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SUPPORTING INFORMATION

Symmetrical Bis(fulvene) Chromophores: Model Compounds for Acceptor-Donor-Acceptor Dye Architectures

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Experimental

General. All solvents, starting materials and reagents were purchased from either Aldrich Chemical Co. or TCI America as reagent grade or higher quality and used as received. Literature procedures were used to prepare 9,9-dioctylfluorene-2,7-dicarboxaldehyde,[1] 2,5-bis(hexyloxy)terephthaldehyde,[2] 2,2'-bithiophene-5,5'-dicarbaldehyde,[3] and 1,3-diphenylcyclopentadiene.[4] Premium grade silica gel used for column chromatography was purchased from Sorbent Technologies (60Å, 40-63 μm (230X400 Mesh)). All ^{1}H and ^{13}C NMR spectra were obtained under ambient conditions using an Agilent Technologies 400 MHz instrument. Proton and ^{13}C NMR spectra were referenced using the peak for TMS (0.03%, $\delta = 0$, ^{1}H) or the peak for $CDCl_3$ ($\delta = 77.0$, ^{13}C). High resolution MS data was obtained using an Agilent Technologies LCMS-TOF with reserpine as an internal standard. UV-Vis spectra were obtained under ambient conditions using quartz cells and a Cary-50 UV-Vis spectrophotometer. Single crystal X-ray diffraction data for bis(fulvene) **3** was obtained at 100 K using a Bruker SMART APEX CCD diffractometer. For details of the single crystal X-ray diffraction study, see pages 13-40 below.

Bis(fulvene) 1. A mixture of 1,3-diphenylcyclopentadiene (1.00 g, 4.58 mmol) and terephthaldehyde (0.31 g, 2.27 mmol) were combined in MeOH (20 mL). Pyrrolidine (0.57 mL, 6.94 mmol) was added and the resulting slurry stirred at room temperature for 16 hours. A brown precipitate was recovered by vacuum filtration, washed with 10 mL of cold MeOH, and vacuum dried to give **1** as a crude brown solid. Purification was achieved with flash column chromatography using hexanes (to remove a small amount of unreacted diphenylcyclopentadiene), followed by elution with 20% ethyl acetate/hexanes to give **1** as a brown solid (0.99 g, 81%). The brown solid was crystallized from 50/50 C_6H_6/MeOH to give **1** as a crystalline brown solid (0.43 g, 35%). Mp: 200-201° C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19-7.69 (overlapping m, 26 H, Ph*H* and exocyclic fulvene-C*H*); 7.03, 6.96 (broad m, 4 H, fulvene-C*H*). Selected ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 145.0, 141.7, 137.8, 137.3, 135.8, 135.1, 131.0, 129.4, 128.7, 128.5, 128.3, 128.1, 127.1, 126.2, 114.2 (*C* and *C*H). LC-TOF MS (APCI) m/z: $[M+H]^+$ calcd for $C_{42}H_{30}$, 535.2420; found, 535.2418.

Bis(fulvene) 2. Crude **2** was obtained as an orange solid (0.86 g, 89%) using a similar procedure to that used for the synthesis of **1**, except using 1,3-diphenylcyclopentadiene (0.50 g, 2.29 mmol), 9,9-dioctyl-9H-fluorene-3,6-dicarbaldehyde (0.51 g, 1.14 mmol) and pyrrolidine (0.30 mL, 3.65 mmol) and sonicating the reaction mixture at room temperature for 16 hours. Flash column chromatography (same method as for **1**) gave **2** as an orange solid (0.54 g, 56%). Crystalline **2** was also obtained from 50/50 C_6H_6/MeOH (0.15 g, 15%). Mp: 138-139 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.82 (overlapping m, 28 H, Ph*H* and exocyclic fulvene-C*H*); 7.09, 7.03 (broad m, 4 H, fulvene-C*H*); 2.06 (m, 4 H, octyl-CC*H*$_2$); 1.18, 1.10 (overlapping m, 20 H, octyl-C*H*$_2$); 0.78, 0.74 (t, overlapping with m, 10 H, octyl-*Me* and octyl-C*H*$_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 146.7, 144.0, 141.7, 141.6, 139.2, 136.6, 136.1, 135.3, 130.0, 129.5, 128.7, 128.4, 128.3, 127.9, 127.7, 127.0, 126.1, 125.4, 120.4, 114.6 (*Ph*, *C*CH_2, and fulvene –*C* and –*C*H); 55.3, 40.4, 31.7, 30.2, 29.3, 24.0, 22.6, 14.0 (octyl –*Me* and *C*H_2). LC-TOF MS (APCI) m/z: $[M+H]^+$ calcd for $C_{65}H_{66}$, 847.5237; found, 847.5236.

Bis(fulvene) 3. Crude **3** was obtained as a black solid (1.56 g, 71%) using a similar procedure to that used for the synthesis of **1**, except using 1,3-diphenylcyclopentadiene (1.30 g, 5.96 mmol), 2,5-bis(hexyloxy)terephthalaldehyde (0.99 g, 2.96 mmol) and pyrrolidine (0.74 ml, 9.01 mmol). Attempts to obtain **3** as a crystalline material using a variety of solvents resulted in a significant loss of yield. However, crystallization of **3** from

50/50 C_6H_6/MeOH gave crystals suitable for single crystal X-ray analysis. Flash column chromatography (same method as for **1** and **2**) on remaining crude **3** (0.96 g) gave a black solid (0.54 g, 25 %). Mp: 160-161° C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95-7.63 (overlapping m, 28 H, Ph*H* and fulvene- C*H*); 3.96 (t, 4 H, OCH_2, *J* = 6 Hz); 1.71 (m, 4 H, OCH_2CH_2); 1.35, 1.21 (m, 12 H, CH_2); 0.79 (t, 6 H, Me, *J* = 7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 146.7, 144.1, 141.7, 136.0, 135.3, 134.0, 129.3, 128.7, 128.5, 128.3, 128.0, 127.9, 127.0, 126.1, 115.5, 114.3 (*Ph* and fulvene -*C* and –*C*H); 69.3 (O*C*H_2); 31.6, 29.3, 25.8, 22.6, 14.1 (*C*H_2 and *Me*). LC-TOF MS (APCI) m/z: $[M+H]^+$ calcd for $C_{54}H_{54}O_2$, 735.4197; found, 735.4200.

Bis(fulvene) 4. Bis(fulvene) **4** was obtained as a dark purple solid (0.50 g, 75%) using a similar procedure to that used for the synthesis of **3**, except using 1,3-diphenylcyclopentadiene (0.47 g, 2.15 mmol), 2,2'-bithiophene-5,5'-dicarbaldehyde (0.24 g, 1.52 mmol) and pyrrolidine (0.30 ml, 3.65 mmol). Analysis (^{1}H NMR) indicated >95% purity, and further purification by column chromatography was not carried out. Mp: 215-216 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.93−7.79 (m, 30 H, Ph*H*, fulvene-*H*, and bithiophene-*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 142.1, 141.9, 141.7, 141.6, 140.8, 135.9, 135.2, 135.1, 129.5, 129.3, 128.5, 128.1, 127.6, 127.1, 126.3, 125.3, 113.1. LC-TOF MS (APCI) m/z: $[M+H]^+$ calcd for $C_{44}H_{30}S_2$, 623.1862; found, 847.1857.

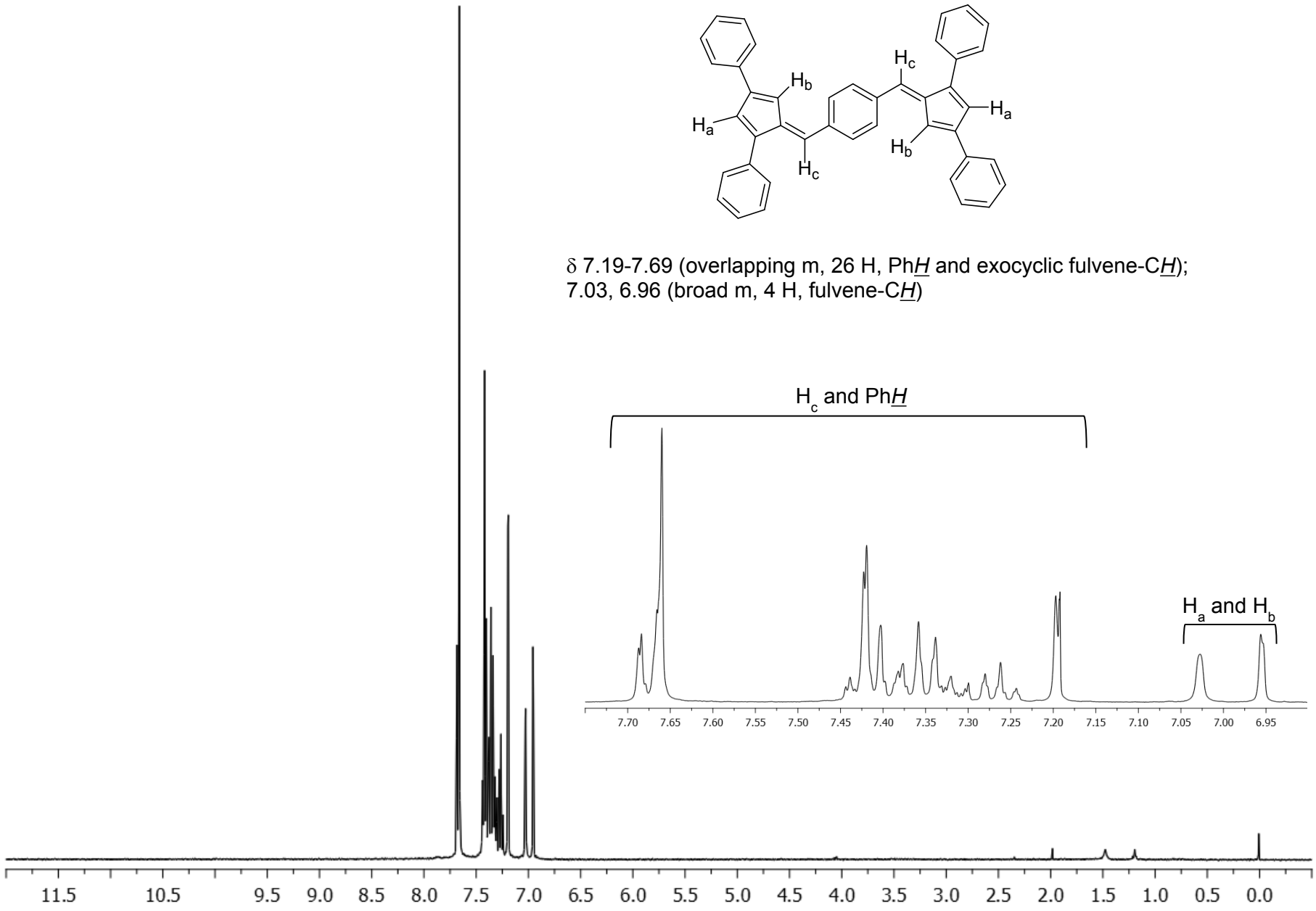


Figure S1. 400 MHz ^{1}H NMR spectrum of bis(fulvene) 1 in $CDCl_3$.

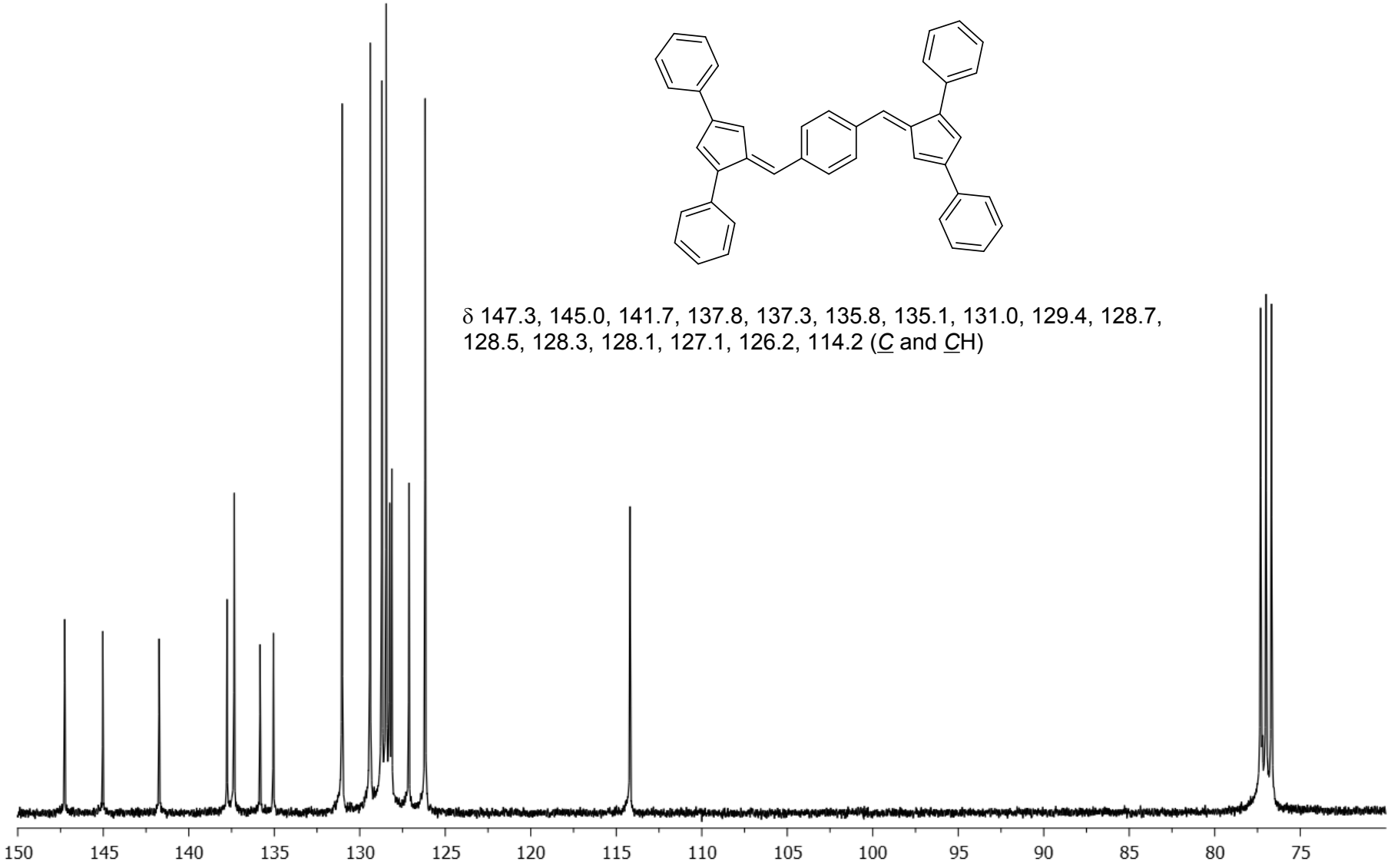
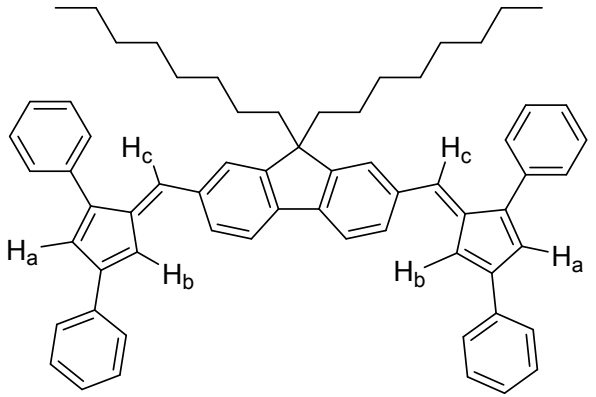


Figure S2. 100 MHz ^{13}C NMR spectrum of bis(fulvene) 1 in $CDCl_3$.

δ 7.30-7.82 (overlapping m, 28 H, Ph*H* and exocyclic fulvene-C*H*); 7.09, 7.03 (broad m, 4 H, fulvene-C*H*); 2.06 (m, 4 H, octyl-CCH_2); 1.18, 1.10 (overlapping m, 20 H, octyl-CH_2); 0.78, 0.74 (t, overlapping with m, 10 H, octyl-*Me* and octyl-CH_2)



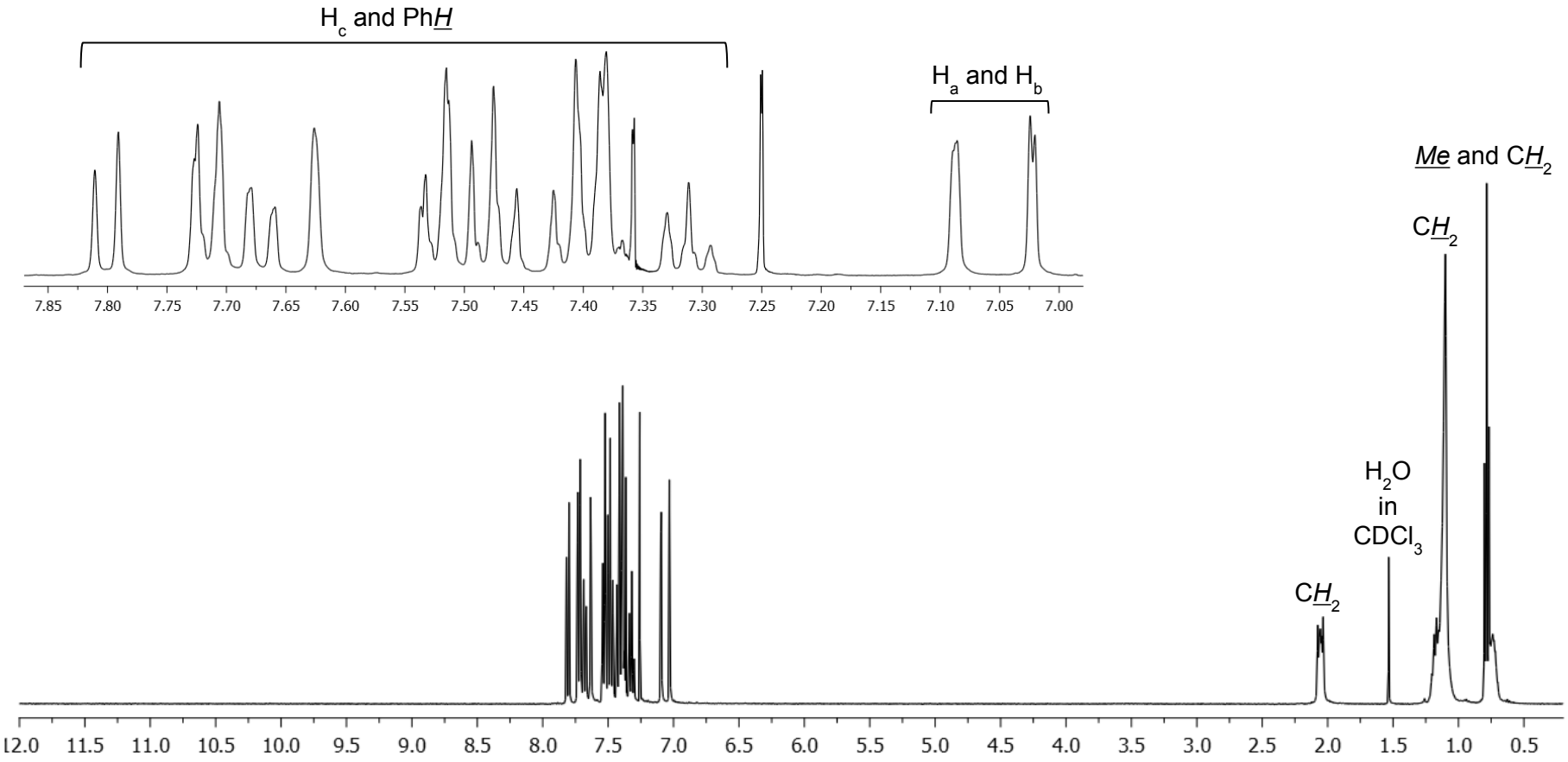
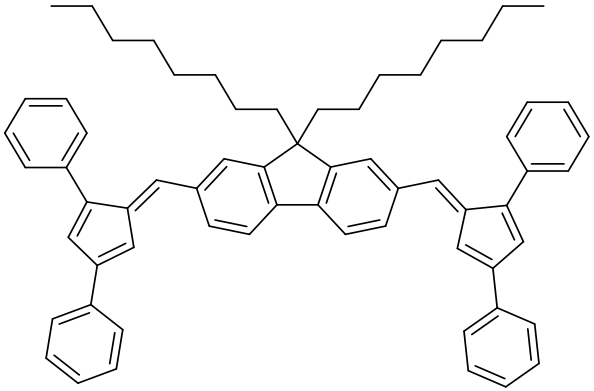


Figure S3. 400 MHz ^{1}H NMR spectrum of bis(fulvene) 2 in $CDCl_3$.

δ 151.9, 146.7, 144.0, 141.7, 141.6, 139.2, 136.6, 136.1, 135.3, 130.0, 129.5, 128.7, 128.4, 128.3, 127.9, 127.7, 127.0, 126.1, 125.4, 120.4, 114.6 (*Ph*, *C*CH_2, and fulvene –*C* and –*C*H); 55.3, 40.4, 31.7, 30.2, 29.3, 24.0, 22.6, 14.0 (octyl –*Me* and *C*H_2)



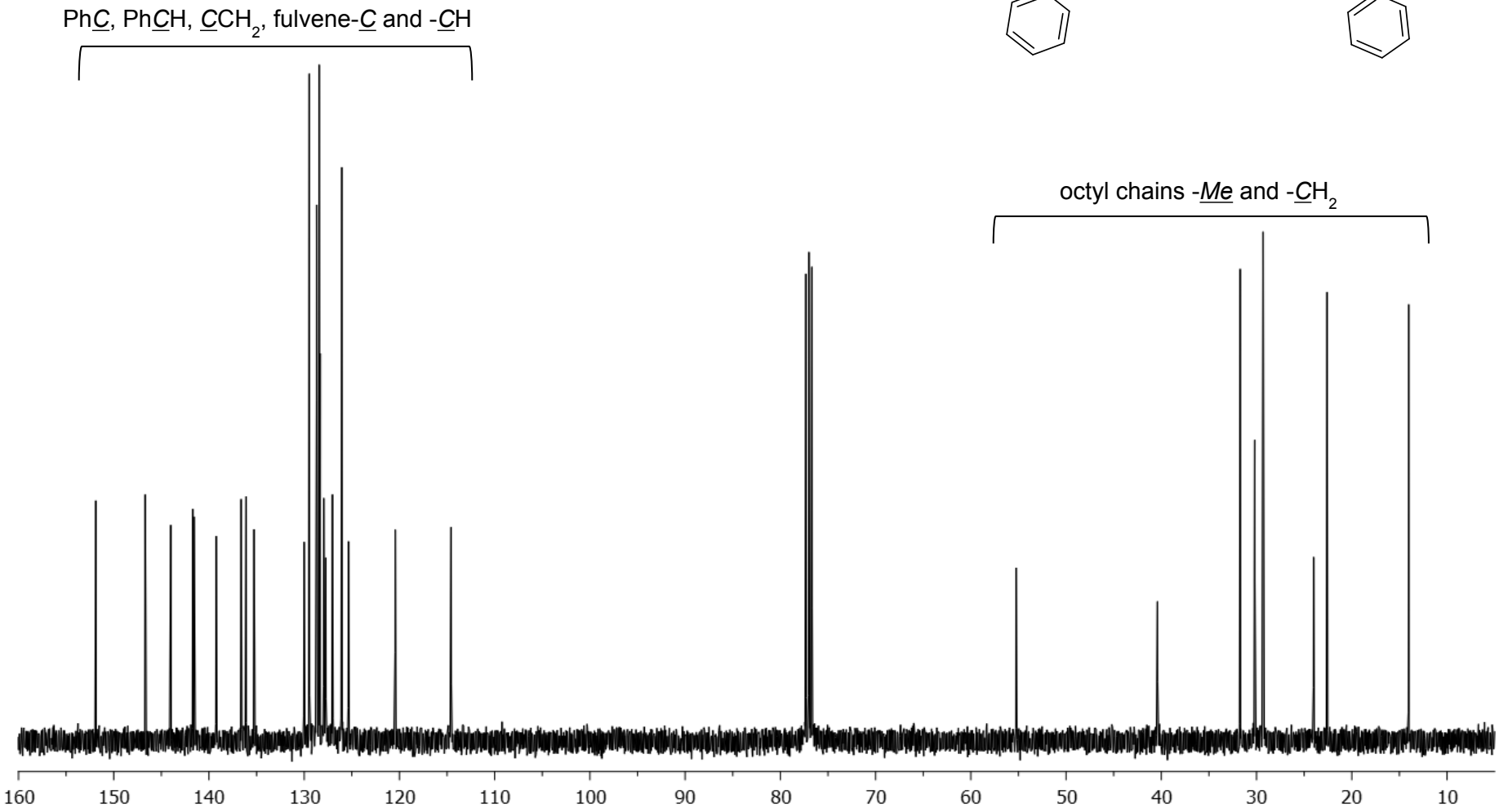


Figure S4. 100 MHz ^{13}C NMR spectrum of bis(fulvene) 2 in $CDCl_3$.

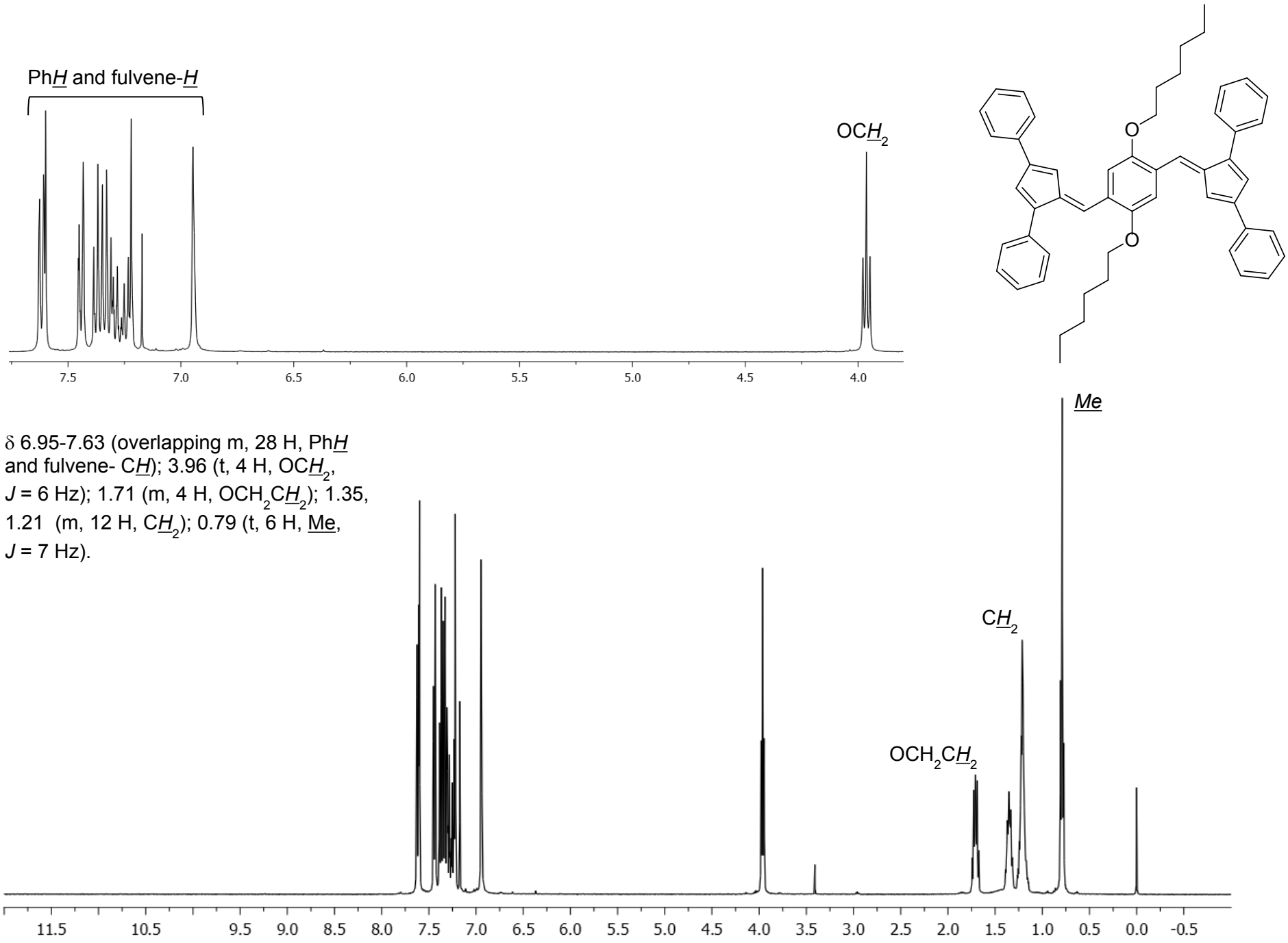


Figure S5. 400 MHz ^{1}H NMR spectrum of bis(fulvene) 3 in $CDCl_3$.

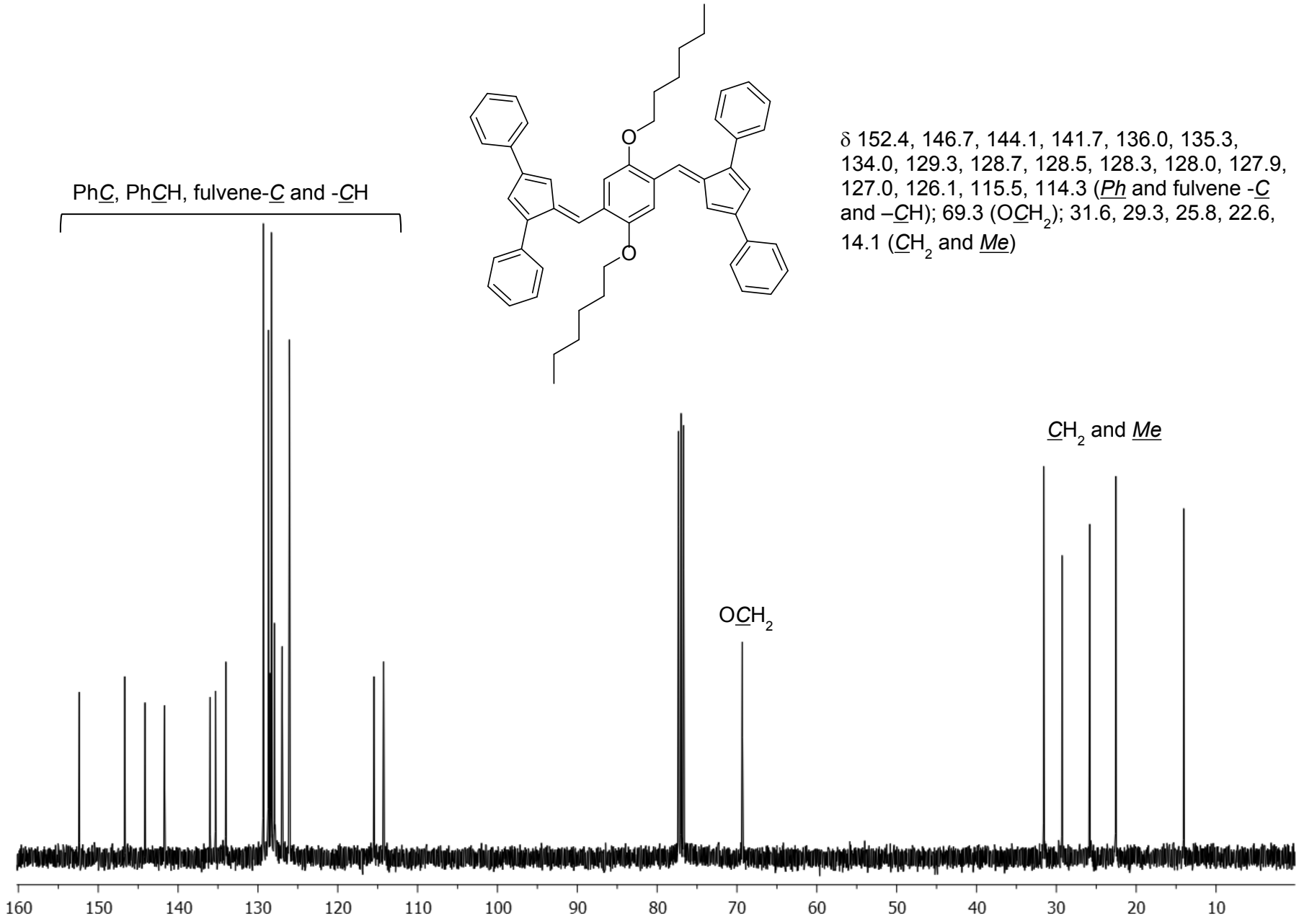


Figure S6. 100 MHz ^{13}C NMR spectrum of bis(fulvene) 3 in $CDCl_3$.

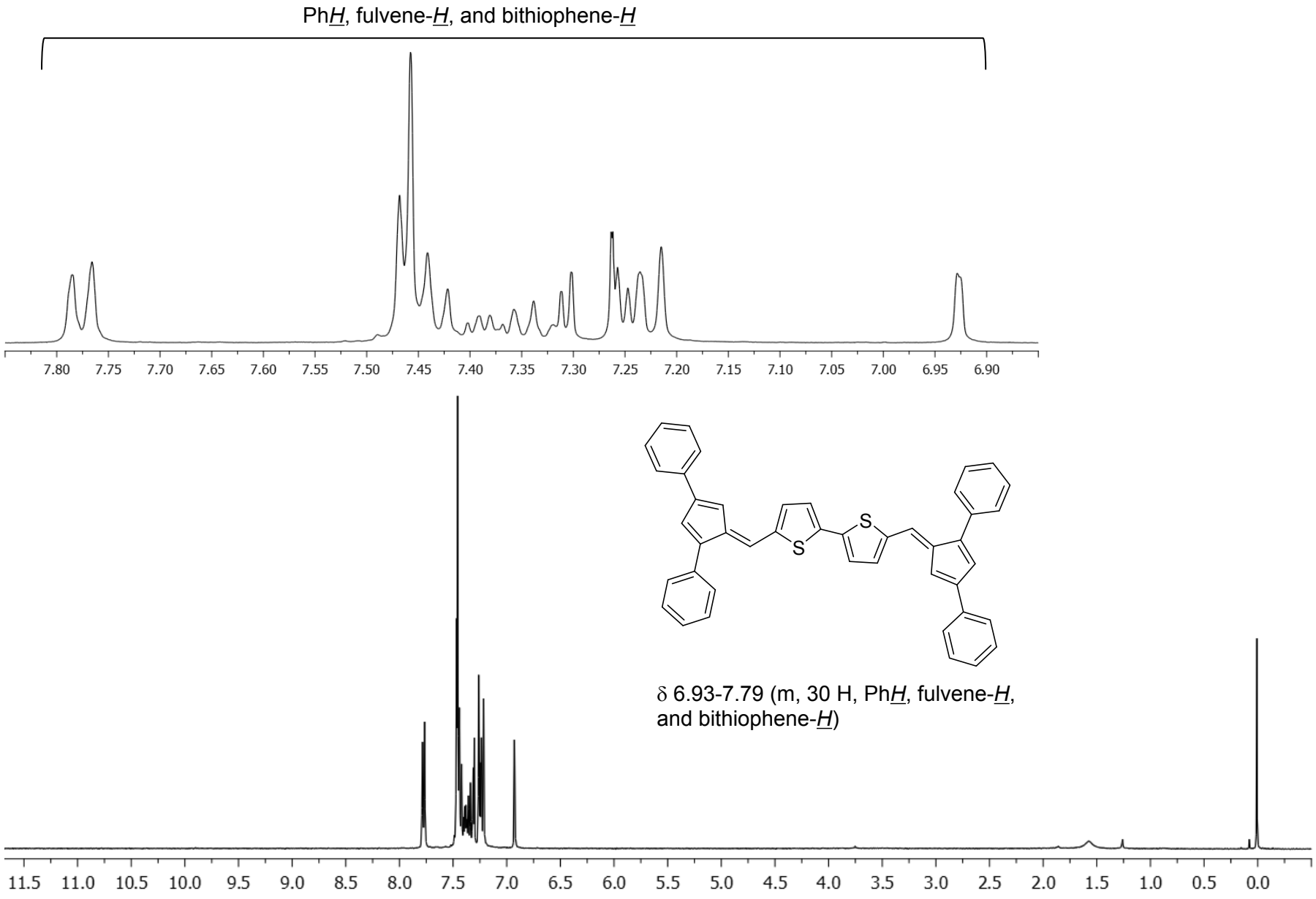
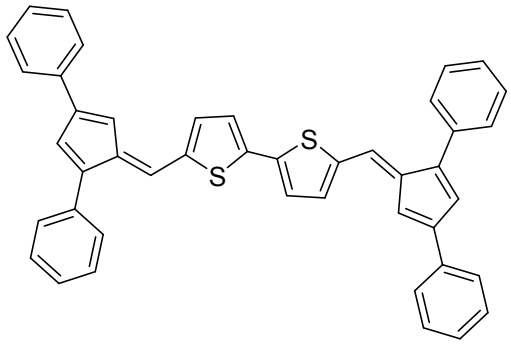


Figure S7. 400 MHz ^{1}H NMR spectrum of bis(fulvene) 4 in $CDCl_3$.

δ 146.8, 142.1, 141.9, 141.7, 141.6, 140.8, 135.9, 135.2, 135.1, 129.5, 129.3, 128.5, 128.1, 127.6, 127.1, 126.3, 125.3, 113.1



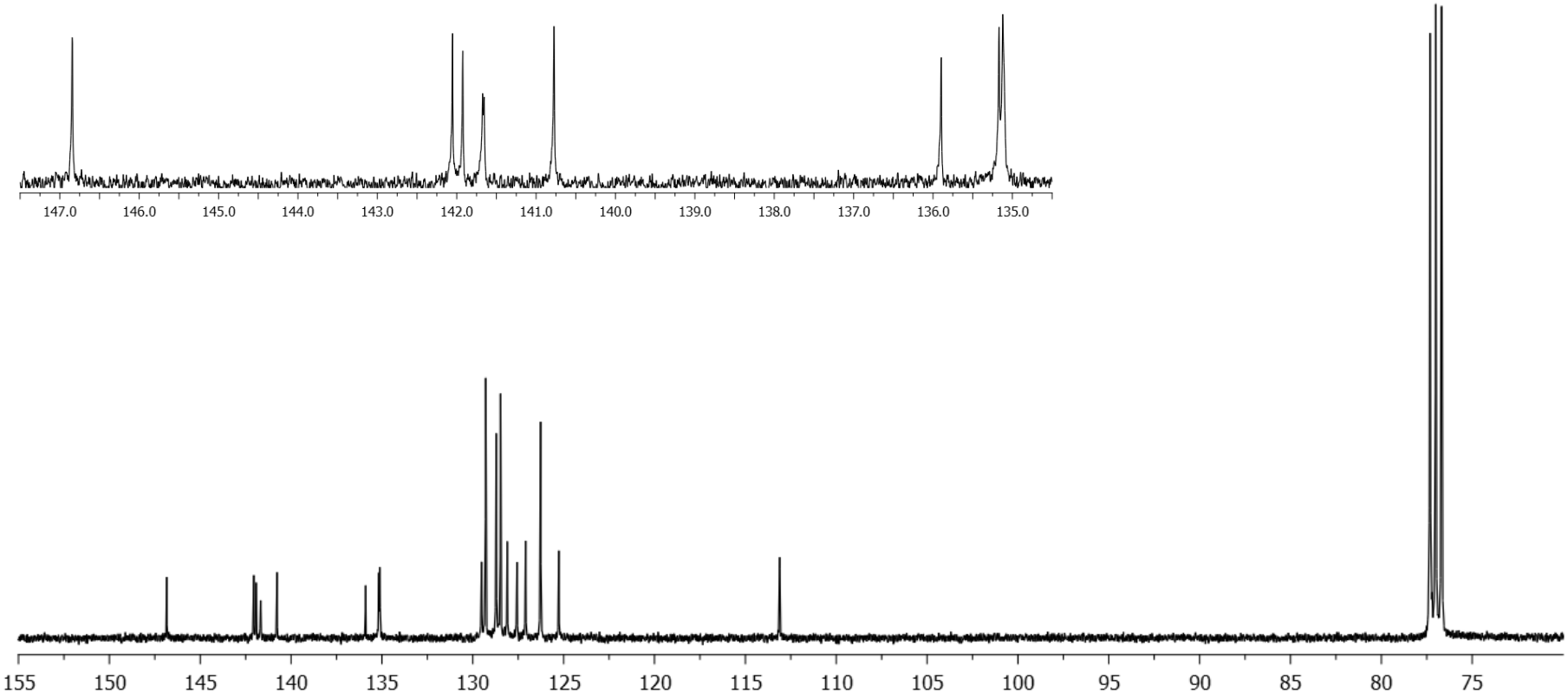


Figure S8. 100 MHz ^{13}C NMR spectrum of bis(fulvene) 4 in $CDCl_3$.

X-Ray Crystallographic Data for Bis(fulvene) 2

Crystals of bis(fulvene) **3** suitable for single crystal X-ray diffraction were obtained from 50/50 C_6H_6/MeOH. A red rectangular prismatic crystal of **3** measuring 0.44 × 0.13 × 0.11 mm^3 was mounted on a MiTeGen MicroGrabber mount using Paratone-N oil. Data was collected at 100 K using a Bruker SMART APEX CCD diffractometer. Data sets were processed using the APEX2 software suite (Bruker, version 2013.6-2).[5] Space group determinations were based on systematic absences and intensity statistics (XPREP, Bruker AXS Inc.),[5] and all data sets were corrected for absorption using SADABS (Bruker, version 2012/1).[5] All structures were solved using direct methods and difference map techniques, and were refined by full-matrix least squares procedures on F^2 (SHELXS and SHELXL, Sheldrick 2013).[6] All non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms were treated as idealized contributions and refined using a riding model. Thermal ellipsoid views and packing diagrams were prepared using Mercury.[7] Crystallographic data for **3** was deposited in the Cambridge Crystallographic Data Center (CCDC) with publication number 1007436. Copies of the crystallography data can be obtained, free of charge, from the CCDC website (www.ccdc.cam.ac.uk).

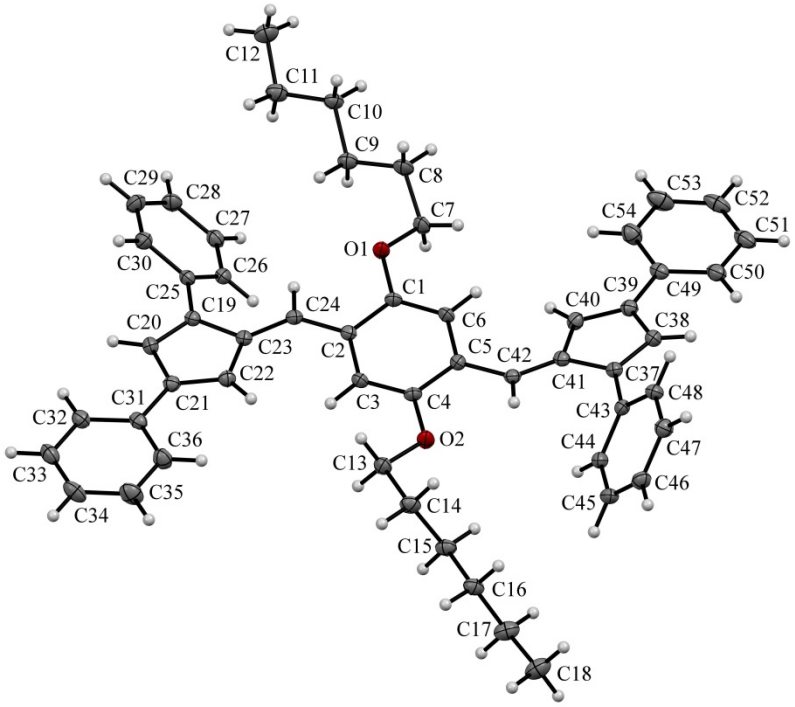


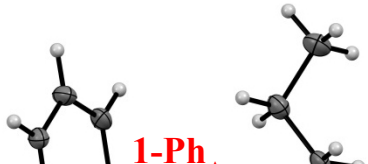
Figure S9. Thermal ellipsoid view of bis(fulvene) 3 (50% probability ellipsoids). Torsion angles O1C7C8C9 (57.7(2)°) and O2C13C14C15 (58.5(2)°) indicate a gauche conformation for both of the O-hexyl zigzag chains with respect to the direction of the respective O1-C7 or O2-C13 bonds. The angle between the mean plane of the zigzag chain (C13-C18) and the mean plane of the central Ph ring (C1-C6) is much larger (74.23°) compared to the same angle for the mean plane of the zigzag chain defined by C7-C12 (30.29°).

Table S1. Sample and crystal data for bis(fulvene) 3.

Chemical formula	$C_{54}H_{54}O_2$	
Formula weight	734.97	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.110 x 0.130 x 0.440 mm	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.0302(19) Å	α = 79.160(2)°
	b = 14.195(3) Å	β = 75.233(2)°
	c = 15.533(3) Å	γ = 77.829(2)°
Volume	2069.2(7) $Å^3$	
Z	2	
Density (calculated)	1.180	
Absorption coefficient	0.070 mm^{-1}	
F(000)	788	
Theta range for data collection	1.87 to 28.05°	
Index ranges	-13<=h<=13, -18<=k<=18, -20<=l<=20	
Reflections collected	43327	
Independent reflections	9982 [R(int) = 0.0569]	
Coverage of independent reflections	99.4%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9920 and 0.9700	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9982 / 0 / 505	
Goodness-of-fit on F^2	1.022	
Final R indices	6836 data; I>2σ(I)	R1 = 0.0505, wR2 = 0.1198
	all data	R1 = 0.0825, wR2 = 0.1389
Largest diff. peak and hole	0.324 and -0.262 $eÅ^{-3}$	

Selected Bond Distances (Å)

C1-O1 = 1.376(2)
O1-C7 = 1.434(2)
C1-C2 = 1.411(2)
C3-C4 = 1.383(2)



Selected Bond Angles (°)

C19-C20-C21 = 109.76(13)
C22-C21-C20 = 107.88(12)
C21-C22-C23 = 109.51(13)
C22-C23-C19 = 105.52(12)

Figure S10. Thermal ellipsoid view of bis(fulvene) 3 depicting selected bond distances and angles. Substituent angles represent the angles between the least squares planes of the Ph and fulvene rings as well as between the least squares planes defined by 6 carbon atoms of each alkyl chain. Shortest intermolecular contacts are noted between H3-H22 (1.98 Å) and H6-H7B (1.97 Å). Thermal ellipsoids are shown at the 50% probability level.

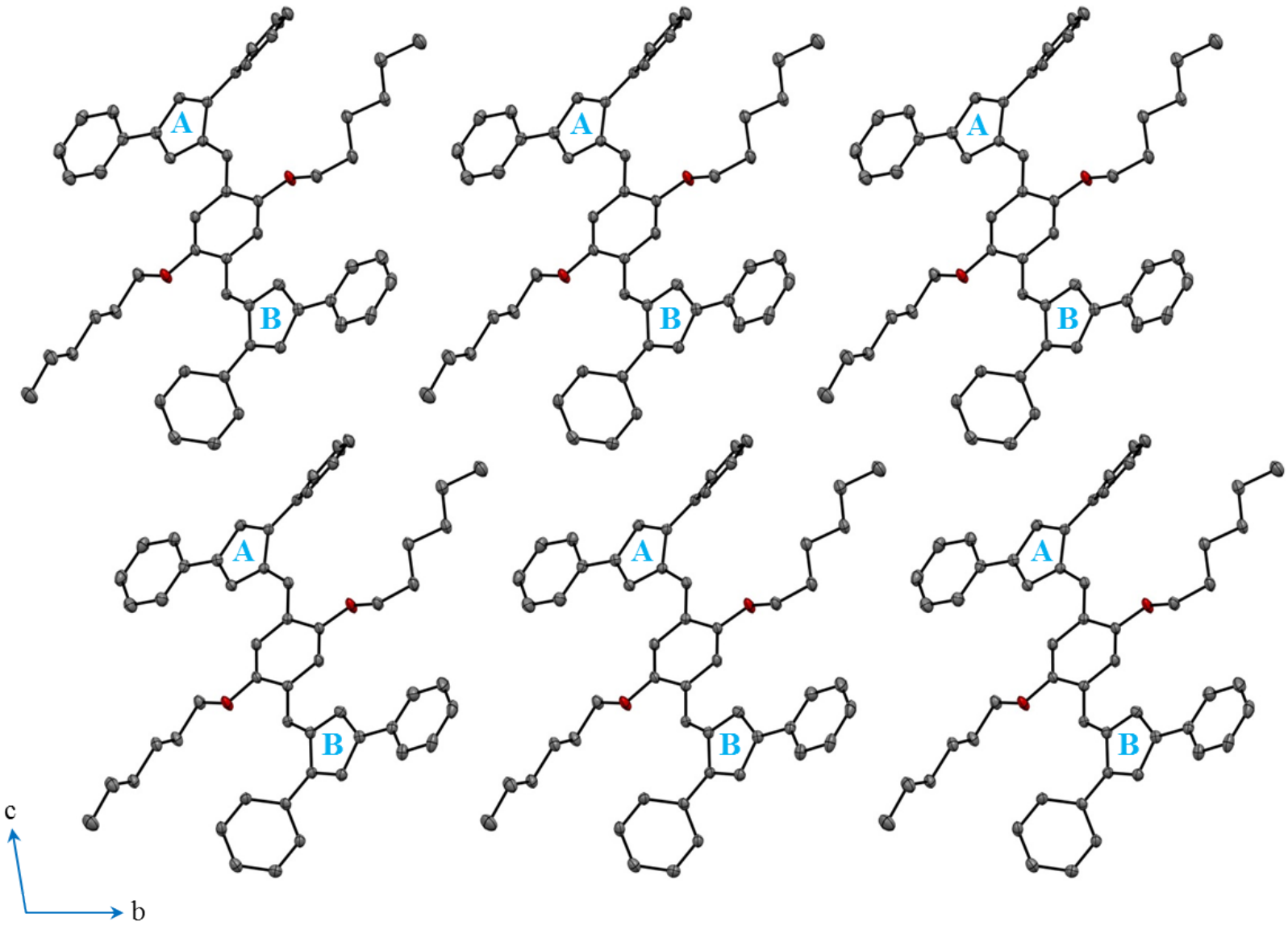


Figure S11. Packing view of bis(fulvene) 3 , view along the a-axis direction. Molecules are aligned in the same relative orientation along the b-axis direction and align in a head-to-tail fashion with respect to the fulvene rings, A and B, along the c-axis direction. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms were omitted for clarity.

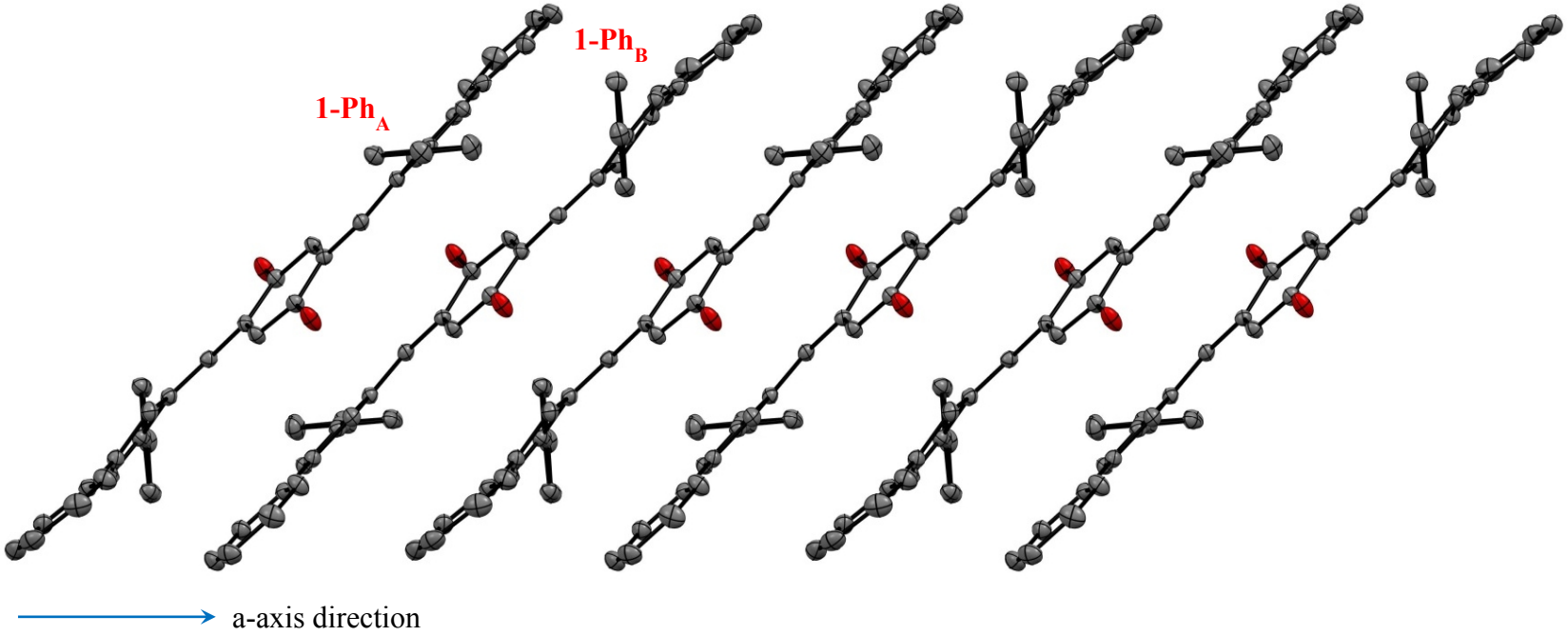


Figure S12. Packing view of bis(fulvene) 3, view perpendicular to the a-axis direction showing large angle (89.4°) between the least squares planes of the 1-Ph$_A$ and 1-Ph$_B$ rings along the a-axis direction. The least squares plane of the central-Ph group is tipped 24.3° with respect to the 100 plane. Thermal ellipsoids are shown at the 50% probability level. The alkyl chains and hydrogen atoms were omitted for clarity.

Table S2. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for bis(fulvene) 3.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
O1	0.71901(12)	0.67710(7)	0.39624(7)	0.0253(3)
O2	0.74540(12)	0.32987(7)	0.62493(7)	0.0254(3)
C1	0.73810(15)	0.58840(10)	0.44952(10)	0.0179(3)
C2	0.68870(14)	0.51206(10)	0.42740(9)	0.0161(3)
C3	0.69228(15)	0.42454(10)	0.48720(10)	0.0182(3)
C4	0.74226(15)	0.41324(10)	0.56433(10)	0.0177(3)
C5	0.79735(14)	0.48825(10)	0.58402(9)	0.0160(3)
C6	0.79251(15)	0.57557(10)	0.52486(10)	0.0187(3)
C7	0.81024(16)	0.74417(11)	0.39157(10)	0.0222(3)
C8	0.74952(18)	0.84136(11)	0.34578(11)	0.0257(4)
C9	0.72845(16)	0.84220(11)	0.25234(10)	0.0228(3)
C10	0.67034(16)	0.94381(11)	0.21086(10)	0.0230(3)
C11	0.63921(18)	0.94748(11)	0.11973(11)	0.0273(4)
C12	0.59507(19)	0.05109(12)	0.07648(12)	0.0342(4)
C13	0.66028(16)	0.26109(11)	0.62271(10)	0.0226(3)
C14	0.65688(16)	0.19068(11)	0.70861(11)	0.0236(3)

Table S2. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for bis(fulvene) 3.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

C15	0.80108(16)	0.13771(11)	0.72082(10)	0.0228(3)
C16	0.79760(16)	0.06687(11)	0.80738(10)	0.0230(3)
C17	0.94174(17)	0.01133(12)	0.81566(11)	0.0304(4)
C18	0.94326(19)	0.94424(13)	0.90433(12)	0.0364(4)
C19	0.54977(15)	0.49649(10)	0.21818(9)	0.0168(3)
C20	0.48054(15)	0.42792(10)	0.20857(10)	0.0182(3)
C21	0.46396(14)	0.35659(10)	0.29024(10)	0.0178(3)
C22	0.52387(15)	0.38302(10)	0.34912(10)	0.0184(3)
C23	0.58109(14)	0.47119(10)	0.30904(9)	0.0164(3)
C24	0.64395(14)	0.52717(10)	0.34327(10)	0.0172(3)
C25	0.58875(15)	0.57872(10)	0.14898(10)	0.0179(3)
C26	0.71955(15)	0.60732(10)	0.13113(10)	0.0191(3)
C27	0.75474(16)	0.68252(11)	0.06303(10)	0.0222(3)
C28	0.66046(17)	0.73020(11)	0.01099(11)	0.0257(4)
C29	0.53083(17)	0.70234(11)	0.02732(11)	0.0275(4)
C30	0.49522(16)	0.62777(11)	0.09571(10)	0.0228(3)
C31	0.39527(15)	0.27147(11)	0.30450(10)	0.0193(3)

Table S2. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for bis(fulvene) 3.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

C32	0.32754(16)	0.25605(11)	0.24115(11)	0.0227(3)
C33	0.26306(17)	0.17540(12)	0.25521(11)	0.0275(4)
C34	0.26460(18)	0.10834(12)	0.33176(11)	0.0299(4)
C35	0.33109(19)	0.12228(12)	0.39526(12)	0.0317(4)
C36	0.39495(17)	0.20292(12)	0.38180(11)	0.0262(4)
C37	0.93778(15)	0.51734(10)	0.78712(10)	0.0174(3)
C38	0.99979(15)	0.59181(10)	0.79214(10)	0.0194(3)
C39	0.03031(15)	0.65068(11)	0.70343(10)	0.0186(3)
C40	0.98447(15)	0.61148(11)	0.64517(10)	0.0195(3)
C41	0.91920(15)	0.52856(10)	0.69365(10)	0.0176(3)
C42	0.84200(14)	0.47557(10)	0.66782(9)	0.0169(3)
C43	0.89516(15)	0.44051(10)	0.86064(10)	0.0174(3)
C44	0.92350(15)	0.34251(11)	0.84822(10)	0.0198(3)
C45	0.88771(16)	0.27032(11)	0.91894(11)	0.0234(3)
C46	0.82209(16)	0.29390(11)	0.00386(11)	0.0235(3)
C47	0.79331(16)	0.39070(11)	0.01757(10)	0.0234(3)
C48	0.82897(15)	0.46317(11)	0.94679(10)	0.0206(3)

Table S2. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for bis(fulvene) 3.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

C49	0.10081(15)	0.73546(11)	0.68196(10)	0.0203(3)
C50	0.17763(16)	0.75261(11)	0.73923(11)	0.0249(3)
C51	0.24931(17)	0.83047(12)	0.71773(12)	0.0297(4)
C52	0.24489(18)	0.89348(12)	0.63866(12)	0.0316(4)
C53	0.16703(19)	0.87890(12)	0.58181(12)	0.0337(4)
C54	0.09596(17)	0.80066(12)	0.60321(11)	0.0281(4)

Table S3. Bond lengths (Å) for bis(fulvene) 3.

O1-C1	1.3762(17)	O1-C7	1.4341(17)
O2-C4	1.3667(17)	O2-C13	1.4362(17)
C1-C6	1.380(2)	C1-C2	1.4111(19)
C2-C3	1.4041(19)	C2-C24	1.452(2)
C3-C4	1.383(2)	C3-H3	0.95
C4-C5	1.410(2)	C5-C6	1.397(2)
C5-C42	1.4501(19)	C6-H6	0.95
C7-C8	1.509(2)	C7-H7A	0.99
C7-H7B	0.99	C8-C9	1.517(2)
C8-H8A	0.99	C8-H8B	0.99
C9-C10	1.524(2)	C9-H9A	0.99
C9-H9B	0.99	C10-C11	1.515(2)
C10-H10A	0.99	C10-H10B	0.99

Table S3. Bond lengths (Å) for bis(fulvene) 3.

C11-C12	1.522(2)	C11-H11A	0.99
C11-H11B	0.99	C12-H12A	0.98
C12-H12B	0.98	C12-H12C	0.98
C13-C14	1.507(2)	C13-H13A	0.99
C13-H13B	0.99	C14-C15	1.523(2)
C14-H14A	0.99	C14-H14B	0.99
C15-C16	1.517(2)	C15-H15A	0.99
C15-H15B	0.99	C16-C17	1.518(2)
C16-H16A	0.99	C16-H16B	0.99
C17-C18	1.522(2)	C17-H17A	0.99
C17-H17B	0.99	C18-H18A	0.98
C18-H18B	0.98	C18-H18C	0.98
C19-C20	1.358(2)	C19-C25	1.475(2)
C19-C23	1.486(2)	C20-C21	1.464(2)
C20-H20	0.95	C21-C22	1.357(2)
C21-C31	1.468(2)	C22-C23	1.4528(19)
C22-H22	0.95	C23-C24	1.3613(19)
C24-H24	0.95	C25-C30	1.397(2)
C25-C26	1.400(2)	C26-C27	1.388(2)
C26-H26	0.95	C27-C28	1.386(2)

Table S3. Bond lengths (Å) for bis(fulvene) 3.

C27-H27	0.95	C28-C29	1.386(2)
C28-H28	0.95	C29-C30	1.386(2)
C29-H29	0.95	C30-H30	0.95
C31-C36	1.396(2)	C31-C32	1.401(2)
C32-C33	1.387(2)	C32-H32	0.95
C33-C34	1.378(2)	C33-H33	0.95
C34-C35	1.386(2)	C34-H34	0.95
C35-C36	1.384(2)	C35-H35	0.95
C36-H36	0.95	C37-C38	1.358(2)
C37-C43	1.468(2)	C37-C41	1.486(2)
C38-C39	1.466(2)	C38-H38	0.95
C39-C40	1.360(2)	C39-C49	1.465(2)
C40-C41	1.456(2)	C40-H40	0.95
C41-C42	1.358(2)	C42-H42	0.95
C43-C48	1.398(2)	C43-C44	1.400(2)
C44-C45	1.384(2)	C44-H44	0.95
C45-C46	1.384(2)	C45-H45	0.95
C46-C47	1.388(2)	C46-H46	0.95
C47-C48	1.387(2)	C47-H47	0.95
C48-H48	0.95	C49-C54	1.393(2)

Table S3. Bond lengths (Å) for bis(fulvene) 3.

C49-C50	1.398(2)	C50-C51	1.387(2)
C50-H50	0.95	C51-C52	1.381(2)
C51-H51	0.95	C52-C53	1.386(3)
C52-H52	0.95	C53-C54	1.388(2)
C53-H53	0.95	C54-H54	0.95

Table S4. Bond angles (°) for bis(fulvene) 3.

C1-O1-C7	118.22(11)	C4-O2-C13	118.35(11)
O1-C1-C6	122.38(13)	O1-C1-C2	116.42(12)
C6-C1-C2	121.01(13)	C3-C2-C1	117.05(13)
C3-C2-C24	124.44(13)	C1-C2-C24	118.45(13)
C4-C3-C2	121.67(13)	C4-C3-H3	119.2
C2-C3-H3	119.2	O2-C4-C3	123.47(13)
O2-C4-C5	115.50(12)	C3-C4-C5	121.01(13)
C6-C5-C4	117.16(13)	C6-C5-C42	123.18(13)
C4-C5-C42	119.34(13)	C1-C6-C5	121.99(13)
C1-C6-H6	119.0	C5-C6-H6	119.0
O1-C7-C8	107.50(12)	O1-C7-H7A	110.2

Table S4. Bond angles (°) for bis(fulvene) 3.

C8-C7-H7A	110.2	O1-C7-H7B	110.2
C8-C7-H7B	110.2	H7A-C7-H7B	108.5
C7-C8-C9	115.90(13)	C7-C8-H8A	108.3
C9-C8-H8A	108.3	C7-C8-H8B	108.3
C9-C8-H8B	108.3	H8A-C8-H8B	107.4
C8-C9-C10	111.98(13)	C8-C9-H9A	109.2
C10-C9-H9A	109.2	C8-C9-H9B	109.2
C10-C9-H9B	109.2	H9A-C9-H9B	107.9
C11-C10-C9	114.00(13)	C11-C10-H10A	108.8
C9-C10-H10A	108.8	C11-C10-H10B	108.8
C9-C10-H10B	108.8	H10A-C10-H10B	107.6
C10-C11-C12	112.42(14)	C10-C11-H11A	109.1
C12-C11-H11A	109.1	C10-C11-H11B	109.1
C12-C11-H11B	109.1	H11A-C11-H11B	107.9
C11-C12-H12A	109.5	C11-C12-H12B	109.5
H12A-C12-H12B	109.5	C11-C12-H12C	109.5
H12A-C12-H12C	109.5	H12B-C12-H12C	109.5
O2-C13-C14	106.57(12)	O2-C13-H13A	110.4

Table S4. Bond angles (°) for bis(fulvene) 3.

C14-C13-H13A	110.4	O2-C13-H13B	110.4
C14-C13-H13B	110.4	H13A-C13-H13B	108.6
C13-C14-C15	113.68(13)	C13-C14-H14A	108.8
C15-C14-H14A	108.8	C13-C14-H14B	108.8
C15-C14-H14B	108.8	H14A-C14-H14B	107.7
C16-C15-C14	113.65(12)	C16-C15-H15A	108.8
C14-C15-H15A	108.8	C16-C15-H15B	108.8
C14-C15-H15B	108.8	H15A-C15-H15B	107.7
C15-C16-C17	112.60(13)	C15-C16-H16A	109.1
C17-C16-H16A	109.1	C15-C16-H16B	109.1
C17-C16-H16B	109.1	H16A-C16-H16B	107.8
C16-C17-C18	113.96(14)	C16-C17-H17A	108.8
C18-C17-H17A	108.8	C16-C17-H17B	108.8
C18-C17-H17B	108.8	H17A-C17-H17B	107.7
C17-C18-H18A	109.5	C17-C18-H18B	109.5
H18A-C18-H18B	109.5	C17-C18-H18C	109.5
H18A-C18-H18C	109.5	H18B-C18-H18C	109.5
C20-C19-C25	125.34(13)	C20-C19-C23	107.33(12)

Table S4. Bond angles (°) for bis(fulvene) 3.

C25-C19-C23	127.31(13)	C19-C20-C21	109.76(13)
C19-C20-H20	125.1	C21-C20-H20	125.1
C22-C21-C20	107.88(12)	C22-C21-C31	126.70(14)
C20-C21-C31	125.42(13)	C21-C22-C23	109.51(13)
C21-C22-H22	125.2	C23-C22-H22	125.2
C24-C23-C22	131.01(13)	C24-C23-C19	123.37(13)
C22-C23-C19	105.52(12)	C23-C24-C2	131.08(14)
C23-C24-H24	114.5	C2-C24-H24	114.5
C30-C25-C26	117.94(13)	C30-C25-C19	119.45(13)
C26-C25-C19	122.54(13)	C27-C26-C25	120.97(14)
C27-C26-H26	119.5	C25-C26-H26	119.5
C28-C27-C26	120.17(14)	C28-C27-H27	119.9
C26-C27-H27	119.9	C27-C28-C29	119.62(14)
C27-C28-H28	120.2	C29-C28-H28	120.2
C30-C29-C28	120.25(14)	C30-C29-H29	119.9
C28-C29-H29	119.9	C29-C30-C25	121.05(14)
C29-C30-H30	119.5	C25-C30-H30	119.5
C36-C31-C32	117.52(14)	C36-C31-C21	121.19(14)

Table S4. Bond angles (°) for bis(fulvene) 3.

C32-C31-C21	121.29(14)	C33-C32-C31	120.85(15)
C33-C32-H32	119.6	C31-C32-H32	119.6
C34-C33-C32	120.70(15)	C34-C33-H33	119.6
C32-C33-H33	119.6	C33-C34-C35	119.33(15)
C33-C34-H34	120.3	C35-C34-H34	120.3
C36-C35-C34	120.21(16)	C36-C35-H35	119.9
C34-C35-H35	119.9	C35-C36-C31	121.38(15)
C35-C36-H36	119.3	C31-C36-H36	119.3
C38-C37-C43	126.45(13)	C38-C37-C41	107.36(13)
C43-C37-C41	126.18(13)	C37-C38-C39	109.67(13)
C37-C38-H38	125.2	C39-C38-H38	125.2
C40-C39-C49	126.54(14)	C40-C39-C38	108.03(13)
C49-C39-C38	125.42(13)	C39-C40-C41	109.15(13)
C39-C40-H40	125.4	C41-C40-H40	125.4
C42-C41-C40	130.59(13)	C42-C41-C37	123.37(13)
C40-C41-C37	105.66(12)	C41-C42-C5	129.35(14)
C41-C42-H42	115.3	C5-C42-H42	115.3
C48-C43-C44	117.80(13)	C48-C43-C37	120.47(13)

Table S4. Bond angles (°) for bis(fulvene) 3.

C44-C43-C37	121.69(13)	C45-C44-C43	121.15(14)
C45-C44-H44	119.4	C43-C44-H44	119.4
C44-C45-C46	120.38(14)	C44-C45-H45	119.8
C46-C45-H45	119.8	C45-C46-C47	119.33(14)
C45-C46-H46	120.3	C47-C46-H46	120.3
C48-C47-C46	120.39(15)	C48-C47-H47	119.8
C46-C47-H47	119.8	C47-C48-C43	120.95(14)
C47-C48-H48	119.5	C43-C48-H48	119.5
C54-C49-C50	117.69(14)	C54-C49-C39	121.34(14)
C50-C49-C39	120.96(14)	C51-C50-C49	121.37(16)
C51-C50-H50	119.3	C49-C50-H50	119.3
C52-C51-C50	120.05(16)	C52-C51-H51	120.0
C50-C51-H51	120.0	C51-C52-C53	119.48(15)
C51-C52-H52	120.3	C53-C52-H52	120.3
C52-C53-C54	120.38(17)	C52-C53-H53	119.8
C54-C53-H53	119.8	C53-C54-C49	121.01(16)
C53-C54-H54	119.5	C49-C54-H54	119.5

Table S5. Torsion angles (°) for bis(fulvene) 3.

C7-O1-C1-C6	28.7(2)	C7-O1-C1-C2	-156.17(13)
O1-C1-C2-C3	-172.67(13)	C6-C1-C2-C3	2.5(2)
O1-C1-C2-C24	10.1(2)	C6-C1-C2-C24	-174.72(13)
C1-C2-C3-C4	-0.2(2)	C24-C2-C3-C4	176.89(14)
C13-O2-C4-C3	-17.4(2)	C13-O2-C4-C5	164.13(13)
C2-C3-C4-O2	178.90(13)	C2-C3-C4-C5	-2.7(2)
O2-C4-C5-C6	-178.33(13)	C3-C4-C5-C6	3.2(2)
O2-C4-C5-C42	-4.7(2)	C3-C4-C5-C42	176.81(13)
O1-C1-C6-C5	172.85(13)	C2-C1-C6-C5	-2.0(2)
C4-C5-C6-C1	-0.8(2)	C42-C5-C6-C1	-174.20(14)
C1-O1-C7-C8	-168.37(13)	O1-C7-C8-C9	-57.69(18)
C7-C8-C9-C10	-178.54(13)	C8-C9-C10-C11	-176.52(13)
C9-C10-C11-C12	-174.38(14)	C4-O2-C13-C14	-166.56(12)
O2-C13-C14-C15	-58.48(17)	C13-C14-C15-C16	179.95(13)
C14-C15-C16-C17	177.07(14)	C15-C16-C17-C18	176.39(14)
C25-C19-C20-C21	178.42(13)	C23-C19-C20-C21	-0.07(16)
C19-C20-C21-C22	0.05(17)	C19-C20-C21-C31	-179.53(13)
C20-C21-C22-C23	0.00(16)	C31-C21-C22-C23	179.56(13)
C21-C22-C23-C24	176.32(15)	C21-C22-C23-C19	-0.04(16)
C20-C19-C23-C24	-176.65(13)	C25-C19-C23-C24	4.9(2)

Table S5. Torsion angles (°) for bis(fulvene) 3.

C20-C19-C23-C22	0.06(15)	C25-C19-C23-C22	-178.39(13)
C22-C23-C24-C2	7.7(3)	C19-C23-C24-C2	-176.46(14)
C3-C2-C24-C23	9.7(2)	C1-C2-C24-C23	-173.25(15)
C20-C19-C25-C30	39.4(2)	C23-C19-C25-C30	-142.42(15)
C20-C19-C25-C26	-137.47(16)	C23-C19-C25-C26	40.7(2)
C30-C25-C26-C27	0.4(2)	C19-C25-C26-C27	177.35(14)
C25-C26-C27-C28	-0.5(2)	C26-C27-C28-C29	0.0(2)
C27-C28-C29-C30	0.5(2)	C28-C29-C30-C25	-0.5(2)
C26-C25-C30-C29	0.0(2)	C19-C25-C30-C29	-176.97(14)
C22-C21-C31-C36	-5.0(2)	C20-C21-C31-C36	174.50(14)
C22-C21-C31-C32	174.95(15)	C20-C21-C31-C32	-5.6(2)
C36-C31-C32-C33	-0.1(2)	C21-C31-C32-C33	179.96(14)
C31-C32-C33-C34	-0.2(2)	C32-C33-C34-C35	0.2(3)
C33-C34-C35-C36	0.1(3)	C34-C35-C36-C31	-0.5(3)
C32-C31-C36-C35	0.5(2)	C21-C31-C36-C35	-179.59(15)
C43-C37-C38-C39	177.92(13)	C41-C37-C38-C39	-2.80(16)
C37-C38-C39-C40	0.70(17)	C37-C38-C39-C49	-178.05(14)
C49-C39-C40-C41	-179.48(14)	C38-C39-C40-C41	1.78(16)
C39-C40-C41-C42	169.60(15)	C39-C40-C41-C37	-3.39(16)
C38-C37-C41-C42	-169.86(14)	C43-C37-C41-C42	9.4(2)

Table S5. Torsion angles (°) for bis(fulvene) 3.

C38-C37-C41-C40	3.78(16)	C43-C37-C41-C40	-176.94(13)
C40-C41-C42-C5	-2.3(3)	C37-C41-C42-C5	169.63(14)
C6-C5-C42-C41	-19.7(2)	C4-C5-C42-C41	167.10(14)
C38-C37-C43-C48	42.7(2)	C41-C37-C43-C48	-136.45(15)
C38-C37-C43-C44	-134.91(16)	C41-C37-C43-C44	45.9(2)
C48-C43-C44-C45	-0.3(2)	C37-C43-C44-C45	177.41(13)
C43-C44-C45-C46	0.3(2)	C44-C45-C46-C47	-0.4(2)
C45-C46-C47-C48	0.5(2)	C46-C47-C48-C43	-0.4(2)
C44-C43-C48-C47	0.3(2)	C37-C43-C48-C47	-177.39(14)
C40-C39-C49-C54	17.2(2)	C38-C39-C49-C54	-164.31(14)
C40-C39-C49-C50	-161.62(15)	C38-C39-C49-C50	16.9(2)
C54-C49-C50-C51	-1.4(2)	C39-C49-C50-C51	177.40(14)
C49-C50-C51-C52	0.5(2)	C50-C51-C52-C53	0.8(2)
C51-C52-C53-C54	-1.1(3)	C52-C53-C54-C49	0.2(3)
			-177.73(15)
C50-C49-C54-C53	1.1(2)	C39-C49-C54-C53	

Table S6. Anisotropic atomic displacement parameters (Å^2) for bis(fulvene) 3.

The anisotropic atomic 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}

O1	0.0387(7)	0.0140(5)	0.0300(6)	0.0060(5)	-0.0204(5)	-0.0118(5)
O2	0.0384(6)	0.0160(5)	0.0277(6)	0.0069(5)	-0.0179(5)	-0.0136(5)

Table S6. Anisotropic atomic displacement parameters (Å^2) for bis(fulvene) 3.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

C1	0.0221(7)	0.0121(7)	0.0201(7)	0.0000(6)	-0.0072(6)	-0.0032(6)
C2	0.0173(7)	0.0137(7)	0.0173(7)	-0.0028(6)	-0.0037(6)	-0.0020(5)
C3	0.0221(7)	0.0134(7)	0.0210(7)	-0.0023(6)	-0.0075(6)	-0.0044(6)
C4	0.0212(7)	0.0125(7)	0.0188(7)	0.0011(6)	-0.0060(6)	-0.0026(6)
C5	0.0170(7)	0.0152(7)	0.0163(7)	-0.0027(6)	-0.0048(5)	-0.0020(5)
C6	0.0235(7)	0.0131(7)	0.0225(8)	-0.0023(6)	-0.0086(6)	-0.0057(6)
C7	0.0306(8)	0.0162(8)	0.0236(8)	0.0000(6)	-0.0106(7)	-0.0094(6)
C8	0.0363(9)	0.0141(8)	0.0291(9)	0.0004(6)	-0.0114(7)	-0.0079(6)
C9	0.0271(8)	0.0160(8)	0.0251(8)	-0.0004(6)	-0.0068(6)	-0.0048(6)
C10	0.0270(8)	0.0137(7)	0.0287(8)	0.0013(6)	-0.0094(7)	-0.0042(6)
C11	0.0320(9)	0.0189(8)	0.0299(9)	0.0000(7)	-0.0068(7)	-0.0055(7)
C12	0.0435(10)	0.0238(9)	0.0344(10)	0.0040(7)	-0.0147(8)	-0.0039(8)
C13	0.0272(8)	0.0174(8)	0.0266(8)	0.0003(6)	-0.0105(7)	-0.0087(6)
C14	0.0263(8)	0.0172(8)	0.0272(8)	0.0023(6)	-0.0064(7)	-0.0077(6)
C15	0.0249(8)	0.0160(8)	0.0263(8)	0.0008(6)	-0.0048(6)	-0.0050(6)

C16	0.0266(8)	0.0165(8)	0.0250(8)	-0.0007(6)	-0.0046(6)	-0.0054(6)

Table S6. Anisotropic atomic displacement parameters (Å^2) for bis(fulvene) 3.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

C17	0.0290(9)	0.0245(9)	0.0326(9)	0.0020(7)	-0.0057(7)	-0.0002(7)
C18	0.0376(10)	0.0313(10)	0.0363(10)	0.0054(8)	-0.0131(8)	-0.0005(8)
C19	0.0188(7)	0.0145(7)	0.0172(7)	-0.0030(6)	-0.0048(6)	-0.0012(5)
C20	0.0200(7)	0.0183(7)	0.0182(7)	-0.0042(6)	-0.0060(6)	-0.0037(6)
C21	0.0174(7)	0.0161(7)	0.0198(7)	-0.0020(6)	-0.0042(6)	-0.0030(6)
C22	0.0204(7)	0.0168(7)	0.0183(7)	-0.0005(6)	-0.0054(6)	-0.0042(6)
C23	0.0173(7)	0.0146(7)	0.0176(7)	-0.0029(6)	-0.0050(6)	-0.0015(5)
C24	0.0183(7)	0.0134(7)	0.0194(7)	-0.0014(6)	-0.0056(6)	-0.0010(5)
C25	0.0225(7)	0.0142(7)	0.0185(7)	-0.0039(6)	-0.0058(6)	-0.0032(6)
C26	0.0234(8)	0.0156(7)	0.0198(7)	-0.0037(6)	-0.0084(6)	-0.0015(6)
C27	0.0270(8)	0.0187(8)	0.0236(8)	-0.0037(6)	-0.0068(6)	-0.0076(6)
C28	0.0358(9)	0.0173(8)	0.0259(8)	0.0029(7)	-0.0109(7)	-0.0090(7)
C29	0.0323(9)	0.0212(8)	0.0315(9)	0.0045(7)	-0.0172(7)	-0.0053(7)
C30	0.0235(8)	0.0187(8)	0.0284(8)	-0.0010(6)	-0.0105(6)	-0.0049(6)
C31	0.0176(7)	0.0177(7)	0.0225(8)	-0.0059(6)	-0.0024(6)	-0.0029(6)
C32	0.0244(8)	0.0191(8)	0.0261(8)	-0.0045(6)	-0.0068(6)	-0.0045(6)

Table S6. Anisotropic atomic displacement parameters (Å^2) for bis(fulvene) 3.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

C33	0.0296(9)	0.0247(9)	0.0331(9)	-0.0106(7)	-0.0077(7)	-0.0088(7)
C34	0.0349(9)	0.0225(9)	0.0346(10)	-0.0083(7)	-0.0019(7)	-0.0132(7)
C35	0.0429(10)	0.0241(9)	0.0282(9)	0.0008(7)	-0.0041(8)	-0.0150(8)
C36	0.0330(9)	0.0232(8)	0.0251(8)	-0.0016(7)	-0.0077(7)	-0.0113(7)
C37	0.0192(7)	0.0148(7)	0.0186(7)	-0.0024(6)	-0.0064(6)	-0.0010(6)
C38	0.0224(7)	0.0164(7)	0.0211(8)	-0.0032(6)	-0.0083(6)	-0.0024(6)
C39	0.0183(7)	0.0166(7)	0.0206(7)	-0.0022(6)	-0.0044(6)	-0.0030(6)
C40	0.0196(7)	0.0199(8)	0.0190(7)	-0.0008(6)	-0.0056(6)	-0.0035(6)
C41	0.0181(7)	0.0153(7)	0.0189(7)	-0.0032(6)	-0.0044(6)	-0.0005(5)
C42	0.0195(7)	0.0135(7)	0.0169(7)	-0.0016(6)	-0.0047(6)	-0.0007(5)
C43	0.0187(7)	0.0156(7)	0.0195(7)	-0.0011(6)	-0.0089(6)	-0.0021(6)
C44	0.0241(8)	0.0164(7)	0.0203(7)	-0.0037(6)	-0.0091(6)	-0.0005(6)
C45	0.0283(8)	0.0141(7)	0.0301(9)	-0.0023(6)	-0.0136(7)	-0.0010(6)
C46	0.0256(8)	0.0193(8)	0.0263(8)	0.0036(7)	-0.0101(7)	-0.0063(6)
C47	0.0274(8)	0.0225(8)	0.0201(8)	-0.0023(6)	-0.0057(6)	-0.0038(6)
C48	0.0257(8)	0.0144(7)	0.0228(8)	-0.0031(6)	-0.0077(6)	-0.0024(6)

Table S6. Anisotropic atomic displacement parameters (Å^2) for bis(fulvene) 3.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

C49	0.0199(7)	0.0161(7)	0.0243(8)	-0.0049(6)	-0.0026(6)	-0.0030(6)
C50	0.0244(8)	0.0182(8)	0.0333(9)	-0.0059(7)	-0.0079(7)	-0.0027(6)
C51	0.0265(8)	0.0197(8)	0.0460(11)	-0.0125(8)	-0.0075(8)	-0.0042(6)
C52	0.0310(9)	0.0187(8)	0.0433(11)	-0.0102(8)	0.0035(8)	-0.0099(7)
C53	0.0441(11)	0.0210(9)	0.0321(10)	-0.0005(7)	0.0011(8)	-0.0122(8)
C54	0.0342(9)	0.0247(9)	0.0268(9)	-0.0033(7)	-0.0052(7)	-0.0104(7)

Table S7. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for bis(fulvene) 3.

	x/a	y/b	z/c	U(eq)
H3	0.6595	0.3718	0.4744	0.022
H6	0.8277	0.6277	0.5369	0.022
H7A	0.9053	0.7210	0.3568	0.027
H7B	0.8168	0.7501	0.4528	0.027
H8A	0.8120	0.8883	0.3417	0.031
H8B	0.6580	0.8650	0.3844	0.031
H9A	0.6631	0.7975	0.2557	0.027
H9B	0.8191	0.8180	0.2131	0.027
H10A	0.5832	0.9694	0.2525	0.028
H10B	0.7387	0.9872	0.2046	0.028

Table S7. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for bis(fulvene) 3.

	x/a	y/b	z/c	U(eq)
H11A	0.5636	0.9098	0.1267	0.033
H11B	0.7237	0.9163	0.0795	0.033
H12A	0.5753	1.0498	0.0182	0.051
H12B	0.6707	1.0882	0.0677	0.051
H12C	0.5108	1.0821	0.1157	0.051
H13A	0.7010	0.2263	0.5699	0.027
H13B	0.5645	0.2948	0.6189	0.027
H14A	0.5989	0.1419	0.7094	0.028
H14B	0.6113	0.2267	0.7602	0.028
H15A	0.8466	0.1017	0.6693	0.027
H15B	0.8590	0.1865	0.7200	0.027
H16A	0.7360	0.0199	0.8098	0.028
H16B	0.7570	0.1032	0.8592	0.028
H17A	1.0047	0.0587	0.8090	0.037
H17B	0.9795	-0.0280	0.7657	0.037

Table S7. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for bis(fulvene) 3.

H18A	1.0392	-0.0889	0.9050	0.055
H18B	0.8834	-0.1042	0.9109	0.055
H18C	0.9081	-0.0174	0.9542	0.055

Table S7. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for bis(fulvene) 3.

	x/a	y/b	z/c	U(eq)
H20	0.4478	0.4265	0.1567	0.022
H22	0.5278	0.3491	0.4075	0.022
H24	0.6616	0.5863	0.3056	0.021
H26	0.7852	0.5748	0.1661	0.023
H27	0.8437	0.7013	0.0521	0.027
H28	0.6845	0.7817	-0.0356	0.031
H29	0.4662	0.7345	-0.0085	0.033
H30	0.4058	0.6097	0.1066	0.027
H32	0.3258	0.3014	0.1879	0.027
H33	0.2173	0.1663	0.2116	0.033
H34	0.2205	0.0531	0.3409	0.036
H35	0.3328	0.0763	0.4482	0.038
H36	0.4395	0.2118	0.4261	0.031
H38	1.0203	0.6039	0.8451	0.023
H40	0.9936	0.6345	0.5828	0.023
H42	0.8130	0.4225	0.7109	0.02
H44	0.9681	0.3252	0.7902	0.024
H45	0.9083	0.2042	0.9091	0.028
H46	0.7970	0.2444	1.0523	0.028

Table S7. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for bis(fulvene) 3.

	x/a	y/b	z/c	U(eq)
H47	0.7489	0.4074	1.0758	0.028
H48	0.8081	0.5291	0.9570	0.025
H50	1.1808	0.7100	0.7940	0.03
H51	1.3015	0.8405	0.7574	0.036
H52	1.2948	0.9464	0.6234	0.038
H53	1.1623	0.9227	0.5279	0.04
H54	1.0432	0.7914	0.5636	0.034

Computational Methods and Results

All calculations were performed using Gaussian 09[8] and GaussView 05.[9] Density-functional geometry optimizations and vibrational frequency calculations were performed using Becke's three-parameter exchange functional[10] along with the local/non-local correlation functional by Lee, Yang, and Parr[11] in conjunction with the standard 6-311G basis set.[12] Minimum-energy geometries were confirmed by the presence of no imaginary vibrational frequencies. Electronic excited state and subsequent spectrum calculations were performed using time-dependent DFT calculations using the same functional and basis set. Only singlet states were included in the excited state calculations.

All four molecular geometries were optimized with no imaginary vibrational frequencies. The gas-phase geometries show a 22 - 29º angle between the central group and the fulvene ring planes, somewhat larger than seen in the crystal structures. Calculations of the UV-vis spectra show an average deviation of 35 nm for the predicted λ_{max} of the most low energy peak (Table S8). However, because the HOMO-LUMO transition typically has a lower extinction coefficient, the HOMO-LUMO gap does not necessarily track with λ_{max} (Table S8). Plots of the HOMOs and LUMOs for **1** – **4** are shown below. The plots show that the fulvene moiety contains significant electron probability for both HOMO and LUMO for all four derivatives, although in **4** the thiophene ring also has significant electronic population. In **4**, both the HOMO and LUMO extend over most of the molecule, whereas in the other molecules both the HOMO and LUMO are more localized. This may account for its relatively low HOMO-LUMO gap.

Table S8. Comparison of calculated and experimental (UV-Vis) data for bis(fulvenes) 1-4.

Fulvene	λ_{max} (calculated), nm	Δ(Theo – Expt), nm	HOMO-LUMO Gap, eV

1	440	+35	2.13
2	456	+32	2.29
3	435	-22	2.16
4	563	+54	1.91

Calculated UV-Vis Spectra

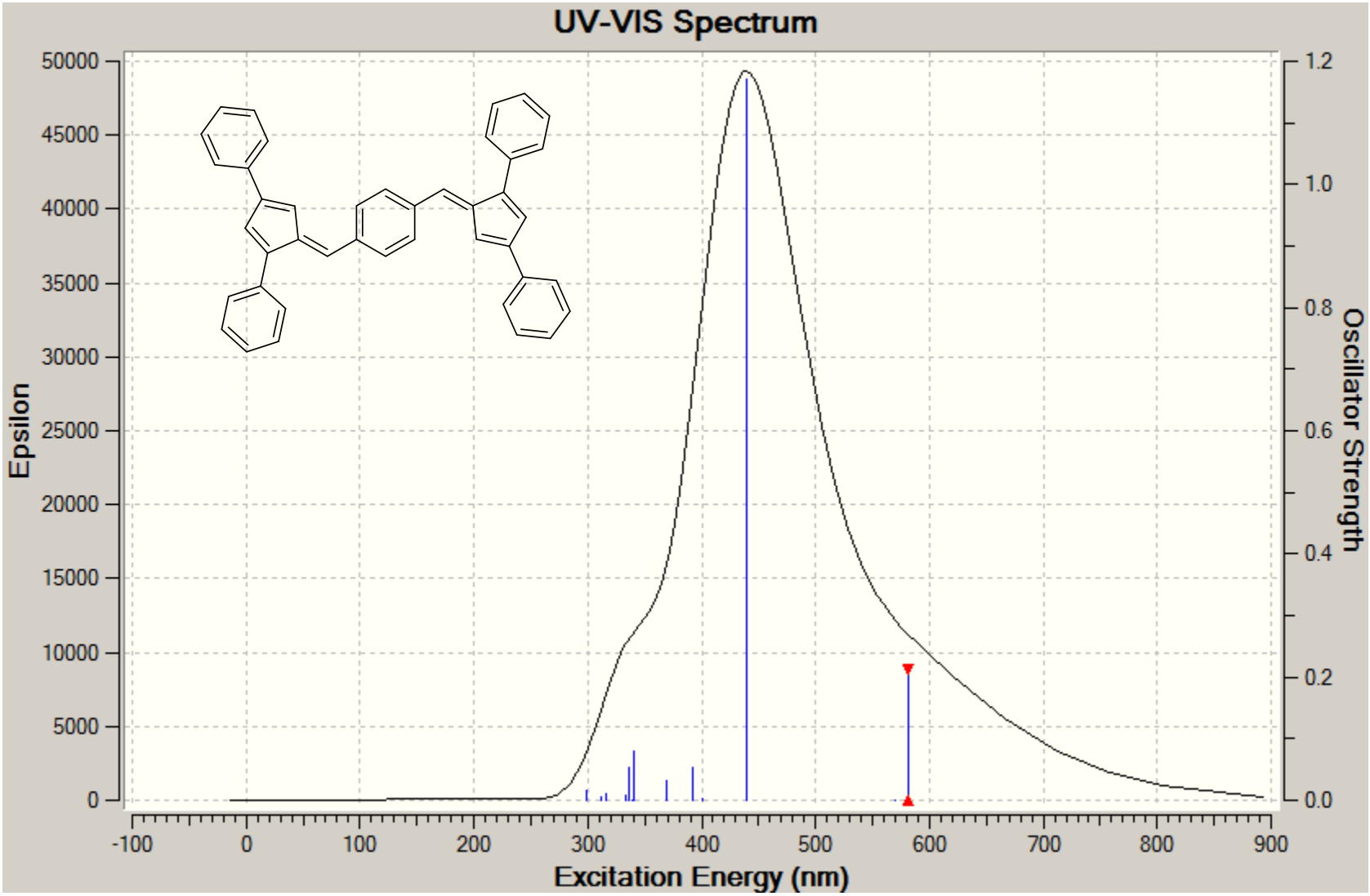


Figure S13. Calculated UV-Vis spectrum of bis(fulvene) 1.

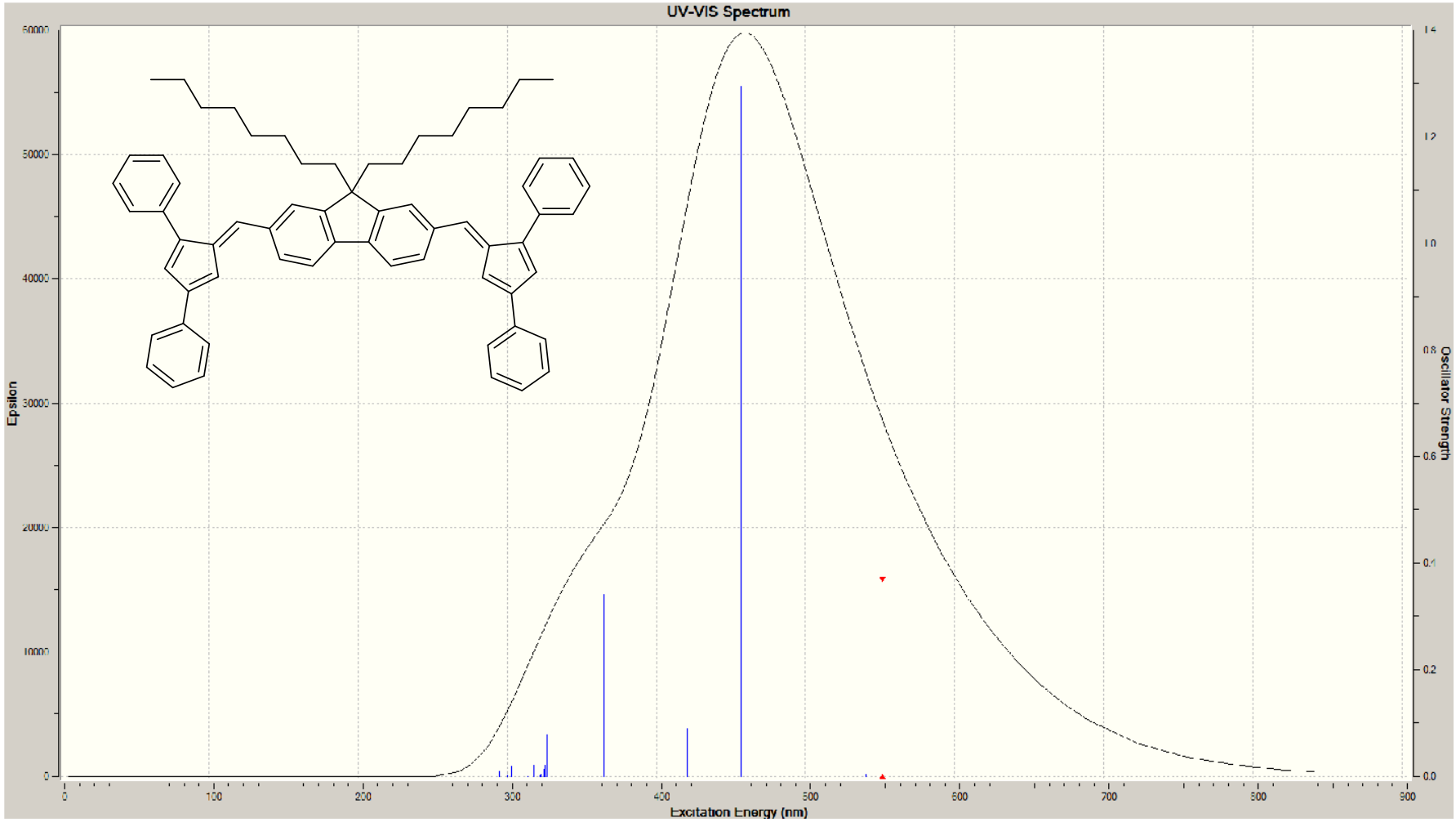


Figure S14. Calculated UV-Vis spectrum of bis(fulvene) 2.

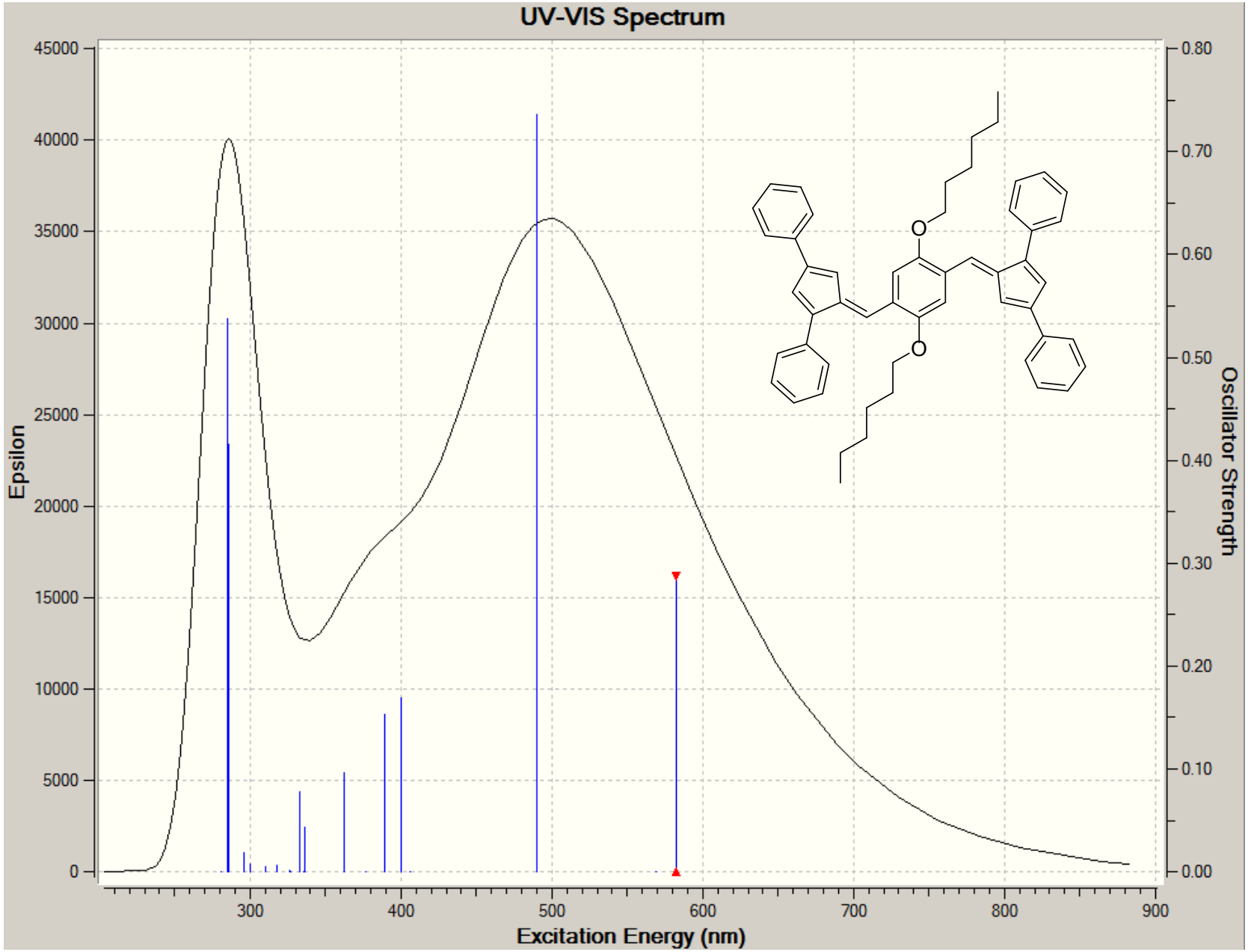


Figure S15. Calculated UV-Vis spectrum of bis(fulvene) 3.

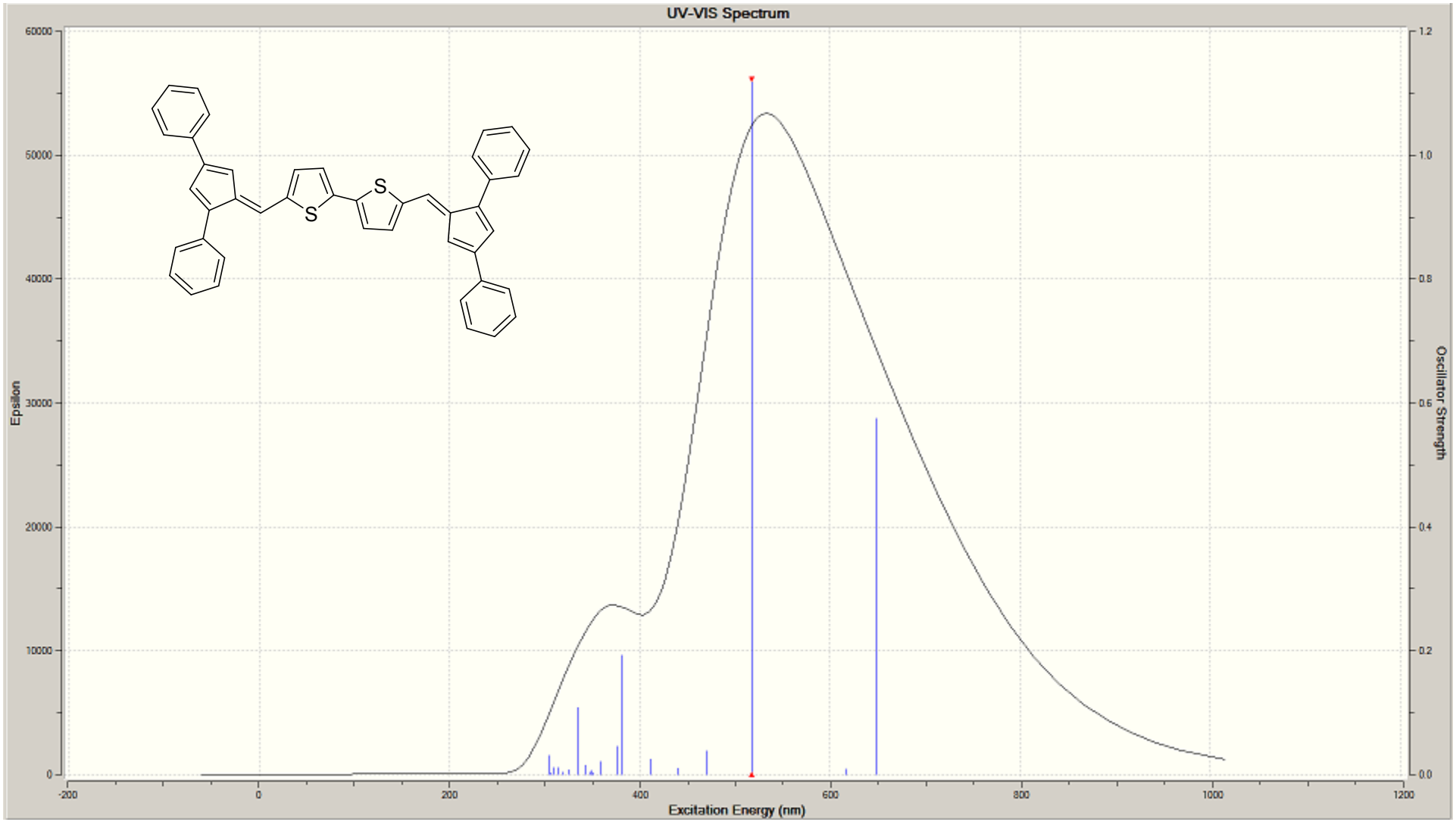


Figure S16. Calculated UV-Vis spectrum of bis(fulvene) 4.

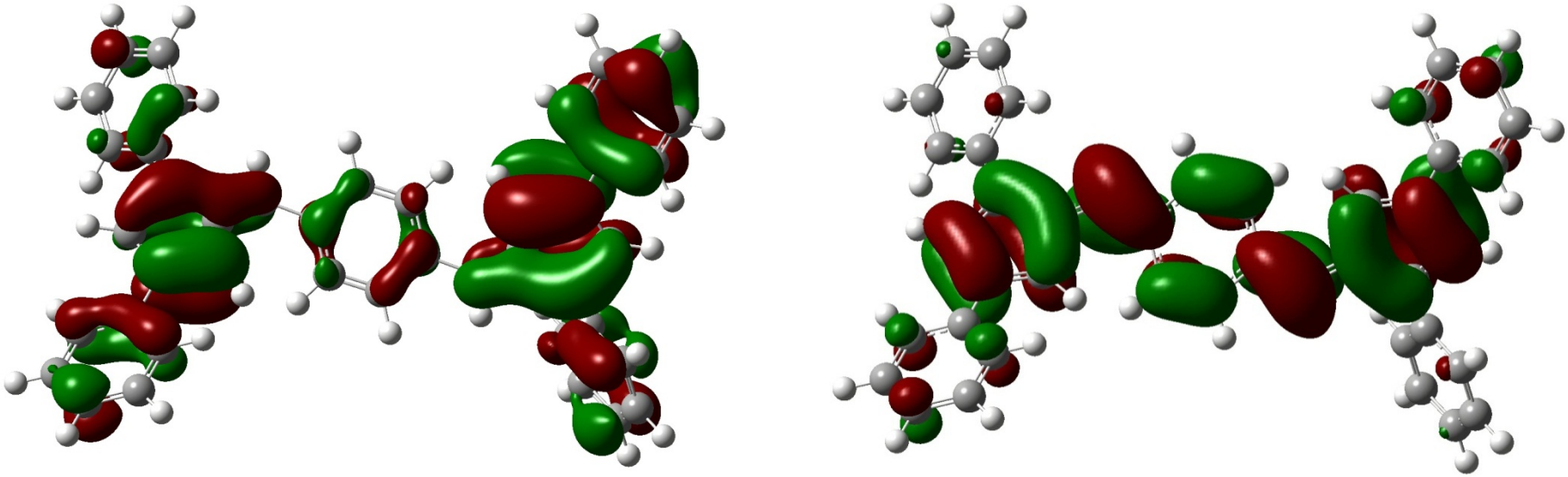


Figure S17. HOMO (left) and LUMO (right) plots of bis(fulvene) 1.

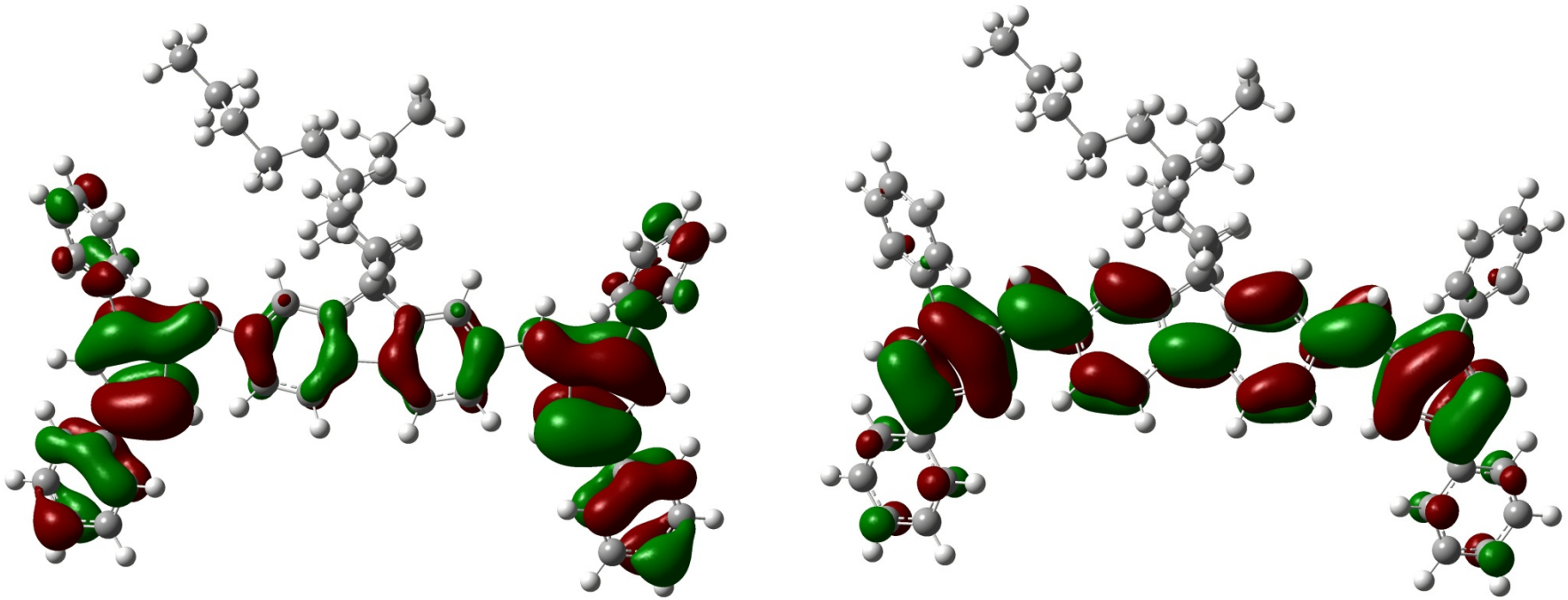


Figure S18. HOMO (left) and LUMO (right) plots of bis(fulvene) 2.

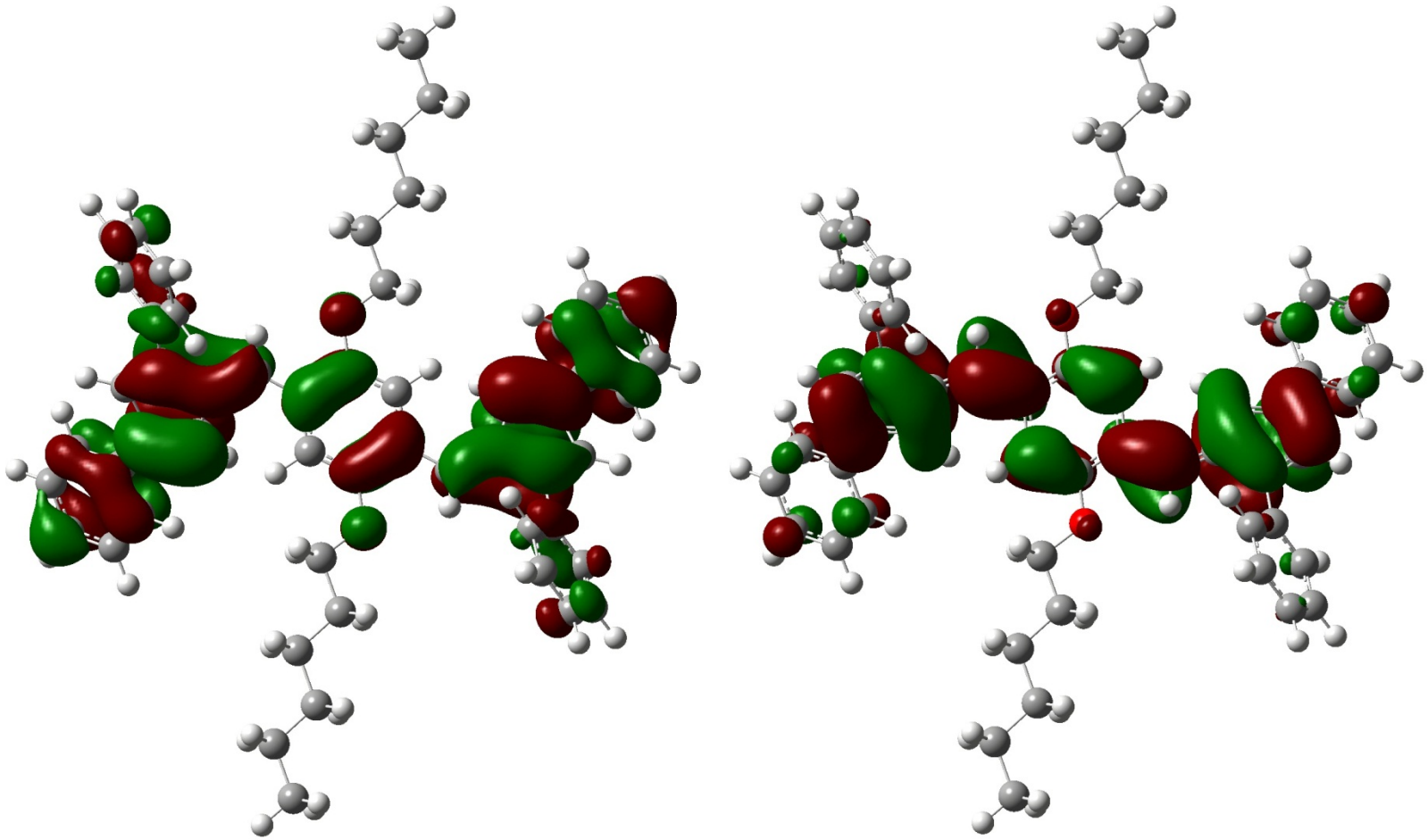


Figure S19. Homo (left) and LUMO (right) plots of bis(fulvene) 3.

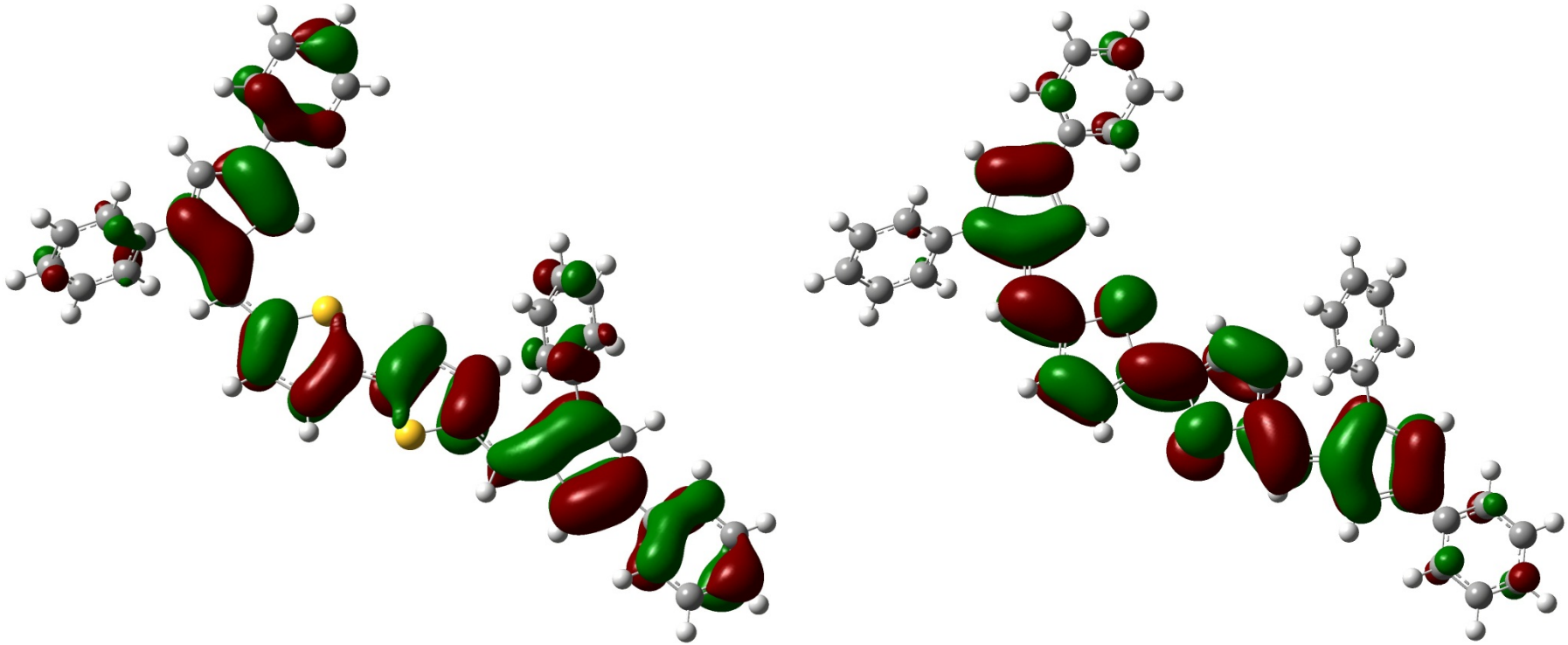


Figure S20. HOMO (left) and LUMO (right) plots of bis(fulvene) 4.

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