H, =CH), 6.77 (d, ^3J = 8.9 Hz, 2H, C_6H_4), 6.71 (d, ^3J = 15.9 Hz, 1H, =CH), 3.05 (s, 6H, NMe_2), 1.99 (s, 3H, Me,); 0.03 (s, 9H, TMS). ^{13}C[^{1}H] NMR (125 MHz, $CDCl_3$): 156.4, 150.7, 149.4, 147.8, 147.5, 146.2, 144.7, 139.5, 138.5, 133.5, 128.4, 126.9, 126.5, 125.6, 123.5, 120.9, 120.7, 119.6, 119.0, 112.3, 40.3, 14.5, -0.6. Anal. Calcd. for $C_{64}H_{58}F_{12}N_4S_4Si_2$: C, 59.33; H, 4.51; N, 4.32. Found: C, 59.87; H, 4.86; N, 4.79. HRMS: *m/z* 1294.2875 $[M]^+$ calcd for $C_{64}H_{58}F_{12}N_4Si_2S_4$ 1294.2891.

Spectroscopic characterization of 1(c,o). Compound **1(c,o)** was generated by irradiation (λ = 436 nm) of a [d^{12}]-cyclohexane solution of **1(o,o)** for 30 min. Selected data. ^{1}H NMR (500 MHz, [d^{12}]-cyclohexane): 8.48; 8.46 (2 x d, ^3J = 5 Hz, 2H, Py^6), 8.49; 8.42 (2 x s, 2H, Py^3), 7.58 (d, ^3J = 15.7 Hz, 1H, =CH(**c**)), 7.25 (s, 1H, thio(**o**)), 7.21 (s, 1H, thio(**o**)), 7.09; 6.95 (2 x

dd, ^3J = 5.1 Hz, 2H, Py[5]), 6.92 (d, ^3J = 15.9 Hz, 1H, =CH(**o**)), 6.70 (s, 1H, thio(**c**)), 6.33 (s, 1H, thio(**c**)), 2.97;2.96 (2 x s, 12 H, NMe_2), 2.04;1.96 (2 x s, 6H, Me).

Numbering



X-ray Crystallography. Single crystals for X-ray diffraction studies were grown by slow evaporation of a CH_2Cl_2 solution of complex **1(o,o)** at 20°C. The sample (0.32 x 0.28 x 0.28) was studied on an Oxford Diffraction Xcalibur Saphir 3 diffractometer with graphite monochromatized MoKα radiation. The data collection (Crysalis 2004) and refinement parameters are presented in the Table. The structure was solved with SIR-97[4] which reveals the non hydrogen atoms of the molecule. After anisotropic refinement, all the hydrogen atoms are found with a Fourier Difference. The whole structure was refined with SHELXL97[5] by the full-matrix least-square techniques (use of F square magnitude ; x , y, z, β_{ij} for Si, S, C, F and N atoms, x, y, z in riding mode for H atoms ; 388 variables and 4381 observations with I>2.0σ(I). The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC-640444. These data can be obtained free of charge at www.cccdc.cam.ac.uk/conts/retrieving.html [of from Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table S1. Crystallographic Data for **1(o,o).**

	1(o,o)
formula	$C_{64}H_{58}F_{12}N_4S_4Si_2$
fw	1295.6
Cryst syst	monoclinic
Space group	$P2_1/n$
a, Å	10.45582(5)
b, Å	19.8097(9)
c, Å	14.9154(7)
β, deg	100.277(4)
V, Å^3	3040.5(2)
Z	2
ρ_{calcd}, g cm^{-3}	1.415
μ (Mo K_α), mm^{-1}	2.77
Temp K	100(1)
F(000)	1340
cryst. dimens, mm	0.32 x 0.28 x 0.28
θ rang, deg	2.61 – 27.00
Index ranges	-11≤ h ≤13 -25 ≤ k ≤21 -17≤ l ≤19
no. reflns collcd	21731
no. of indep reflns/ R int.	6585/0.0405
no. of indep reflns with $I > 2\sigma(I)$	4381
&GOF (F^2)	1.278
R1 (F) ($I > 2\sigma(I)$)	0.077
R1 (all data)	0.1086
wR2 ($I > 2\sigma(I)$)	0.2527
wR2 (all data)	0.2618
largest diff peak/hole e/Å^3	1.476/-0.722

DFT and TD-DFT calculations

DFT calculations were carried out using the parameter-free PBE0 (PBE1PBE) hybrid functional as implemented in the GAUSSIAN 03,Version D02[6] with the LANL2DZ basis set for H, C, F and S atoms, augmented by polarization functions on all atoms except H.

The geometries were optimized starting from crystallographic data for the open form and a standard geometry for the closed one, crystallographic data being not available for the latter one. Excitation energies and oscillator strengths were calculated using Time Dependent DFT (TDDFT) as implemented in the GAUSSIAN03 program. The theoretical electronic spectra

were then plotted using the SWIZARD program[7] and the molecular orbitals plots were done using MOLEKEL4.1.[8]

Optimized Geometry

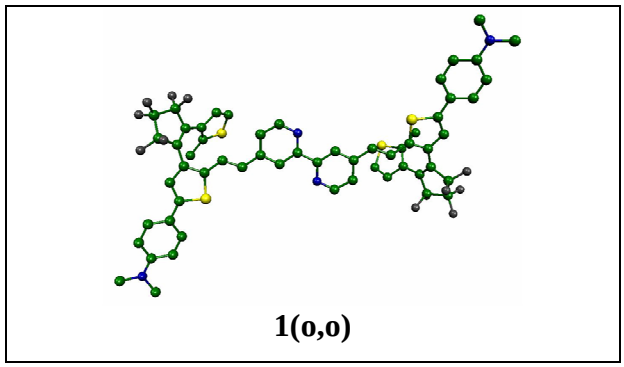


Figure S1. Optimized geometries of **1(o,o)** (antiparallel conformation)

Table S2. Selected experimental and optimized distances of **1(o,o)** (antiparallel form)

Distances	Experimental (Å) *Open form*	Calculated (Å) *Open form*
S_1-C_{11}	1.729	1.744
S_2-C_{26}	1.722	1.730
N_2-C_{15}	1.400	1.378
C_3-C_6	1.484	1.461
C_6-C_7	1.337	1.356
C_7-C_8	1.448	1.443
C_8-C_9	1.385	1.396
C_9-C_{20}	1.477	1.467
C_{20}-C_{24}	1.356	1.361
C_{25}-C_{26}	1.370	1.388
S_1-C_8	1.741	1.742
S_2-C_{27}	1.731	1.727
C_{11}-C_{12}	1.461	1.460
C_{24}-C_{25}	1.463	1.463
C_{27}-C_{28}	1.371	1.368
C_{26}-C_{29}	1.507	1.497
C_8-C_{26}	3.588	3.609

Table S3. Selected experimental and optimized angles of **1(o,o)** (antiparallel form)

Angles (°)	Experimental *Open form*	Calculated *Open form*
C_{11}-S_1-C_8	93.0	93.0
C_{12}-C_{11}-S_1	123.1	121.3
C_{26}-S_2-C_{27}	94.1	92.9
C_7-C_6-C_3	124.9	126.0
C_9-C_8-C_7	129.6	127.8
C_7-C_8-S_1	120.4	122.0
C_{24}-C_{20}-C_9	129.6	129.5
C_{20}-C_{24}-C_{25}	130.1	130.3
C_{25}-C_{26}-C_{29}	130.7	129.6
C_{29}-C_{26}-S_2	119.1	119.9
S_2-C_{27}-Si_1	120.0	120.6
C_{18}-N_2-C_{19}	116.60	119.2

Table S4. Experimental and optimized dihedral angles of **1(o,o)** (antiparallel form)

Dihedral angles (°)	Experimental *Open form*	Calculated *Open form*
C_3-C_6-C_7-C_8	173.31	-178.49
C_8-C_9-C_{20}-C_{24}	48.52	48.93
C_{24}-C_{25}-C_{26}-C_{29}	-0.57	0.50
C_{13}-C_{12}-C_{11}-S_1	-155.7	160.86
S_1-C_8-C_7-C_6	-11.54	9.54
C_{16}-C_{17}-C_{12}-C_{11}	173.16	179.97
S_2-C_{26}-C_{25}-C_{24}	178.82	178.69
C_{13}-C_{12}-C_{11}-C_{10}	26.30	-18.53
C_{25}-C_{24}-C_{20}-C_9	6.28	6.95
C_{20}-C_{24}-C_{25}-C_{26}	44.71	44.11
C_3-C_6-C_7-C_8	173.31	-178.49
C_8-C_9-C_{20}-C_{24}	48,52	48.93

Table S5. TD-DFT calculations of the pyridine fragment of **1(o,o)** as its antiparallel isomer

λ (nm)	oscillator strength	Participating MO
468.4	0.4736	HOMO→LUMO (85%)
382.1	0.4720	HOMO→LUMO+1 (88%)
336.4	0.2290	HOMO-2→LUMO (55%), HOMO-1→LUMO (31%)

Table S6. TD-DFT calculations of the closed pyridine fragment of **1(c,o)**

λ (nm)	oscillator strength	Participating MO
569.2	0.4045	HOMO→LUMO (74%)
410.5	0.2401	HOMO-1 →LUMO (76%), HOMO-2 →LUMO (10%) HOMO-2 →LUMO (7%),
327.6	0.2061	HOMO→LUMO+2 (53%), HOMO-3→LUMO (21%)

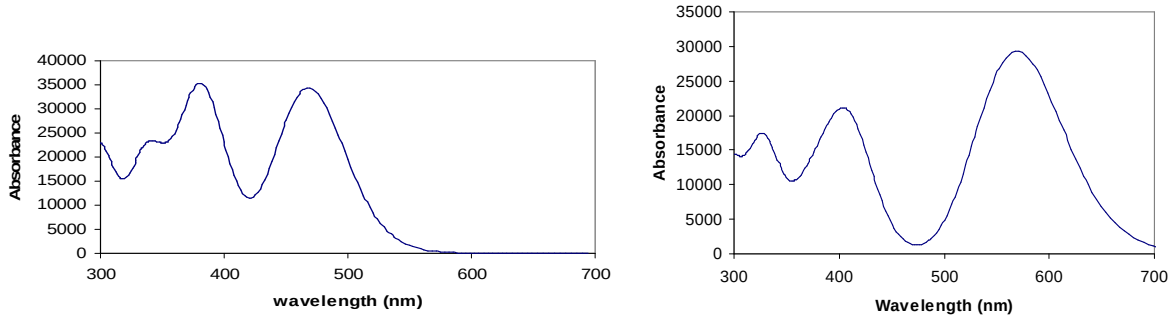


Figure S2. Theoretical electronic spectra of the pyridine fragments of **1**(**o,o**) (antiparallel form) (left) and the corresponding closed form (right)

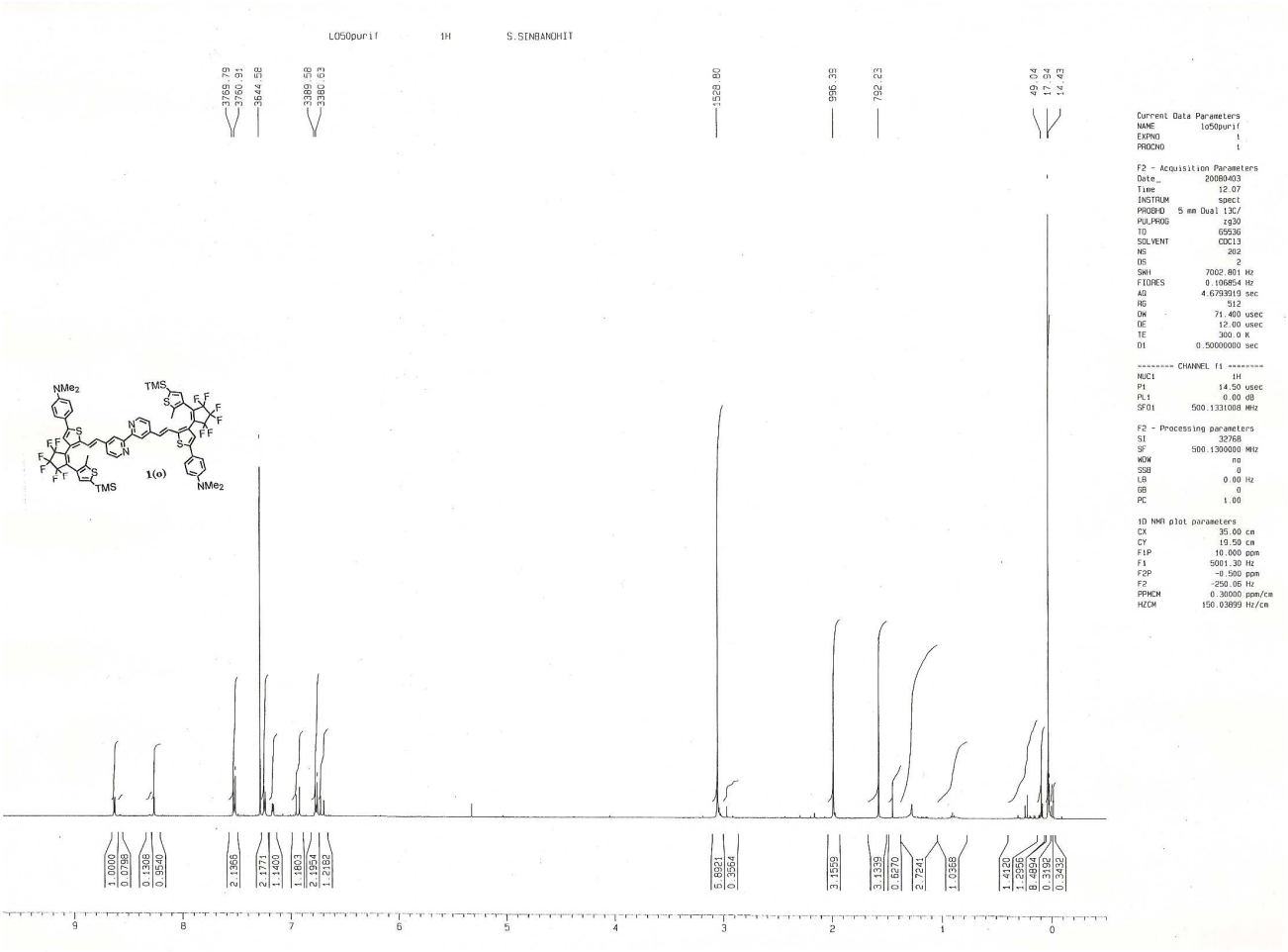


Figure S3. ^{1}H NMR of **1(o,o)** in $CDCl_3$

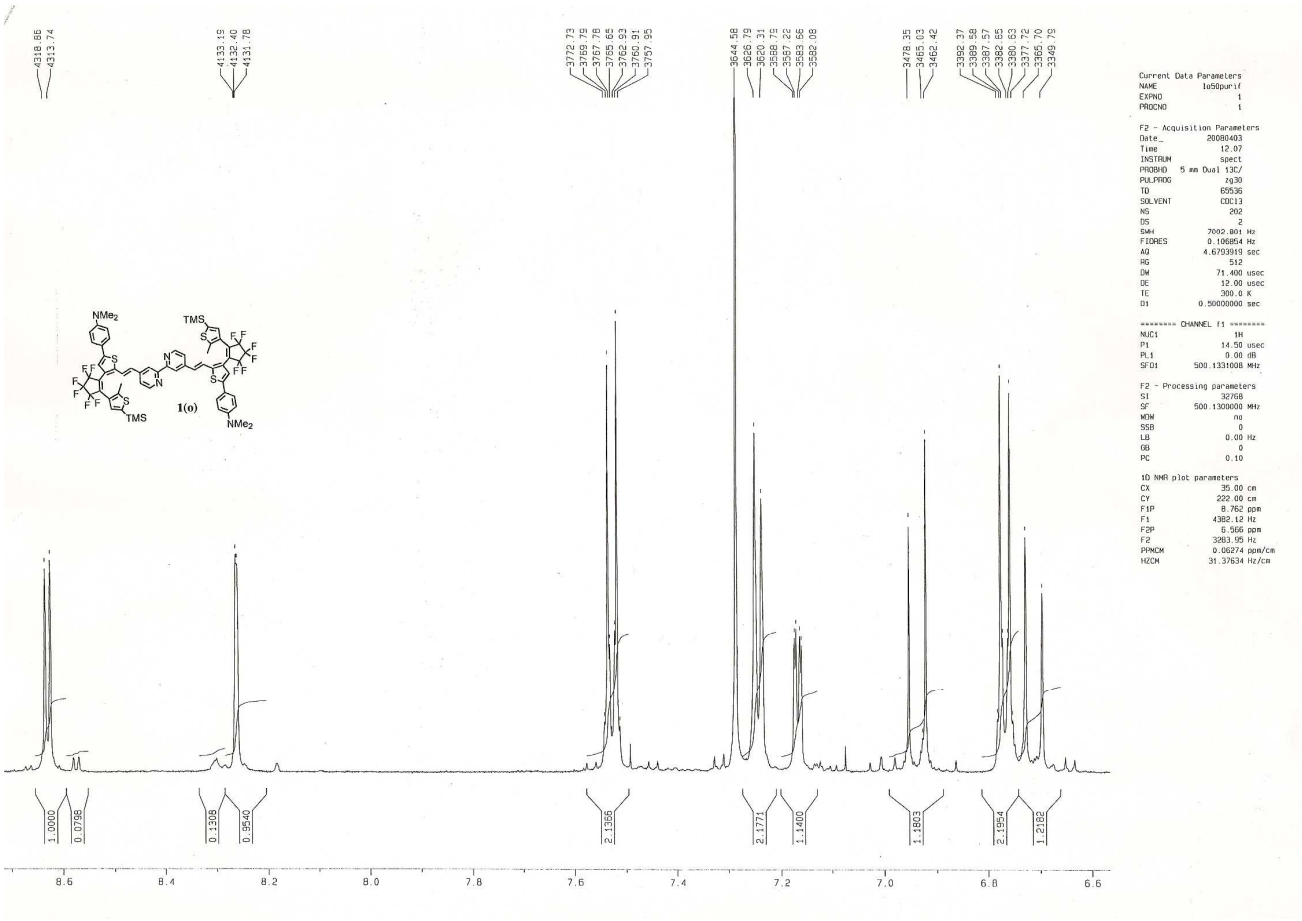


Figure S4. ^{1}H NMR of **1(o,o)** in $CDCl_3$ (aromatic region)

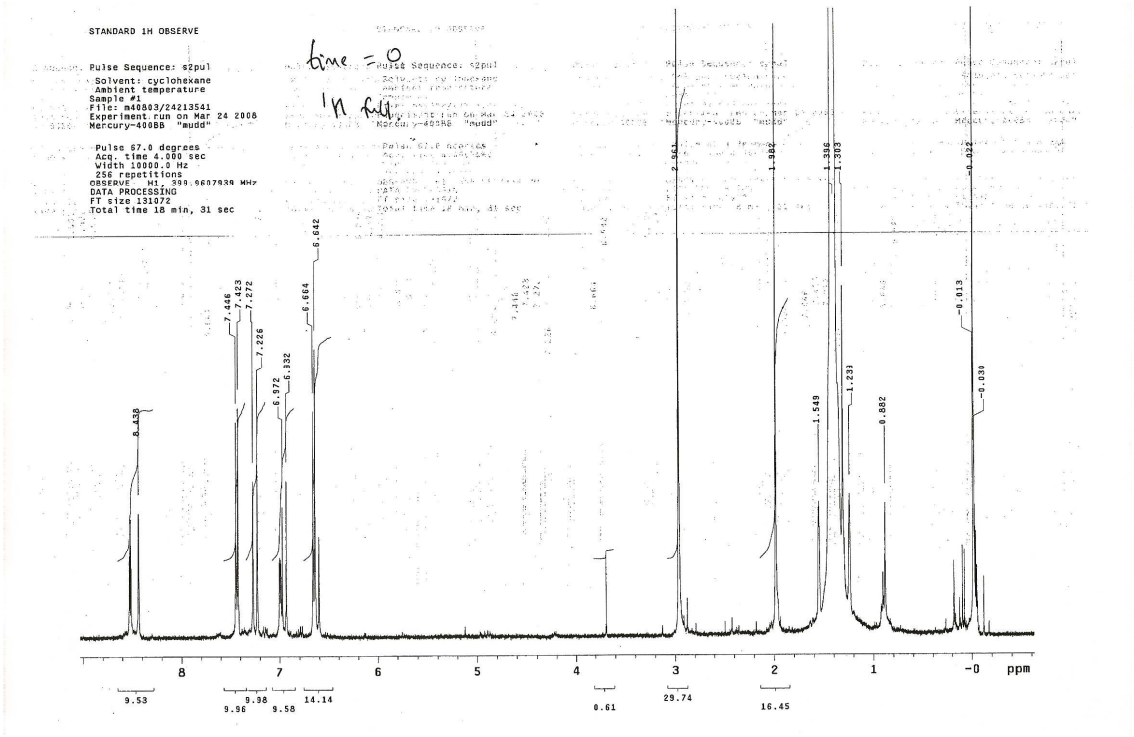


Figure S5. ^{1}H NMR of **1(o,o)** in deuterated cyclohexane

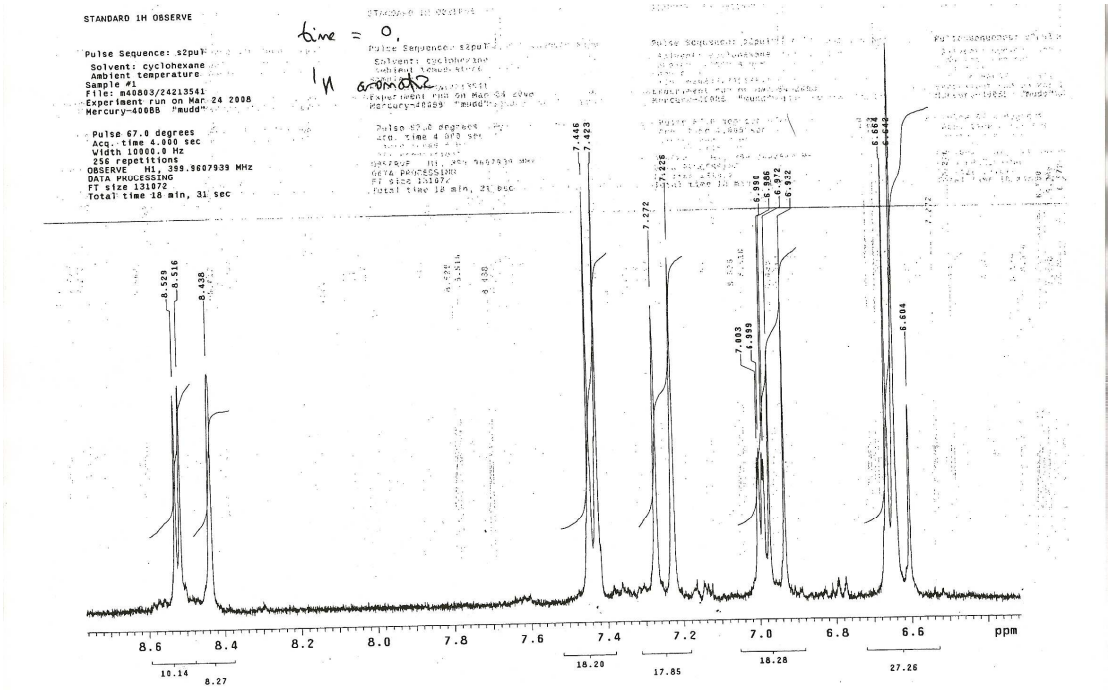


Figure S6. ^{1}H NMR of **1(o,o)** in C_6D_{12} (aromatic region)

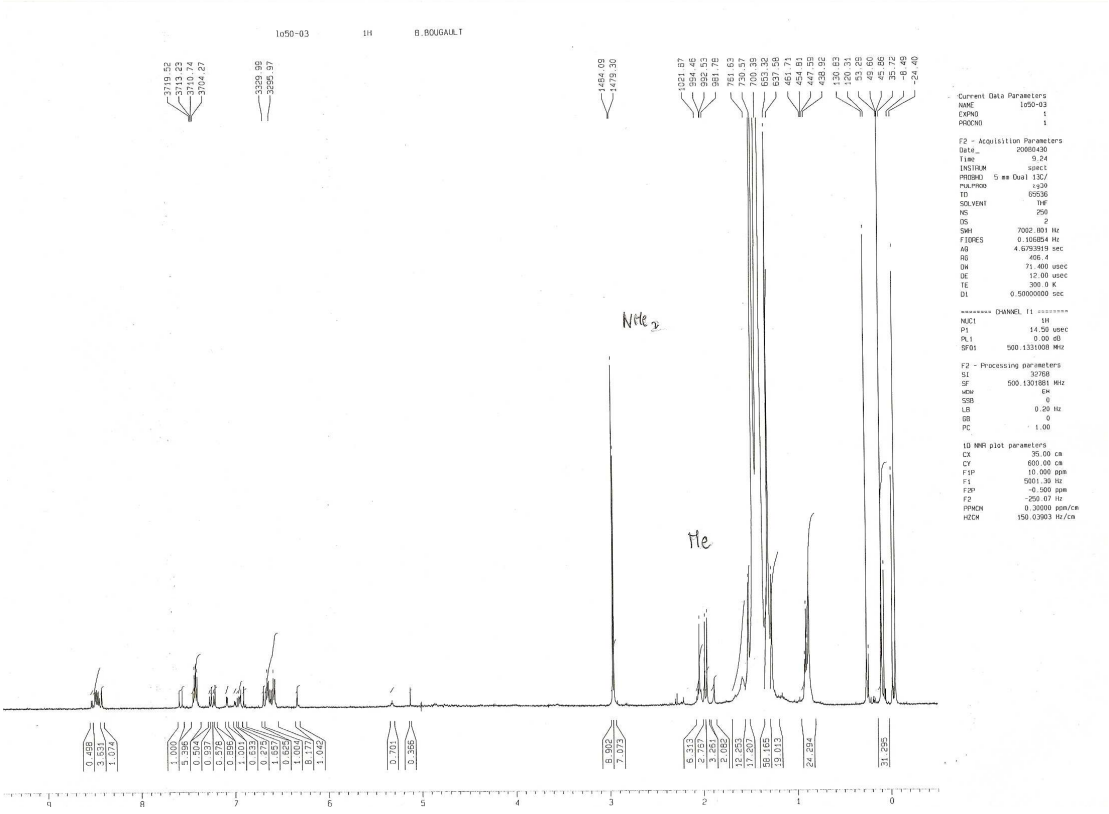


Figure S7. ^{1}H NMR after irradiation of **1(o,o)** in deuterated cyclohexane (PSS)

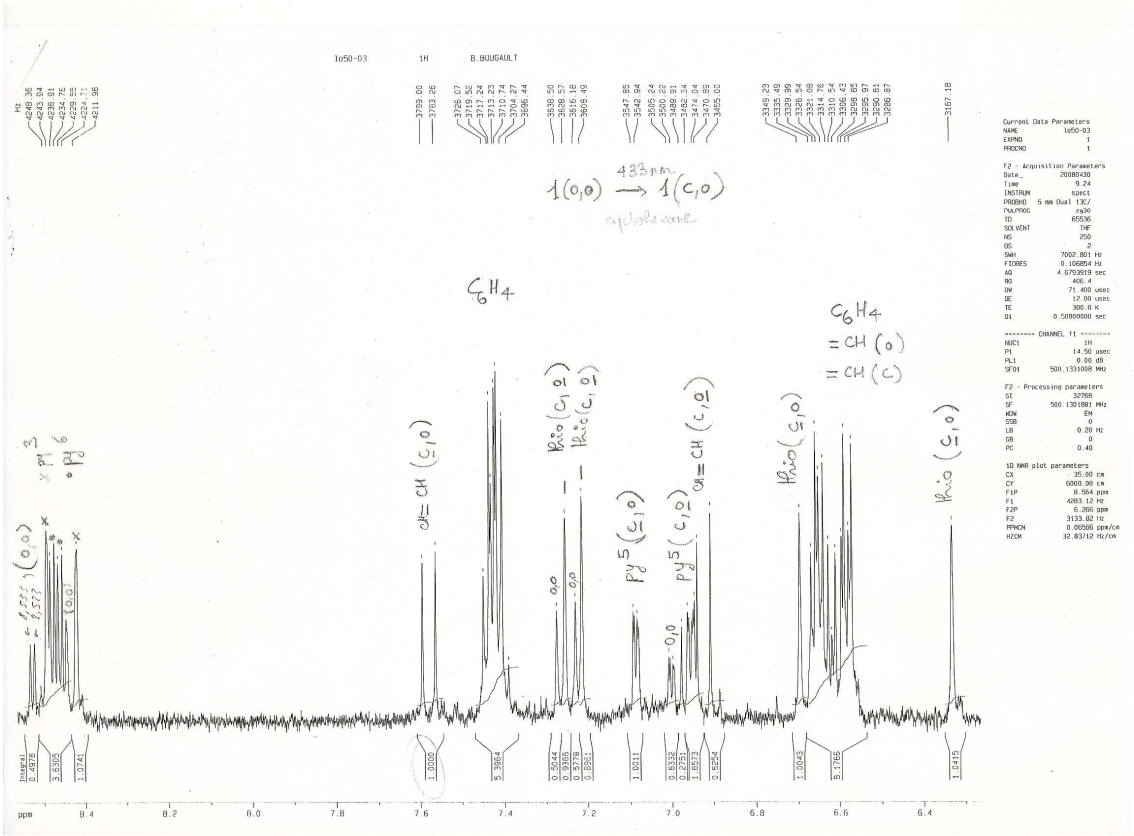


Figure S8. ^{1}H NMR after irradiation of **1(o,o)** in deuterated cyclohexane (aromatic region)

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