Supplementary Information (SI) for Chemical Science.
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SUPPORTING INFORMATION

High Brightness in *Bis*(*tri*-isopropylsilyl)Ethynyl-Functionalized Polycyclic Aromatic Hydrocarbons: Localized Representation Versus Clar's Model

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GENERAL METHODS FOR SYNTHESIS

All reactions were carried out under argon. THF and toluene were distilled over Na/benzophenone. Toluene were kept over activated 3 Å molecular sieves. 1,2-Dichloroethane was dried with activated 3 Å molecular sieves. All commercial reagents were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded at room temperature on Brucker Avance-300 MHz NMR spectrometer. ^{1}H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra were recorded at 75 MHz. Chloroform residual peak was taken as internal reference at 7.26 ppm for ^{1}H NMR and 77 ppm for ^{13}C NMR. *O*-Dichlorobenzene-D4 residual peak was taken as internal reference at 7.19 and 6.97 ppm for ^{1}H NMR and 132.10, 130.04 (3) and 127.20 (3) for ^{13}C NMR. Infrared spectra were recorded from Nicolet 6700 FT-IR spectrometer. MALDI High-resolution mass spectra were performed by the Small Molecule Mass Spectrometry of ICSN (Centre de Recherche de Gif - www.icsn.cnrs-gif.fr).

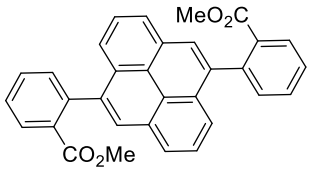
INSTRUMENTS

X-ray diffraction (XRD) measurements were performed using three instruments: (i) a Rigaku *SmartLab* diffractometer equipped with a CuKα source (**TIPS-ATT**), (ii) synchrotron radiation at the BL40XU beamline of SPring-8 (JASRI, project 2024B1520) (**TIPS-PYR**) and (iii) a Bruker *D8 ADVANCE* diffractometer with a MoKα source (**TIPS-DBPYR**). Ultraviolet-visible (UV-vis) absorption spectra and PL spectra were recorded on UV-vis (Lambda 950-PKA, PerkinElmer) and PL (FluoroMax-4, HORIBA Jobin Yvon and FP-8600, JASCO Corporation) spectrophotometers. PL quantum yield was measured using an absolute PL quantum yield measurement system (C11347-01, Hamamatsu Photonics). Emission lifetime was measured using a fluorescence lifetime measurement system (C11367-03 Quantaurus-Tau, Hamamatsu Photonics).

SYNTHESIS

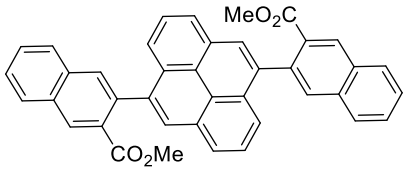
5,10-dibromopyrene was synthesized according to protocols described in the literature.[i]

dimethyl 2,2'-(pyrene-4,9-diyl)dibenzoate **1**



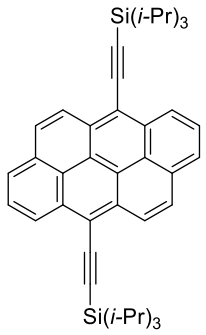
To 100 mL flask, K_3PO_4 (4.24 g, 20 mmol) was dissolved in water (5 mL) under argon, then toluene (50 mL) was added, followed by 5,10-dibromopyrene (1.20 g, 3.33 mmol) and methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (2.62 g, 10 mmol). The mixture was degassed with argon under ultrasound for 10 min. Then, $Pd_2(dba)_3$ (152 mg, 0.167 mmol) and S-Phos (137 mg, 0.333 mmol) were added. The reaction mixture was heated at 100°C for 24 hours. After cooling, the reaction mixture was transferred to an Erlenmeyer flack, diluted with hot chloroform and passed through a pad of silica gel with hot chloroform. The crude solid was put into suspension in dichloromethane and the resulting mixture boiled. Then, acetonitrile was added to precipitate the compound. The solid was filtered then dried to obtain the target molecule as white solid (1.18 g, 75%). Because of the low solubility of the compounds and the existence of two rotamers, obtaining a satisfactory ^{13}C NMR spectrum was not feasible. ^1H NMR (300 MHz, *o*-$C_6D_4Cl_2$) δ = 8.16 – 8.06 (m, 2H), 8.06 – 7.97 (m, 2H), 7.90 – 7.72 (m, 6H), 7.66 – 7.56 (m, 2H), 7.55 – 7.43 (m, 4H), 3.25 (s, 3.6H), 3.17 (s, 2.4H); HRMS (MALDI TOF) calcd for $C_{32}H_{22}O_4$: 470.15130 $[M]^{\cdot+}$, found: 470.15342.

dimethyl 3,3'-(pyrene-4,9-diyl)bis(2-naphthoate) **2**



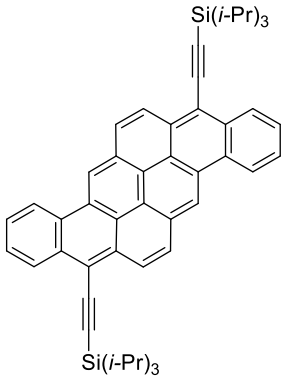
To 100 mL flask, K_3PO_4 (4.24 g, 20 mmol) was dissolved in water (5 mL) under argon, then toluene (50 mL) was added, followed by 5,10-dibromopyrene (1.20 g, 3.33 mmol) and methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-naphthoate (3.12 g, 10 mmol). The mixture was degassed with argon under ultrasound for 10 min. Then, $Pd_2(dba)_3$ (152 mg, 0.167 mmol) and S-Phos (137 mg, 0.333 mmol) were added. The reaction mixture was heated at 100°C for 24 hours. After cooling, the reaction mixture was transferred to an Erlenmeyer flack, diluted with hot chloroform and passed through a pad of silica gel with hot chloroform. The crude solid was put into suspension in dichloromethane and the resulting mixture boiled. Then, acetonitrile was added to precipitate the compound. The solid was filtered then dried to obtain the target molecule as white solid (1.26 g, 66%). Because of the low solubility of the compounds, ^{13}C NMR spectrum couldn't be recorded. ^1H NMR (300 MHz, *o*-$C_6D_4Cl_2$) δ = 8.69 (s, 0.80H), 8.67 (s, 1.20H), 8.16 – 7.77 (m, 14H), 7.63 – 7.49 (m, 4H), 3.35 (s, 3.70H), 3.25 (s, 2.30H); HRMS (MALDI TOF) calcd for $C_{40}H_{26}O_4$: 570.18260 $[M]^{\cdot+}$, found: 570.18304.

TIPS-ATT



A solution of (triisopropylsilyl)acetylene (1.19 g, 6.5 mmol) in THF (10 mL) was cooled to 0 °C. *n*-BuLi (3.93 mL, 6.3 mmol, 1.6 M) was added dropwise, and the mixture was stirred at 0 °C for 30 min. In a separate flask, anthanthrone (200 mg, 0.65 mmol) in THF (70 mL) together with $LaCl_3 \cdot 2LiCl$ (10.8 mL, 6.5 mmol) was degassed with argon for 30 min under sonication and then cooled to –10 °C. The lithiated acetylene solution was cannulated into the cold dione solution, and the reaction mixture was allowed to warm to 0 °C and stirred for 16 h at this temperature. Subsequently, $SnCl_2$ (1.85 g, 9.75 mmol) diluted in HCl (3 M, 8 mL) was added, and the solution was allowed to return to room temperature. After stirring for 2 h, water (80 mL) was added. The resulting mixture was transferred to a separatory funnel with diethyl ether (200 mL). The organic phase was washed five times with water (80 mL each) until the white slurry completely disappeared from the aqueous phase. The organic layer was then concentrated under reduced pressure to dryness. The resulting red solid was purified by column chromatography using cyclohexane and cyclohexane/toluene (95/5) as the eluent to give **TIPS-ATT** as a red solid (277 mg, 67%). ^{1}H NMR (300 MHz, *o*-$C_6D_4Cl_2$) δ 9.27 – 9.16 (m, 2H), 8.89 (d, *J* = 9.2 Hz, 2H), 8.21 – 8.12 (m, 4H), 8.12 – 8.04 (m, 2H), 1.35 (2s, 42H); ^{13}C NMR (75 MHz, o-$C_6D_4Cl_2$) δ 132.83, 131.45, 131.05, 130.32, 129.92, 127.47, 126.71, 125.68, 125.60, 122.32, 121.92, 117.14, 104.51, 104.14, 19.07, 11.85; HRMS (MALDI TOF) calcd for $C_{44}H_{52}Si_2$: 636.36020 $[M]^{\cdot+}$, found: 636.36113; UV/Vis (toluene): λ_{max} (ε) = 491 nm (132,000 L.mol^{-1}.cm^{-1}).

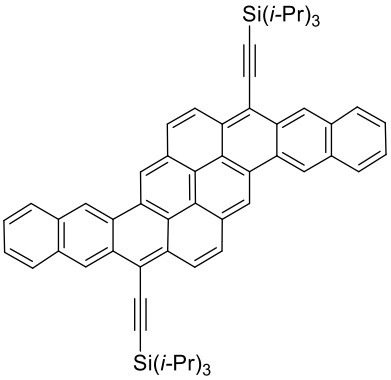
TIPS-PYR



To a flask (200 mL) is added compound **1** (0.90 g, 1.91 mmol) and 1,2-dichloroethane (90 mL) under argon. TfOH (3.39 mL, 38.26 mmol) is added dropwise then the reaction mixture is heated at 95°C for 5h. After returning to room temperature, the reaction mixture is transferred to an Erlenmeyer flask with DCM. A saturated $NaHCO_3$ aqueous solution is added until the pH becomes basic. Water is then added, and the aqueous phase is largely removed from the Erlenmeyer flask. This process is repeated, with fresh water added each time, until the pH of the aqueous solution reaches neutrality. Then, to the chlorinated phase, large amount of MeOH is added. The resulting precipitate is filtered, washed with water then with MeOH. The solid is dried in the oven at 110°C for 3h to furnish a mixture of diketones **3** as an orange solid (0.77 g, 99%). Due to the insolubility of the compound **3**, no NMR spectra could be recorded. IR (solid): $\tilde{\nu}$ = 1704 (s) (C=O of 5-membered ring), 1641 (s) cm^{-1} (C=O of 6-membered ring).

A solution of (triisopropylsilyl)acetylene (0.81 g, 4.43 mmol) in THF (5 mL) was cooled to 0 °C. *n*-BuLi (2.76 mL, 4.43 mmol, 1.6 M) was added dropwise, and the mixture was stirred at 0 °C for 30 min. In a separate flask, dione 3 (300 mg, 0.74 mmol) was suspended in THF (125 mL). The suspension was degassed with argon for 30 min under sonication and then cooled to –10 °C. The lithiated acetylene solution was cannulated into the cold dione suspension, and the reaction mixture was allowed to warm to room temperature. After stirring for 30 min, $SnCl_2$ (1.40 g, 7.40 mmol) diluted in HCl (3 M, 13 mL) was added, and the solution was stirred for 2 h before water (100 mL) was introduced. The resulting mixture was transferred to a separatory funnel with diethyl ether (300 mL). The organic phase was washed five times with water (100 mL each) until the white slurry completely disappeared from the aqueous phase. The organic layer was then concentrated to half its volume, and a large excess of acetonitrile was added. The resulting precipitate was filtered and washed with acetonitrile. The solid was further precipitated sequentially from chloroform/acetonitrile and then chloroform/cyclohexane. Finally, the precipitate was boiled in chloroform and filtered to afford a dark green solid (191 mg, 35%). ^{1}H NMR (300 MHz, *o*-$C_6D_4Cl_2$) δ 9.30 (s, 2H), 9.10 – 8.97 (m, 4H), 8.86 (d, *J* = 9.3 Hz, 2H), 8.15 (d, *J* = 9.4 Hz, 2H), 7.86 – 7.77 (m, 4H), 1.39-1.38 (2s, 42H); HRMS (MALDI TOF) calcd for $C_{52}H_{56}Si_2$: 736.39150 $[M]^{\cdot+}$, found: 736.39278; UV/Vis (toluene): λ_{max} (ε) = 527 nm (208,000 $L.mol^{-1}.cm^{-1}$).

TIPS-DBPYR

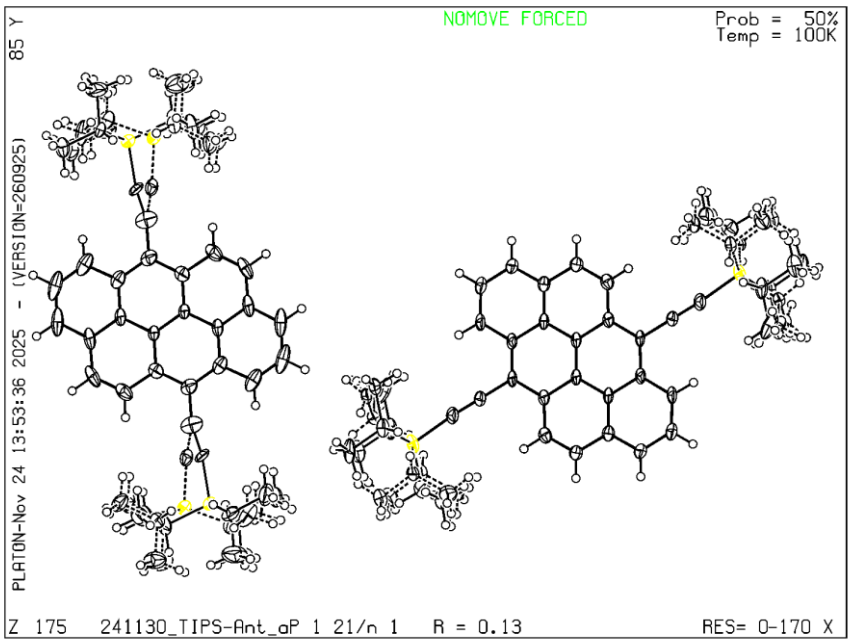


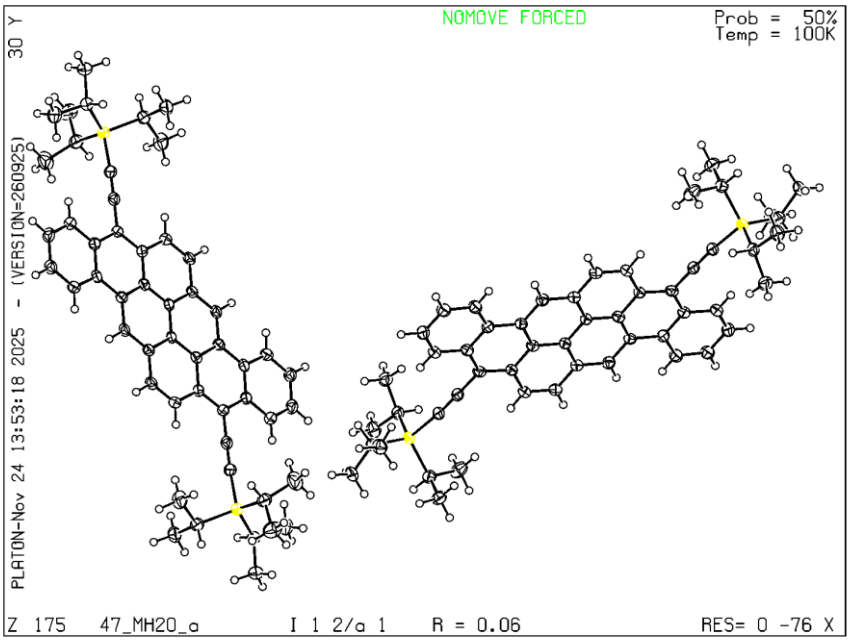
To a flask (200 mL) is added compound **2** (1 g, 1.75 mmol) and 1,2-dichloroethane (100 mL) under argon. TfOH (3.10 mL, 35.08 mmol) is added dropwise then the reaction mixture is heated at 95°C for 5h. After returning to room temperature, the reaction mixture is transferred to an Erlenmeyer flask with DCM. A saturated $NaHCO_3$ aqueous solution is added until the pH becomes basic. Water is then added, and the aqueous phase is largely removed from the Erlenmeyer flask. This process is repeated, with fresh water added each time, until the pH of the aqueous solution reaches neutrality. Then, to the chlorinated phase, large amount of MeOH is added. The resulting precipitate is filtered, washed with water then with MeOH. The solid is dried in the oven at 110°C for 3h to furnish a mixture of diketones **4** as a red solid (0.89 g, 95%). Due to the insolubility of the compound **4**, no NMR spectra could be recorded. IR (solid): $\tilde{\nu}$ = 1704 (s) (C=O of 5-membered ring), 1641 (s) cm^{-1} (C=O of 6-membered ring).

A solution of (triisopropylsilyl)acetylene (0.50 g, 2.76 mmol) in THF (5 mL) was cooled to 0 °C. *n*-BuLi (1.63 mL, 2.60 mmol, 1.6 M) was added dropwise, and the mixture was stirred at 0 °C for 30 min. In a separate flask, dione **4** (200 mg, 0.39 mmol) was suspended in THF (125 mL). The suspension was degassed with argon for 30 min under sonication and then cooled to –10 °C. The lithiated acetylene solution was cannulated into the cold dione suspension, and the reaction mixture was allowed to warm to room temperature. After stirring for 30 min, $SnCl_2$ (0.74 g, 3.90 mmol) diluted in HCl (3 M, 10 mL) was added, and the solution was stirred for 2 h before water (100 mL) was added. The resulting mixture was transferred to a separatory funnel with diethyl ether (300 mL). The organic phase was washed five times with water (100 mL each) until the white slurry completely disappeared from the aqueous phase. The organic layer was then concentrated to half its volume, filtered and washed with acetonitrile and methanol. The solid was further precipitated sequentially from chloroform/acetonitrile and then chloroform/cyclohexane. Finally, the precipitate was boiled in chloroform and filtered to afford a dark blue solid (137 mg, 42%). ^{1}H NMR (300 MHz, *o*-$C_6D_4Cl_2$) δ 9.11 (s, 2H), 9.08 (s, 2H), 8.94 (s, 2H), 8.70 (d, *J* = 9.2 Hz, 2H), 8.15 (d, *J* = 8.3 Hz, 2H), 7.97 (d, *J* = 9.3 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.27 (t, *J* = 7.7 Hz, 2H), 1.53 (s, 42H); HRMS (MALDI TOF) calcd for $C_{60}H_{60}Si_2$: 836.42280 $[M]^{\cdot+}$, found: 836.42485; UV/Vis (toluene): λ_{max} (ε) = 599 nm (148,000 $L.mol^{-1}.cm^{-1}$).

X-RAY CRYSTALLOGRAPHY DATA

Identification	**TIPS-ATT**	**TIPS-PYR**	**TIPS-DBPYR**
CCDC number deposition	**2503088**	**2503087**	**2504051**
Empirical formula	$C_{44}H_{52}Si_2$	$C_{52}H_{56}Si_2$	$C_{60}H_{60}Si_2$
Formula weight (Mw)	637.03	737.14	837.26
Temperature/K	100	100	200
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	I2/a	C2/c
a/Å	6.9570(8)	29.5583(9)	28.6941(14)
b/Å	34.975(4)	7.7632(2)	17.8984(9)
c/Å	15.1996(14)	37.7963(11)	9.3498(5)
α/°	90	90	90
β/°	95.349(9)	110.197(3)	94.361(2)
γ/°	90	90	90
Volume/Å^3	3682.3(7)	8139.7(4)	4788.0(4)
Z	4	8	8
ρ_{calc}g/cm^3	1.149	1.203	1.161
μ/mm^{-1}	1.079	0.168	0.113
F(000)	1376.0	3168.0	1792.0
Crystal size/mm^3	0.07 × 0.01 × 0.01	0.05 × 0.01 × 0.01	0.3 × 0.04 × 0.02
Radiation	CuKα (λ = 1.54184)	Synchrotron (λ = 0.81022)	MoKα (λ = 0.71073)
Reflections collected	35643	39067	113948
Independent reflections	7471	8313	5503
Data/restraints/parameters	7471/0/622	8313/0/499	5503/0/286
Goodness-of-fit on F^2	1.042	1.019	1.046
Final R indexes [I>=2σ (I)]	**R_1 = 0.1329** wR_2 = 0.3508	**R_1 = 0.0601** wR_2 = 0.1370	**R_1 = 0.0565** wR_2 = 0.1405

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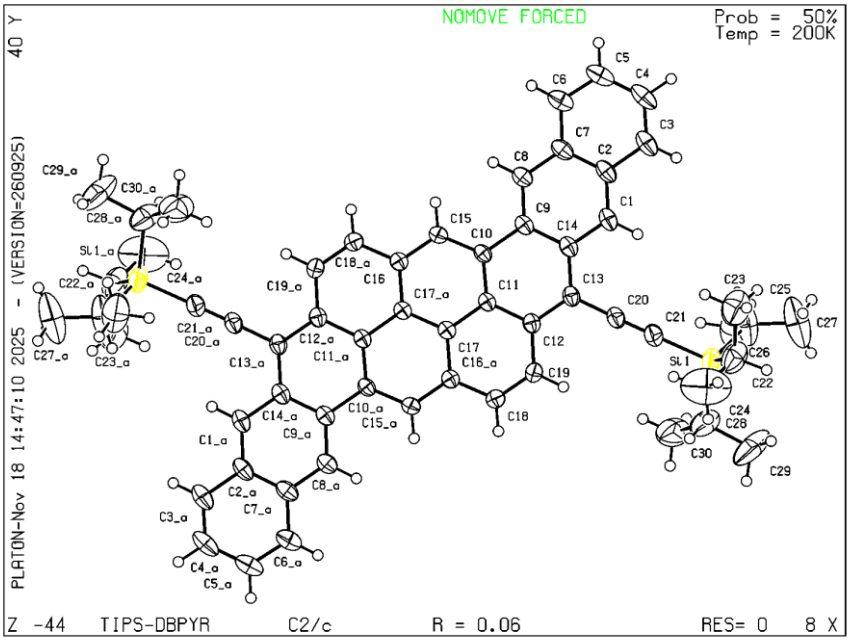
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STABILITY TESTS IN SOLUTION

Stability tests were carried out in toluene solution with a [*C*] = 1x10^{-5} M in ambient laboratory conditions.

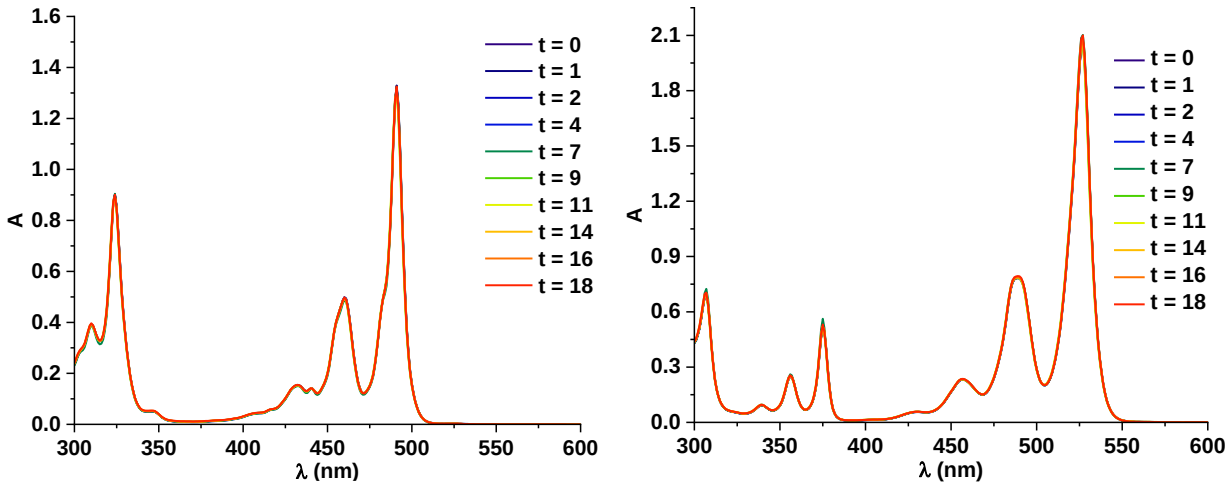


Figure S1. UV/vis spectral evolution as a function of time (in days) of **TIPS-ATT** (left) and **TIPS-PYR** (right).

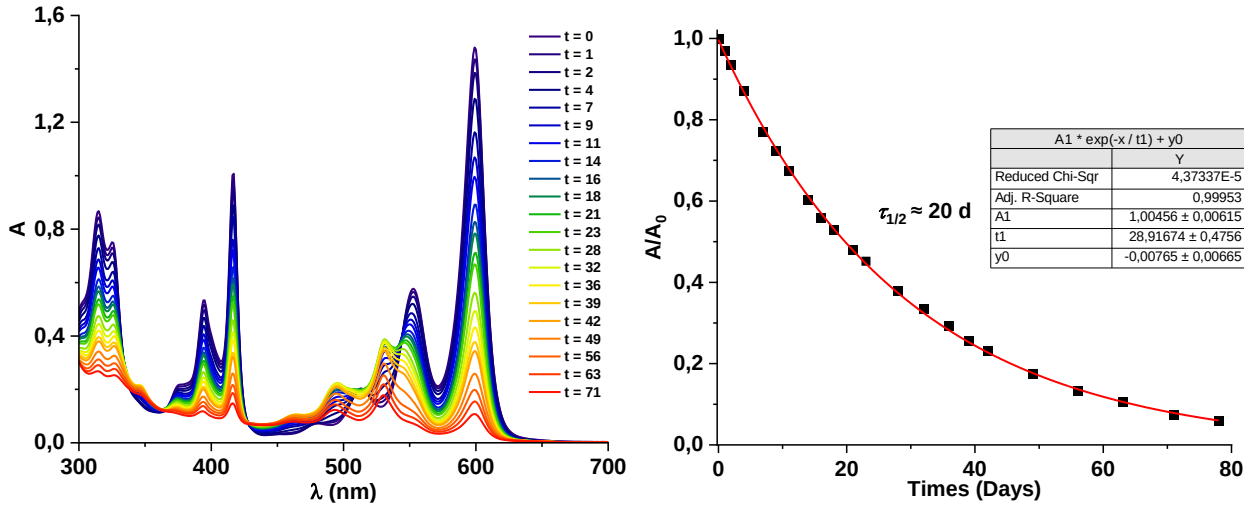


Figure S2. UV/vis spectral evolution as a function of time (in days) (left) and change of absorbance at 599 nm over time (right) of **TIPS-DBPYR**.

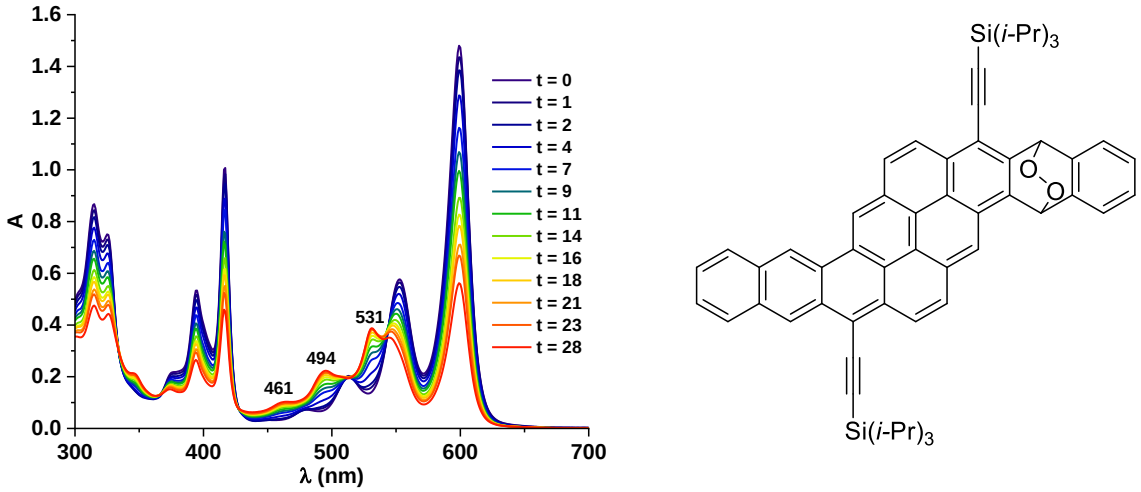


Figure S3. UV/vis spectral evolution up to 28 days (left) of **TIPS-DBPYR** and the structure of the endoperoxide photoproduct (right).

Based on TD-DFT calculations (see Table S5), the photoproduct absorbing at 531, 494 and 461 nm can be attributed of an endoperoxide photoproduct (see above).

Stability tests were carried out in toluene solution with a [*C*] = 1x10^{-5} M with two 6W bench lamp at 365 nm (see below).

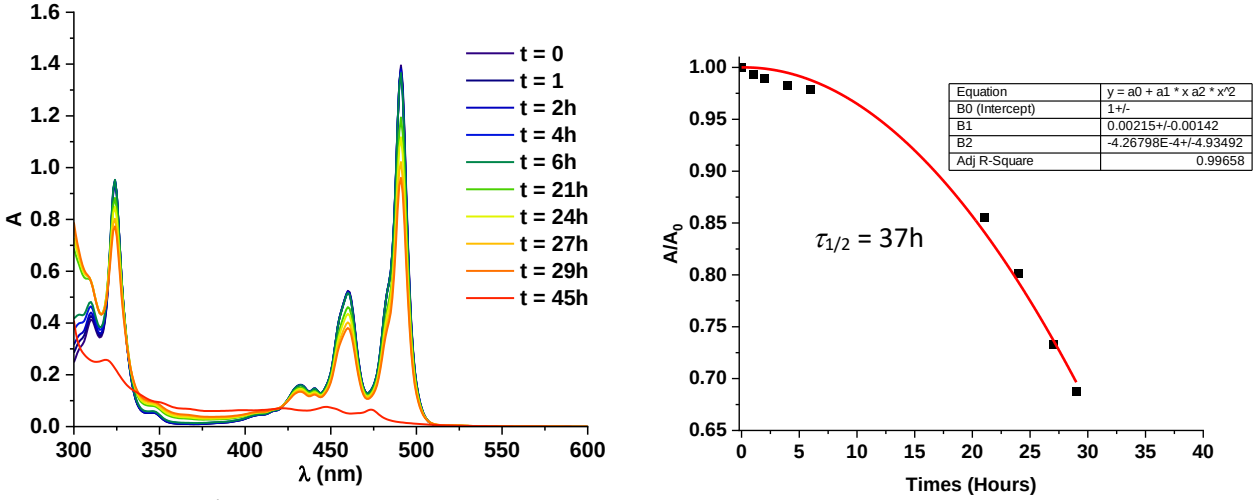


Figure S4. UV/vis spectral evolution (left) and change of absorbance at 491 nm over time (right) of **TIPS-ATT**.

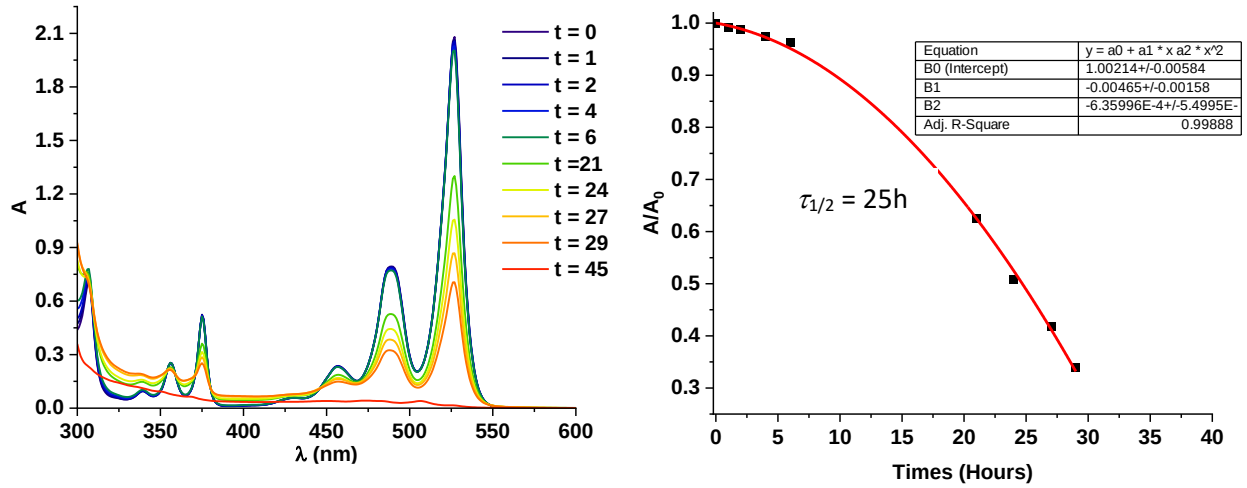


Figure S5. UV/vis spectral evolution (left) and change of absorbance at 527 nm over time (right) of **TIPS-PYR**.

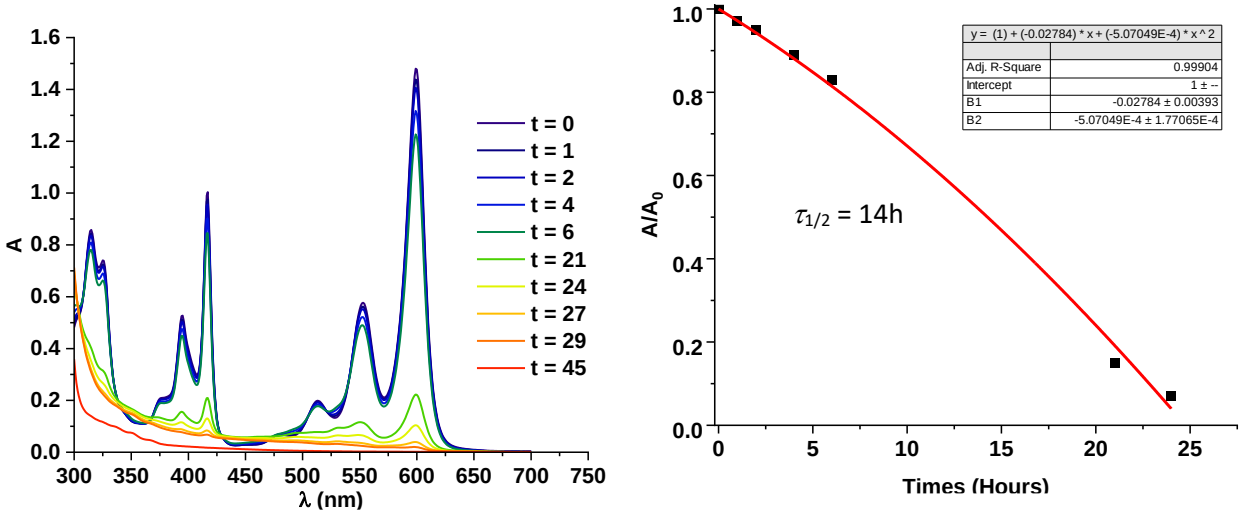
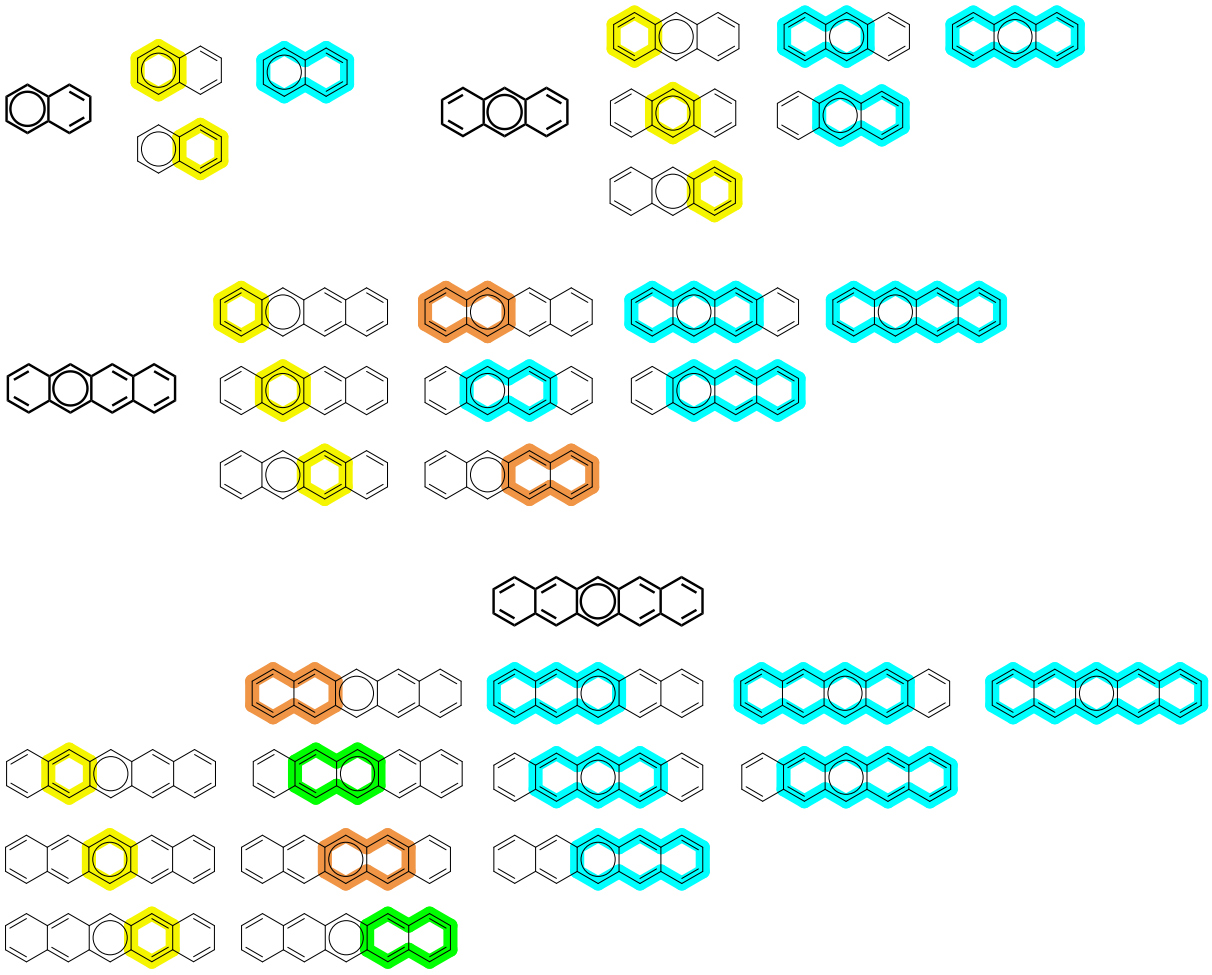


Figure S6. UV/vis spectral evolution (left) and change of absorbance at 599 nm over time (right) of **TIPS-DBPYR**.

RING CURRENT CIRCUITS IN ACENES

Ring current circuits of the same colour neutralize at the fusion bond. In contrast, the blue currents contribute fully.



THEORITICAL CALCULATIONS

The geometries were optimized at the RB3LYP/6-311G(d,p) level for the closed-shell (CS) singlet and UB3LYP/6-311G(d,p) for the triplet, and these optimized structures are used for the further calculations of the singlet and triplet, respectively. The presence of energy minima for the geometry optimization was confirmed by the absence of imaginary modes (no imaginary frequencies). To numerically achieve accurate values, we have used a fine grid. We adopted two model systems, which are main aromatic backbone with or without substituents. The *tri*isopropylsilyl (TIPS) groups were substituted with *tri*methylsilyl (TMS) groups. Molecular orbital calculations were performed using the program Gaussian 16.

The time-dependent density functional theory (TD-DFT) calculations were conducted at the M06-2X/6-311+G(d,p) and the B3LYP/6-311+G(d,p) levels for the excited states calculations including solvent effects in toluene by means of the polarizable continuum model (PCM).

The singlet biradical factor was also calculated by the natural orbital occupation number (NOON) of the LUMO in a spin-unrestricted Hartree-Fock (HF) calculation using 6-31+G(d,p) basis set.[ii] The broken symmetry UHF/6-31+G(d,p) calculations gave LUMO occupation number. According to the Yamaguchi scheme,[iii] the index for singlet biradical character is expressed as

$$y_i = 1 - \frac{2T_i}{1 + T_i^2}$$

where T_i is the orbital overlap between the corresponding orbital pairs and it can be presented using the NOON of HOMO and LUMO.

$$T_i = \frac{n_{HOMO} - n_{LUMO}}{2}$$

NICS values were estimated using the GIAO-B3LYP/6-311+G(d,p) methods. NICS values employ σ-only model to obtain the effect of the π contribution only.[iv]

The current density plotted onto the ACID (anisotropy of the induced current density) were generated using the programs Gaussian 16 and AICD 3.0.4.[v,vi,vii] The ring current analysis was performed with the CSGT method at the B3LYP/6-311+G(d,p) level with IOp(10/93=2). The magnetic field was applied parallel to z-axis (0 0 1). The number of points of cartesian grid was set as 160000.

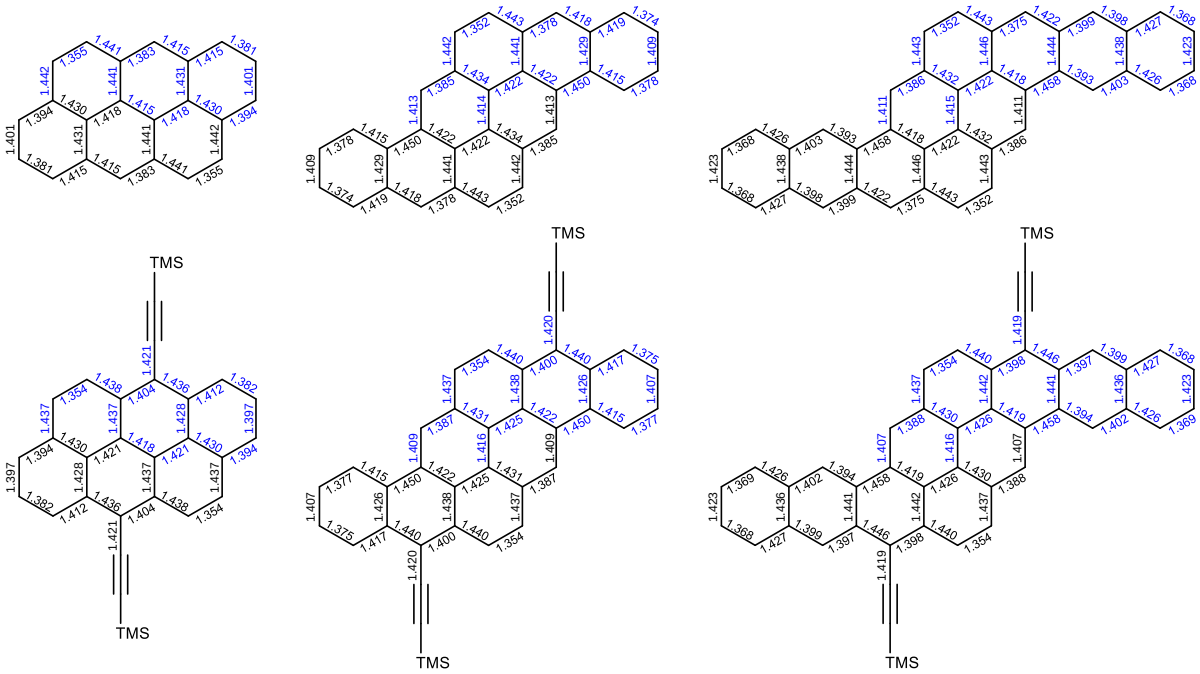


Figure S7. Calculated bond lengths at RB3LYP/6-311G(d,p).

Table S1. Molecular orbitals and energies of the molecules calculated at the B3LYP/6-311+G(d,p) level of theory.

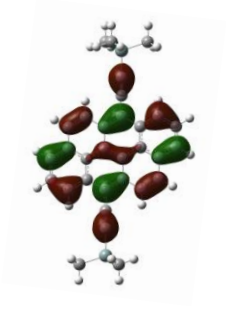
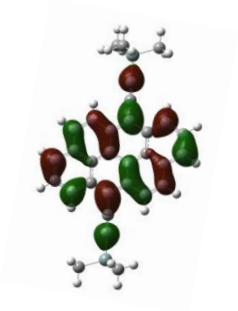
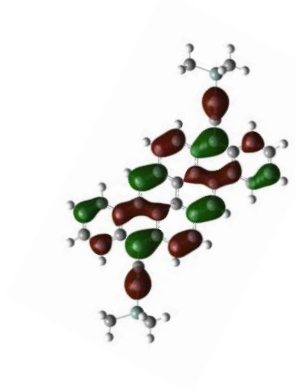
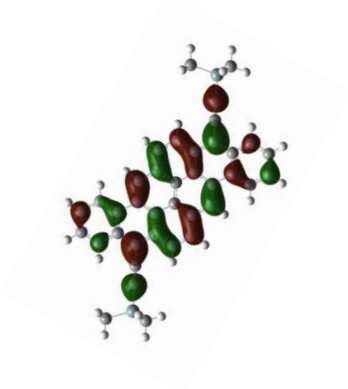
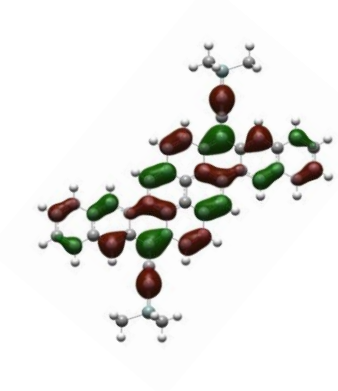
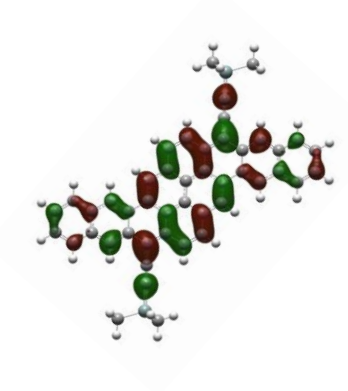
	HOMO	LUMO
TMS-ATT		
E (eV)	-5.15357	-2.6659
TMS-PYR		
E (eV)	-5.05588	-2.76168
TMS-DBPYR		
E (eV)	-4.91465	-2.91407

Table S2. Calculated vertical excitation energies (VEE) in toluene for the first triplet state and the first nine singlet excited states, wavelength and oscillator strength (*f*) of **TMS-ATT**.

	Excited state	M06-2X/6-311+G(d,p)			B3LYP/6-311+G(d,p)		
		VEE (eV)	Wavelength (nm)	*f*	VEE (eV)	Wavelength (nm)	*f*
TMS-ATT	T1	1.3534	916.10	0.0000	1.1567	1071.92	0.0000
	S1	2.5831	479.98	0.9797	2.3261	533.01	0.7862
	S2	3.3944	365.27	0.0095	3.1167	397.80	0.0102
	S3	3.613	343.17	0.0000	3.1207	397.29	0.0000
	S4	3.7655	329.26	0.0000	3.2889	376.98	0.0000
	S5	4.1347	299.86	1.2250	3.732	332.22	0.6957
	S6	4.4156	280.79	0.1023	3.7621	329.56	0.1722
	S7	4.4659	277.62	0.0410	3.9617	312.96	0.2172
	S8	4.5092	274.96	0.0000	3.9774	311.72	0.0000
	S9	4.5536	272.28	0.0003	4.0006	309.91	0.0000

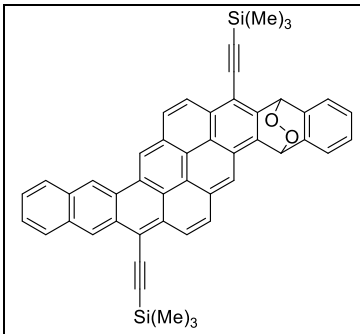
Table S3. Calculated vertical excitation energies (VEE) for the first triplet state and the first fourteen singlet excited states, wavelength and oscillator strength (*f*) of **TMS-PYR**.

	Excited state	M06-2X/6-311+G(d,p)			B3LYP/6-311+G(d,p)		
		VEE (eV)	Wavelength (nm)	*f*	VEE (eV)	Wavelength (nm)	*f*
TMS-PYR	T1	1.2862	963.95	0.0000	1.0895	1137.95	0.0000
	S1	2.4005	516.5	1.8019	2.1448	578.06	1.5288
	S2	3.1145	398.08	0.0005	2.7544	450.14	0.0007
	S3	3.587	345.65	0.0000	2.9921	414.38	0.0000
	S4	3.7169	333.57	0.4699	3.1788	390.04	0.2660
	S5	3.7309	332.32	0.0000	3.2204	385	0.0000
	S6	3.8958	318.25	0.0000	3.3321	372.09	0.0000
	S7	3.9949	310.36	0.0000	3.5417	350.07	0.0000
	S8	4.3928	282.25	0.0000	3.8328	323.48	0.0135
	S9	4.4754	277.03	0.1138	3.8878	318.91	0.0000
	S10	4.5082	275.02	0.0003	3.972	312.15	0.0005
	S11	4.5193	274.35	0.0000	3.982	311.36	0.0000
	S12	4.5464	272.71	1.4352	3.985	311.13	0.0028
	S13	4.683	264.76	0.6678	3.9948	310.36	0.4697
	S14	4.7779	259.5	0.0002	4.0997	302.42	0.0000

Table S4. Calculated vertical excitation energies (VEE) for the first triplet state and the first twenty singlet excited states, wavelength and oscillator strength (*f*) of **TMS-DBPYR**.

	Excited state	M06-2X/6-311+G(d,p)			B3LYP/6-311+G(d,p)		
		VEE (eV)	Wavelength (nm)	*f*	VEE (eV)	Wavelength (nm)	*f*
TMS-DBPYR	T1	1.0348	1198.11	0.0000	0.8545	1450.94	0.0000
	S1	2.0991	590.66	1.6282	1.8369	674.98	1.1574
	S2	2.9194	424.69	0.0024	2.4376	508.62	0.0000
	S3	3.0475	406.84	0.0000	2.4676	502.45	0.0216
	S4	3.2769	378.36	0.0000	2.6832	462.07	0.0000
	S5	3.3328	372.01	1.1007	2.8219	439.37	0.9046
	S6	3.645	340.15	0.0000	3.1181	397.63	0.0000
	S7	3.7386	331.63	0.0000	3.2669	379.52	0.1062
	S8	3.9443	314.33	0.3177	3.2891	376.96	0.0000
	S9	4.0578	305.55	0.0000	3.4585	358.5	0.0000
	S10	4.0794	303.93	0.2012	3.5182	352.41	0.0000
	S11	4.1482	298.88	0.0000	3.538	350.44	0.0305
	S12	4.2478	291.88	1.6773	3.6239	342.13	0.3565
	S13	4.321	286.93	0.0000	3.629	341.65	0.0000
	S14	4.4135	280.92	0.1930	3.7105	334.14	0.0000
	S15	4.4227	280.34	0.0000	3.7321	332.21	1.1078
	S16	4.4338	279.63	0.0002	3.8341	323.37	0.0000
	S17	4.5136	274.69	0.0000	3.8436	322.57	0.0004
	S18	4.5934	269.92	0.7036	3.8882	318.88	0.0000
	S19	4.6152	268.64	0.0000	3.9448	314.3	0.0204
	S20	4.7181	262.78	0.1258	4.079	303.95	0.0000

Table S5. Calculated vertical excitation energies (VEE) in toluene for the first eight singlet excited states, wavelength and oscillator strength (*f*) of a photodegradation product.



Excited state	M06-2X/6-311+G(d,p)		
	VEE (eV)	Wavelength (nm)	*f*
S1	2.4072	515.06	1.8055
S2	2.9942	414.08	0.0065
S3	3.2845	377.49	0.1916
S4	3.7373	331.75	0.0561
S5	3.8114	325.29	0.0350
S6	3.8394	322.93	0.0372
S7	3.9658	312.63	0.4500
S8	4.0998	302.42	0.6475

Table S6. NICS πzz values of **ATT** and **TMS-ATT.**

ATT	NICS(0)πzz	NICS(1)πzz	NICS(1.7)πzz
A	-35.8	-32.9	-20.9
B	-45.1	-39.2	-22.7
C	-12.1	-12.8	-10.4
TMS-ATT	NICS(0)πzz	NICS(1)πzz	NICS(1.7)πzz
A	-31.3	-29.1	-18.8
B	-44.6	-38.4	-22.2
C	-13.7	-13.7	-10.71

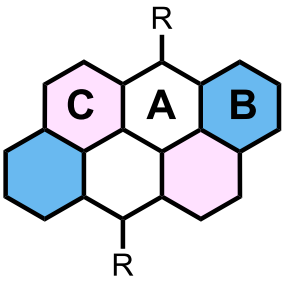


Table S7. NICS πzz values of **PYR** and **TMS-PYR**.

PYR	NICS(0)πzz	NICS(1)πzz	NICS(1.7)πzz
A	-34.6	-31.7	-19.1
B	-39.3	-33.0	-18.9
C	-8.4	-9.6	-8.3
D	-34.4	-31.3	-19.5
TMS-PYR	NICS(0)πzz	NICS(1)πzz	NICS(1.7)πzz
A	-30.4	-28.2	-17.3
B	-39.1	-32.6	-18.6
C	-10.5	-11.0	-9.0
D	-33.2	-30.1	-18.8

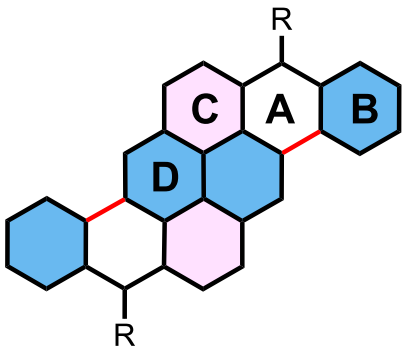
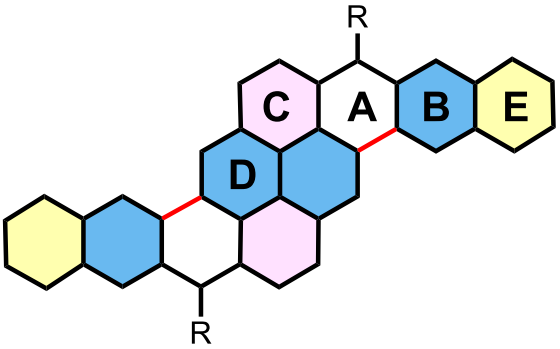


Table S8. NICS πzz values of **DBPYR** and **TMS-DBPYR**.

DBPYR	NICS(0)πzz	NICS(1)πzz	NICS(1.7)πzz
A	-27.2	-25.8	-15.9
B	-43.8	-38.4	-21.9
C	-6.3	-7.8	-6.9
D	-32.7	-29.7	-18.1
E	-35.5	-30.5	-17.6
TMS-DBPYR	NICS(0)πzz	NICS(1)πzz	NICS(1.7)πzz
A	-23.5	-22.6	-14.2
B	-43.4	-37.7	-21.4
C	-8.9	-9.5	-7.8
D	-31.5	-28.4	-17.5
E	-35.4	-30.4	-17.6



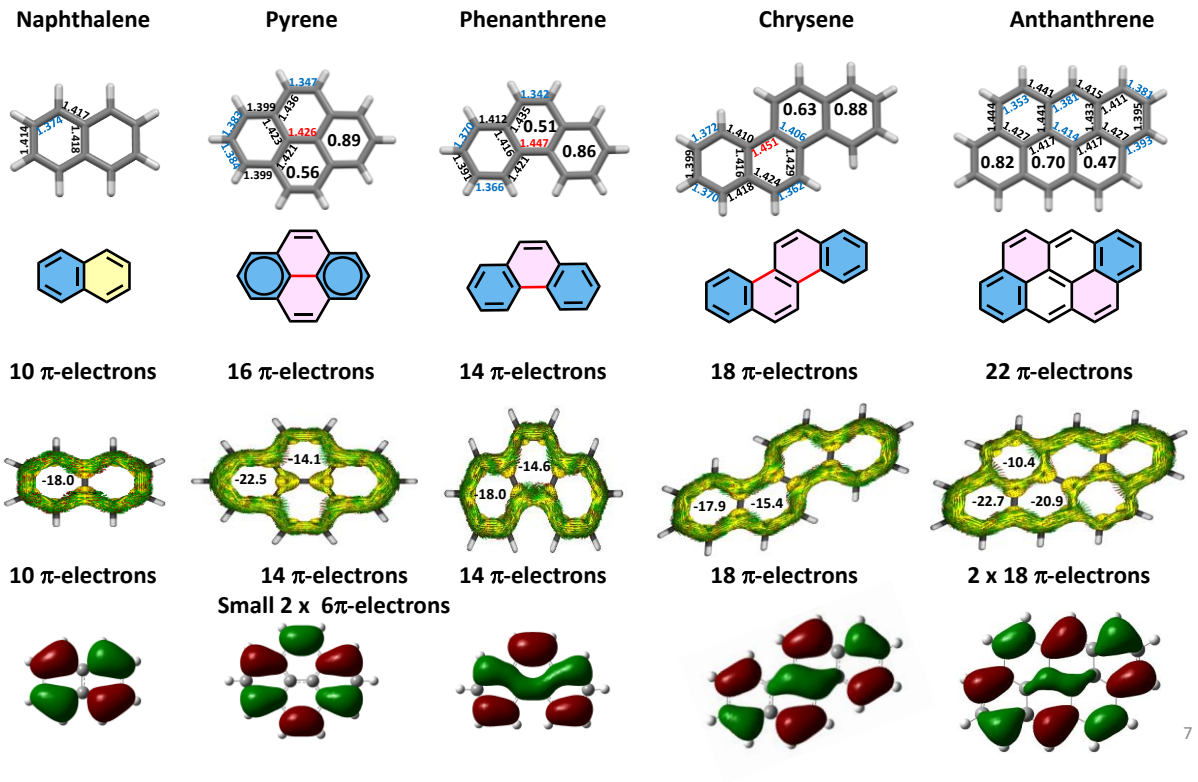
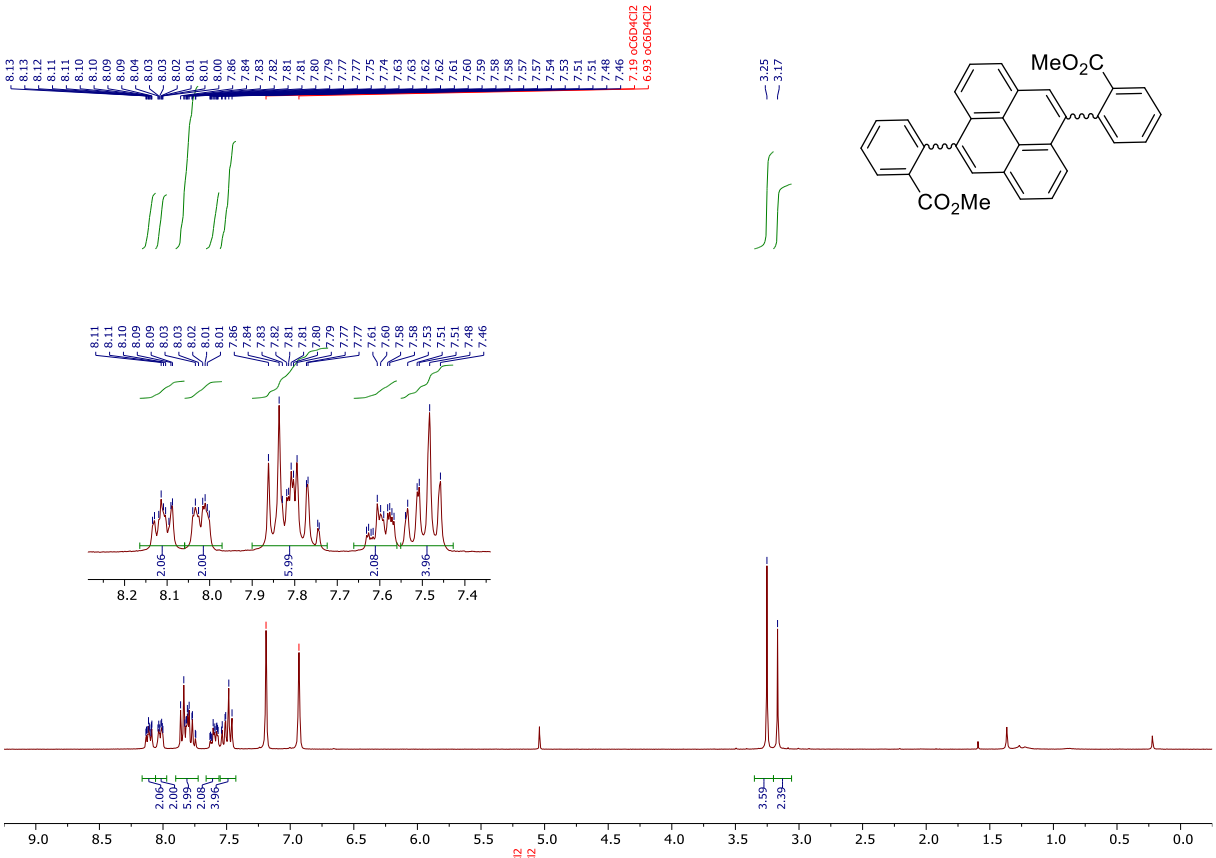
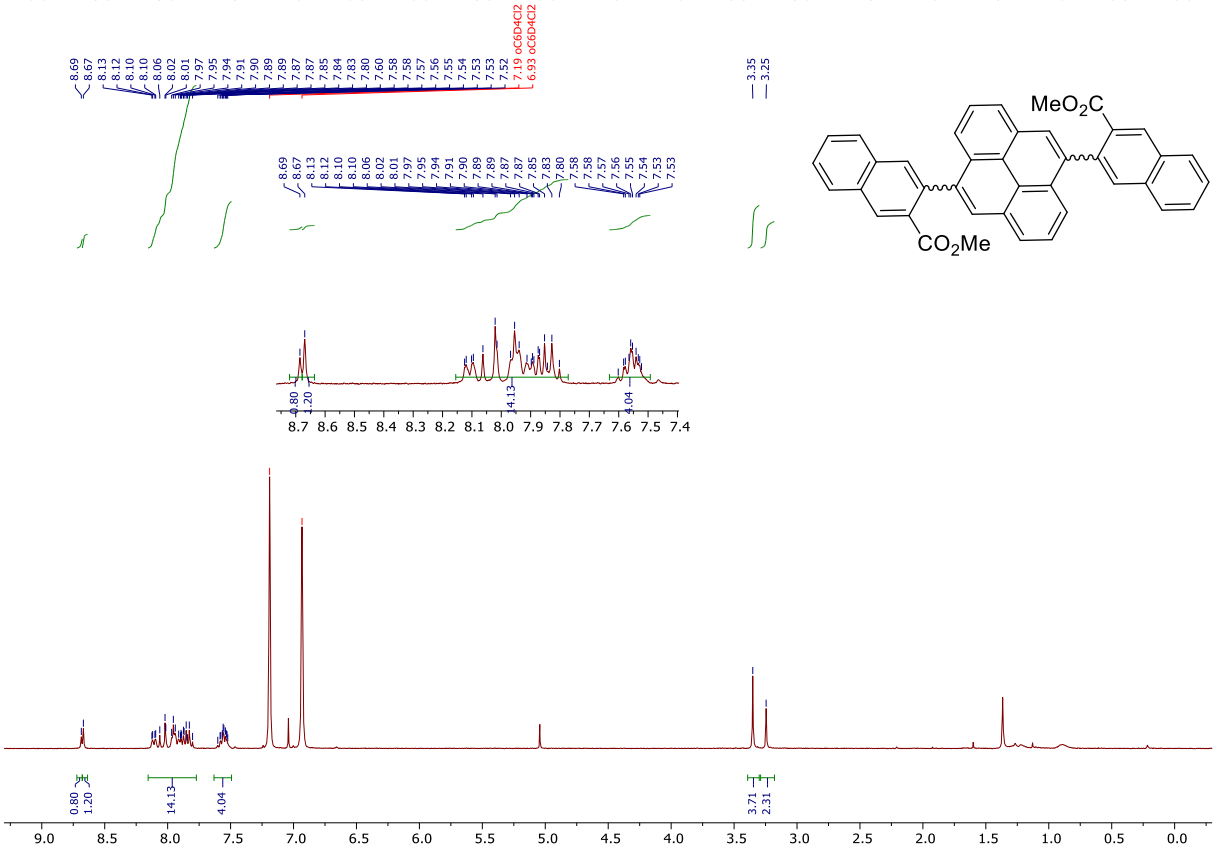
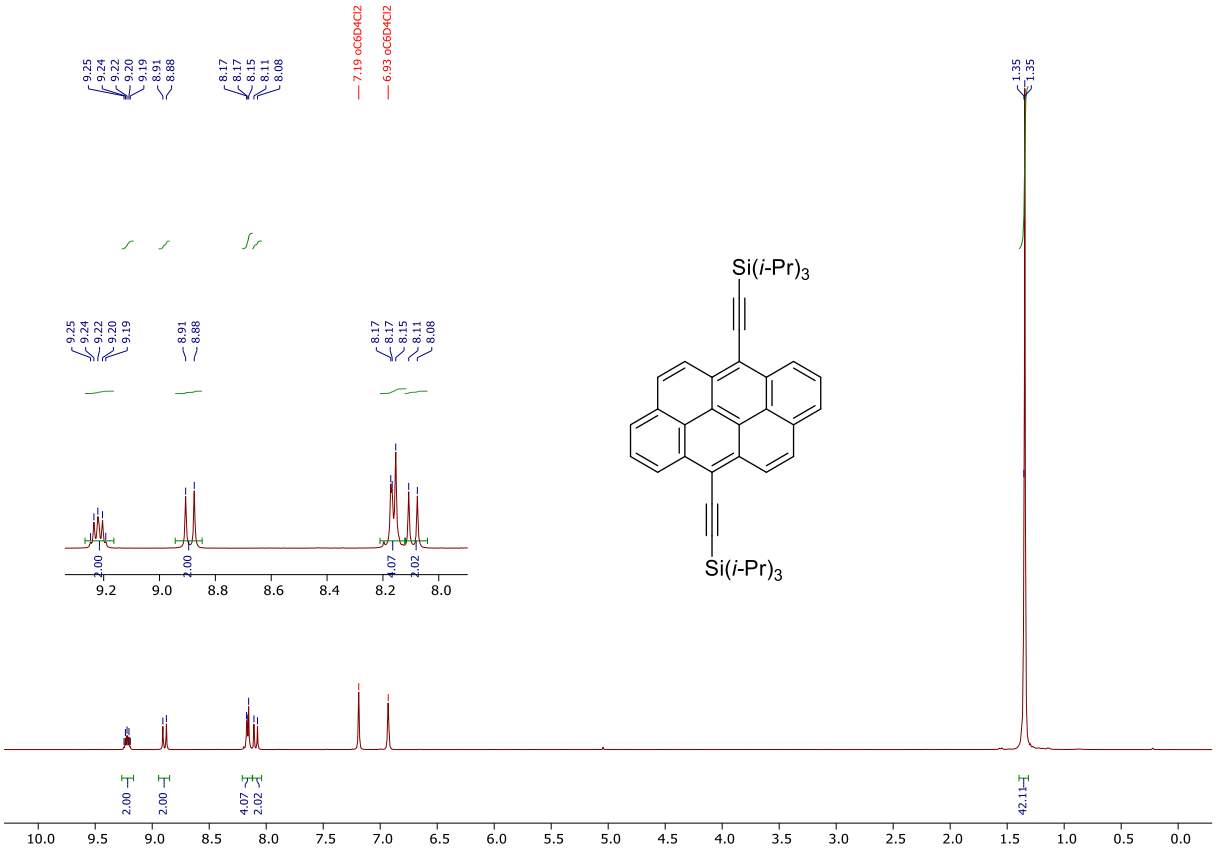


Figure S8. X-ray structures; Fries structures of naphthalene, pyrene, phenanthrene, chrysene and anthanthrene; ACID plots with NICS (1.7)πzz and HOMO orbitals.

NMR SPECTRA



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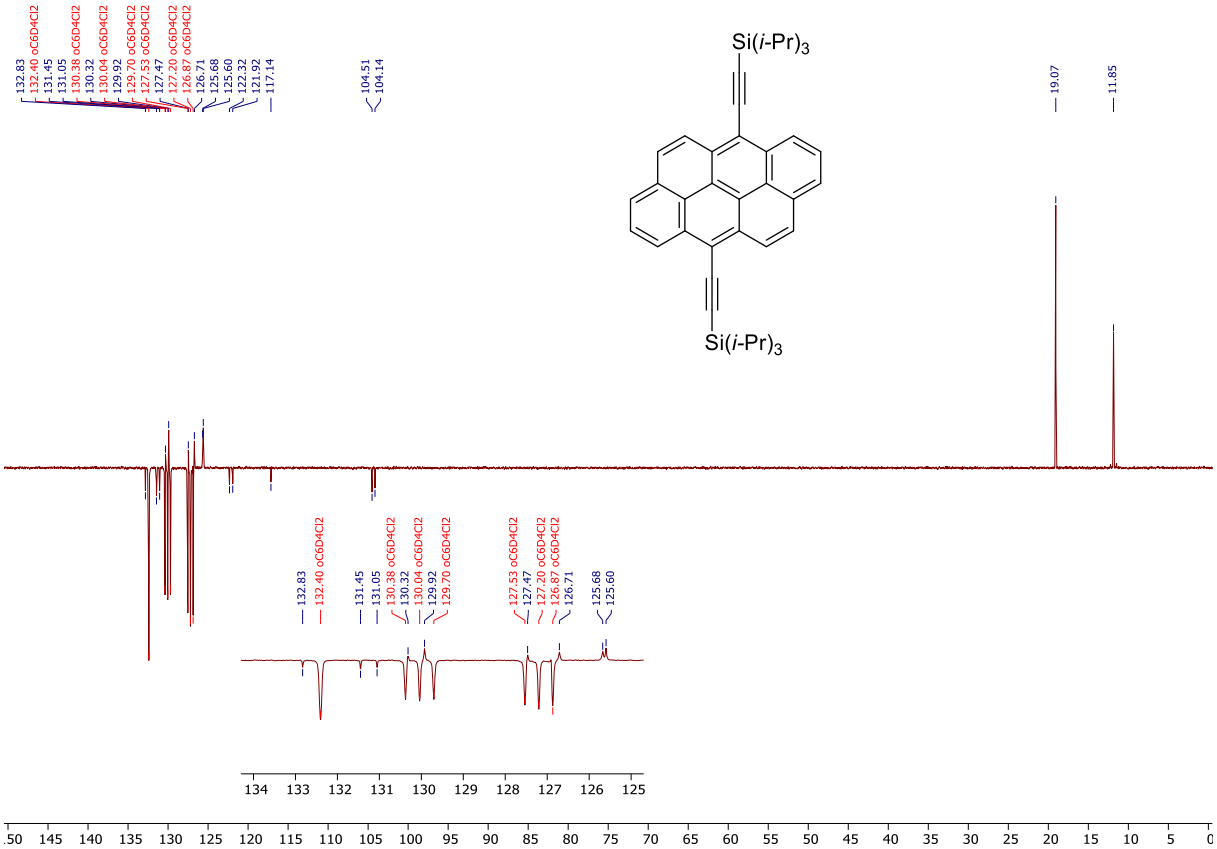
9.22
9.20
9.19
8.91
8.88
8.17
8.17
8.15
8.11
8.08
7.19 oC6D4Cl2
6.93 oC6D4Cl2
1.35
1.35
Si(i-Pr)3
Si(i-Pr)3
2.00
2.00
4.07
2.02
42.11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131.05
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127.47
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126.87 oC6D4Cl2
126.71
125.68
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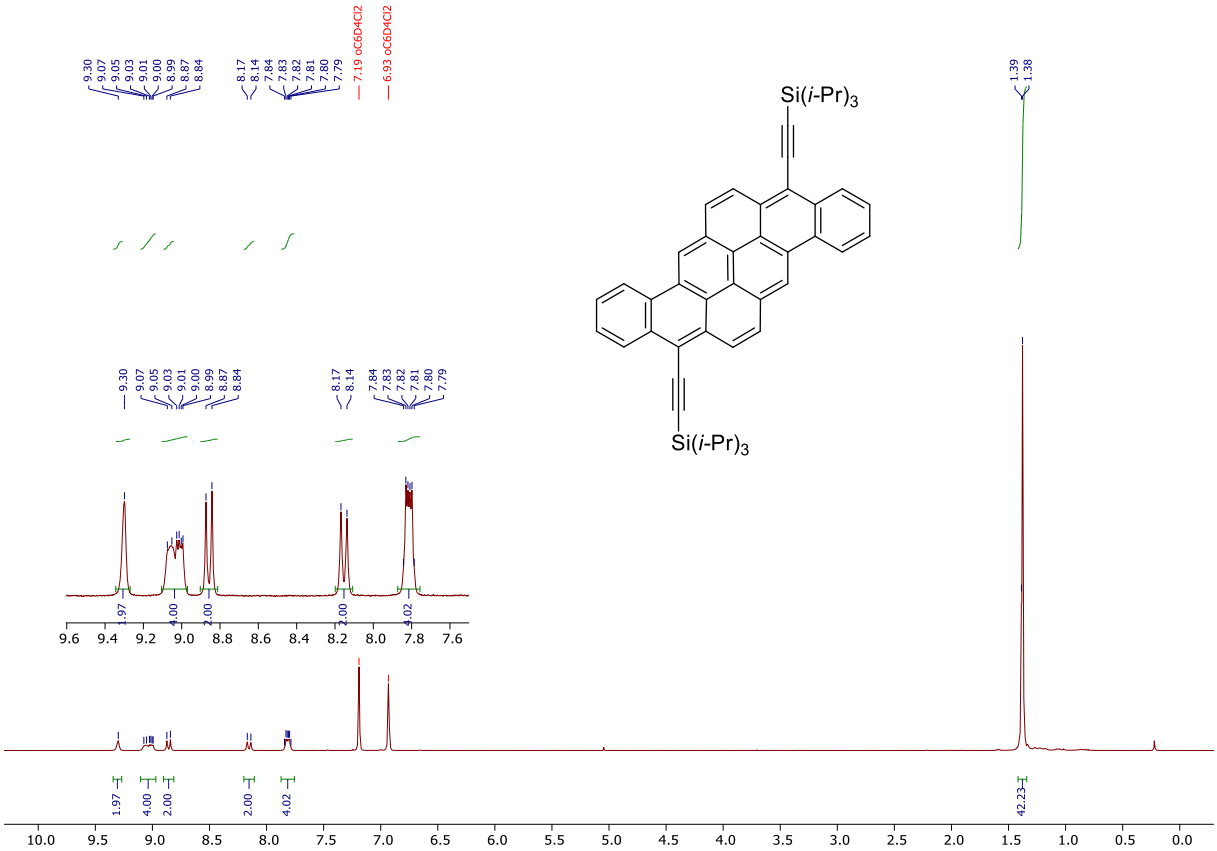
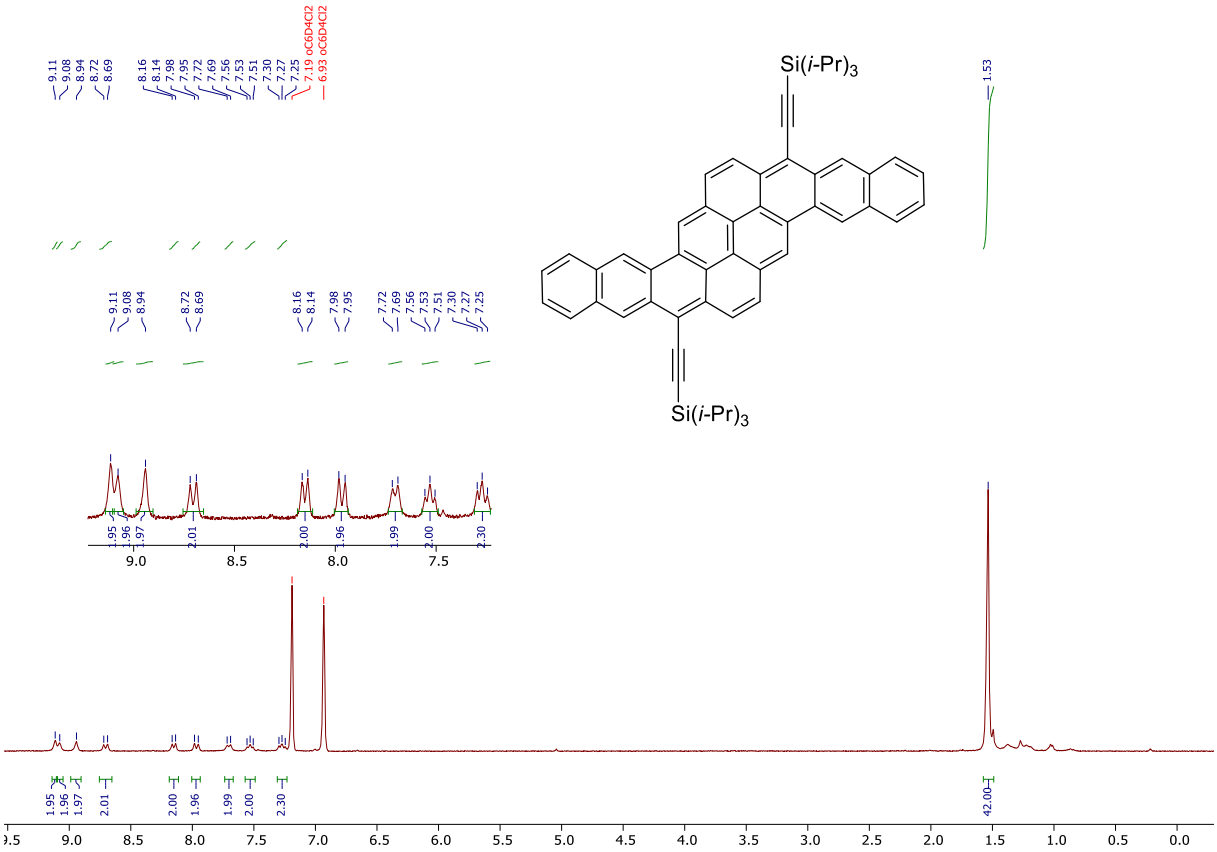
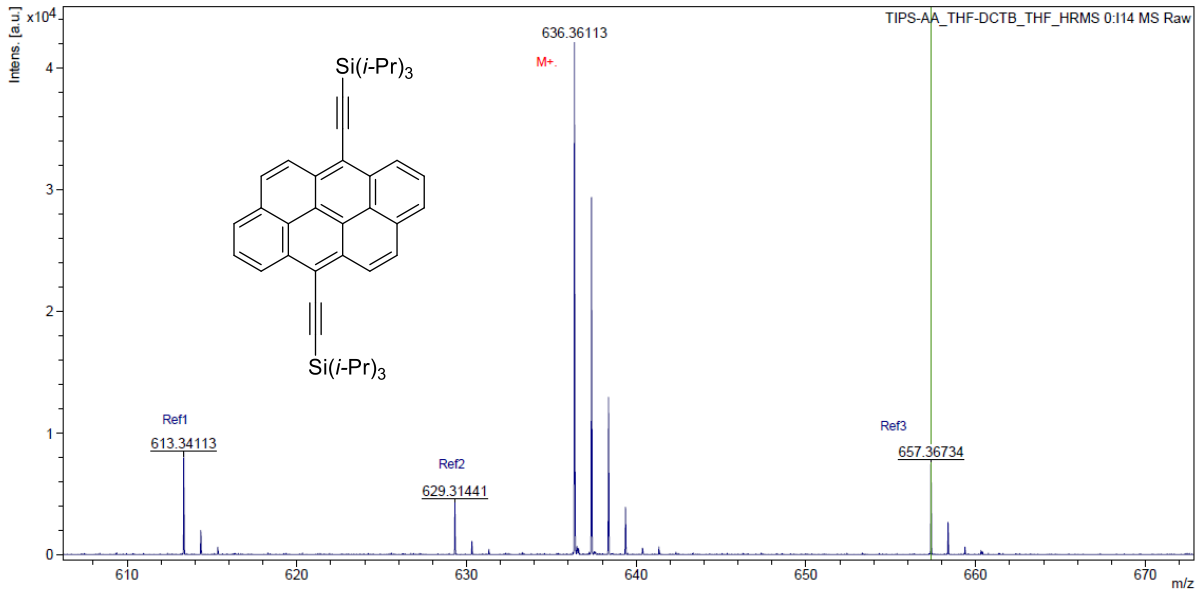
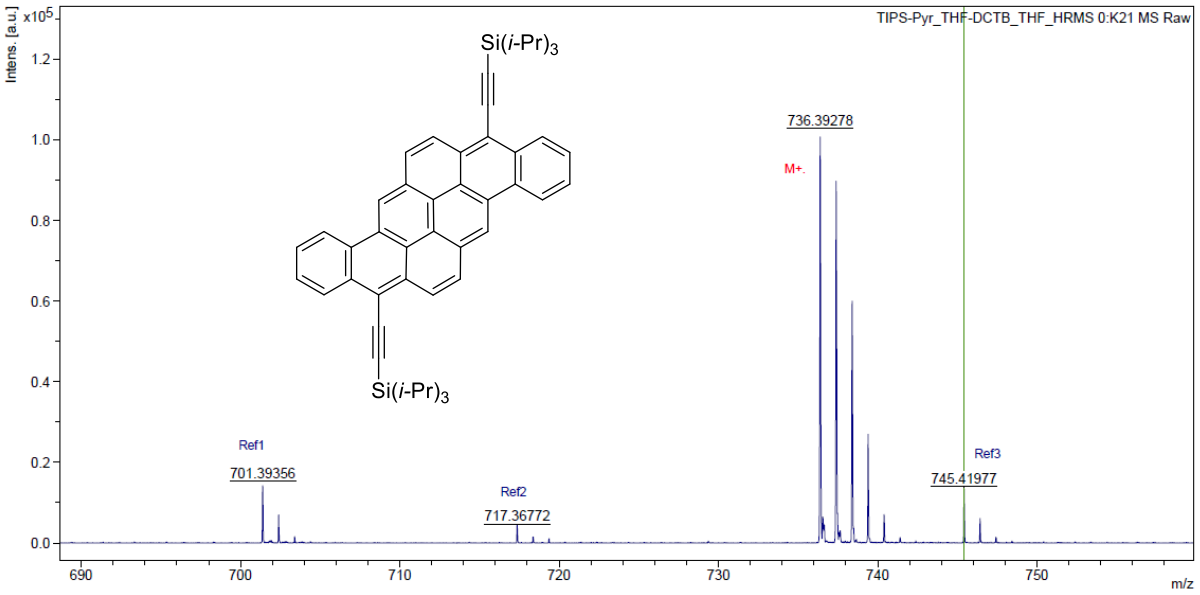
104.51
104.14
Si(i-Pr)3
Si(i-Pr)3
19.07
11.85

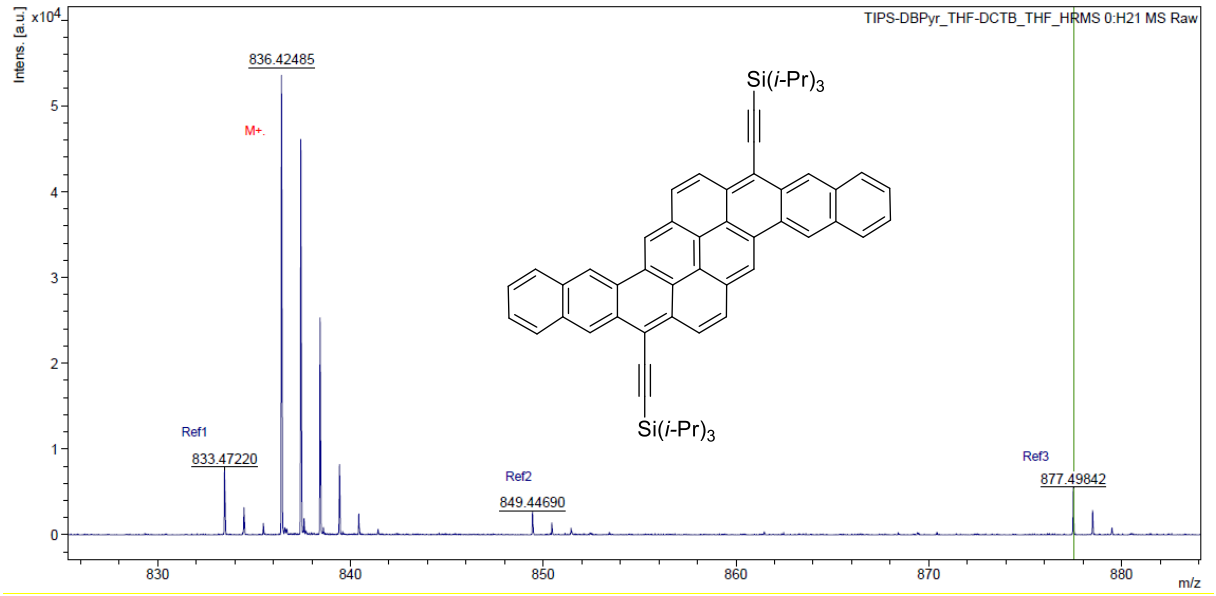

Si(i-Pr)3
Si(i-Pr)3


Si(i-Pr)3
Si(i-Pr)3

HRMS SPECTRA (MALDI)



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M+.
Ref1
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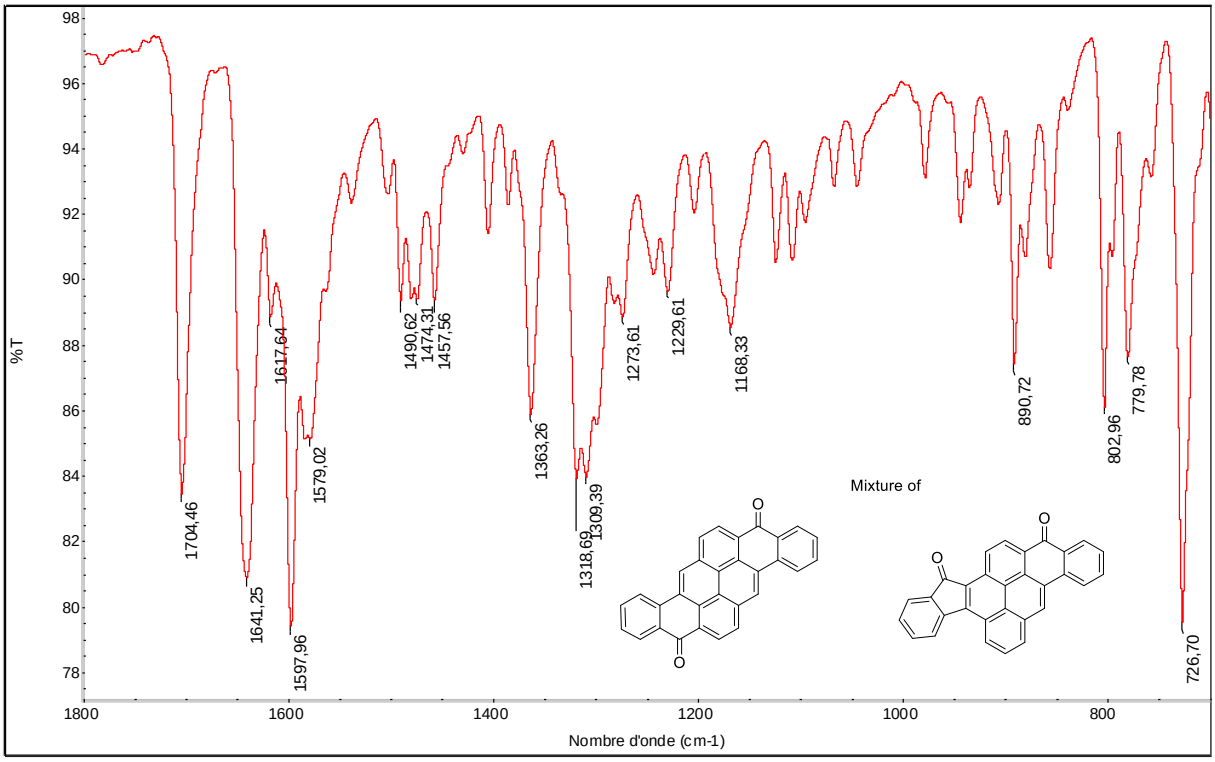
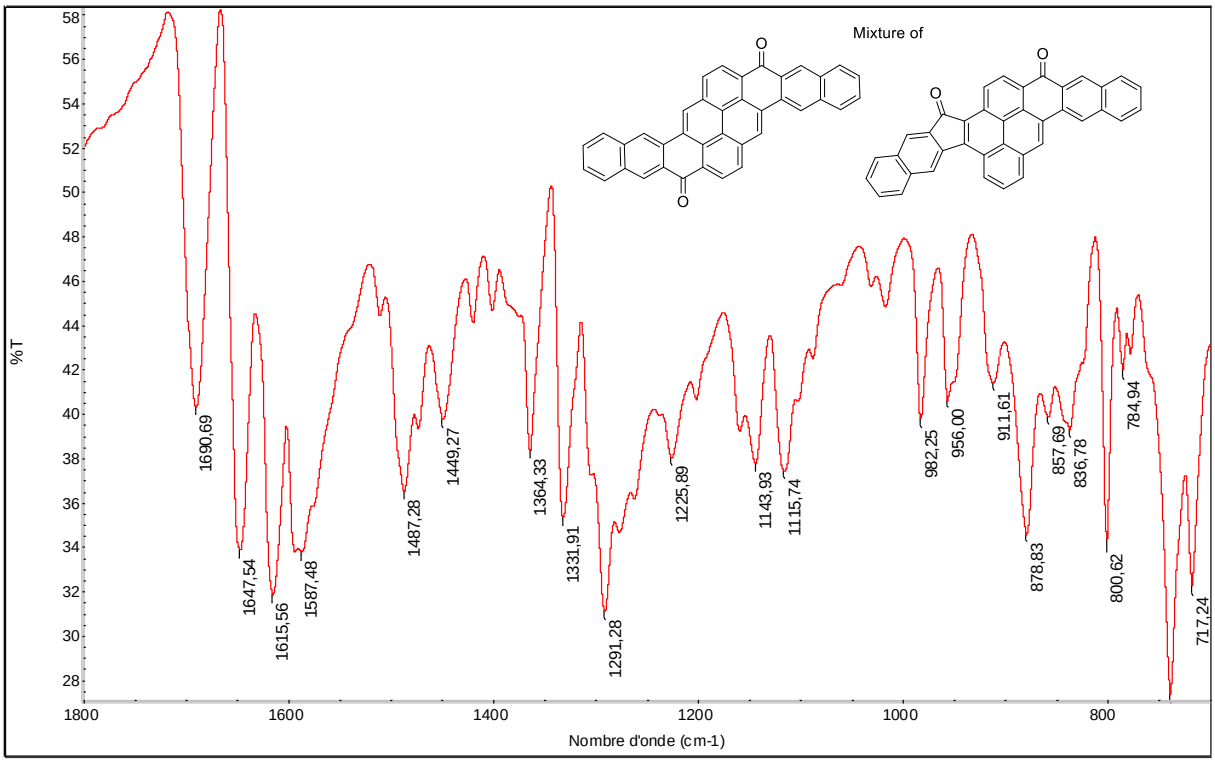
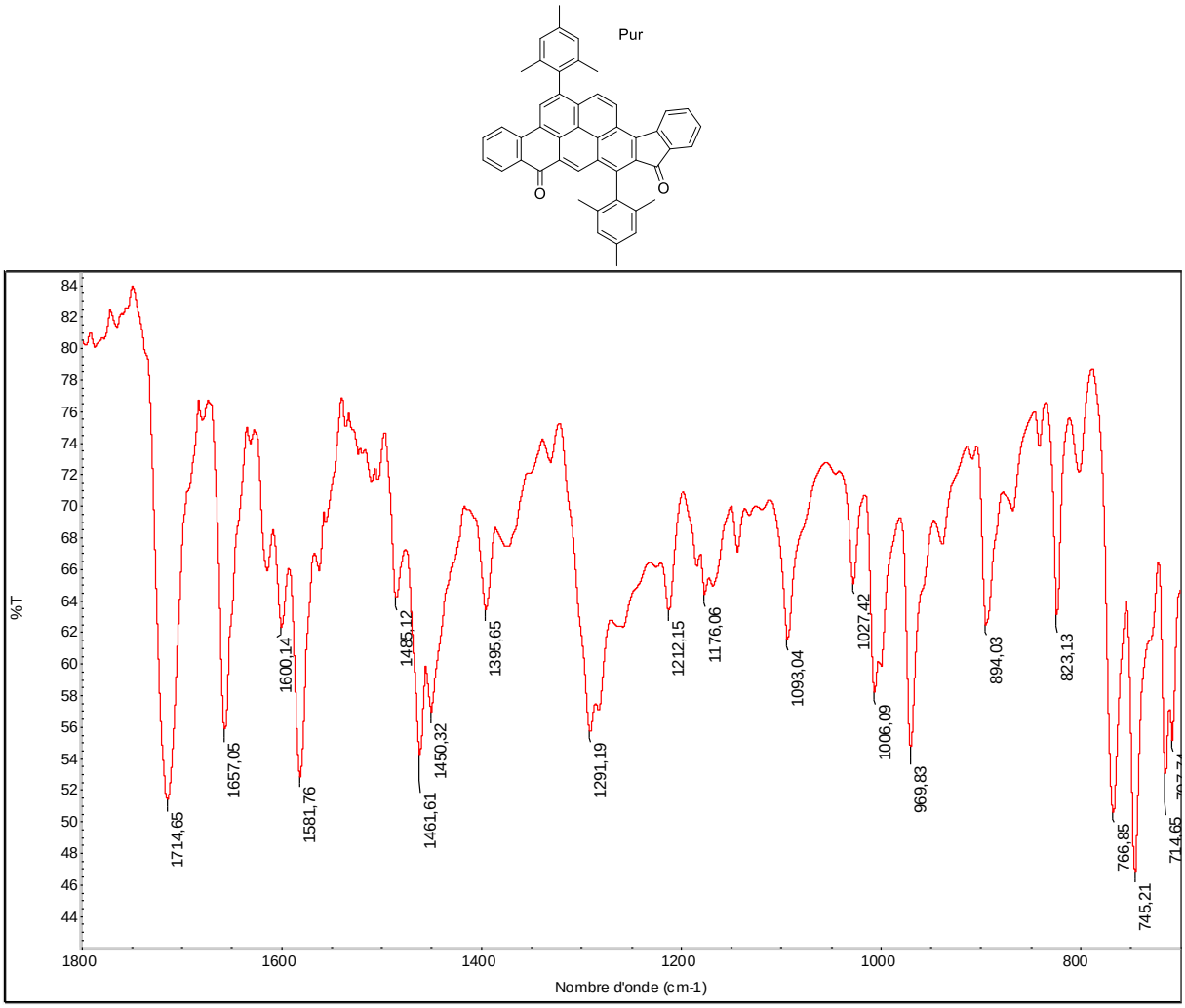
Si(i-Pr)3
Si(i-Pr)3
m/z

INFRARED SPECTRA






Pur
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68
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52
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48
46
44
1800
1600
1400
1200
1000
800
Nombre d'onde (cm-1)
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1600,14
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1006,09
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894,03
823,13
766,85
745,21
714,65

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