Supporting Information

From Solution to Thin Films: Unraveling Excited-State Behavior in Halogenated Diradicaloids

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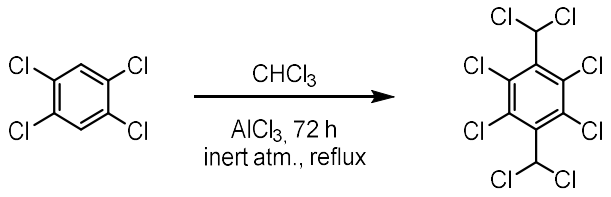
1. Materials and methods

All analyses and operations were performed under ambient conditions unless otherwise specified. 1,2,4,5-tetrafluorobenzene, 1,3,5-trichlorobenzene, Aluminum trichloride, hydrochloride acid (1 M), sodium sulphate and tetrabutylammonium hydroxide (55% w/w) were purchased from Sigma-Aldrich and used as received. Acetonitrile (CH_3CN), tetrahydrofuran (THF), dichloromethane (DCM), chloroform ($CHCl_3$) diethyl ether (Et_2O), methanol (MeOH), *n*-hexane, *n*-pentane and deuterated solvents were purchased from Sigma-Aldrich. Unless otherwise noted, all solvents were dry and of high purity grade and were used as received. THF was distilled prior to use. Compounds **TTH** and **TFH** were prepared following the literatre procedures.[1,2] Nevertheless, in light of the modifications implemented to the original procedures, we reported the versions employed in the present study. NMR spectra were recorded on a Bruker Avance 400 MHz (400 MHz for ^{1}H, 100 MHz for ^{13}C) or on a Bruker Avance 200 MHz (200 MHz for ^{19}F); chemical shifts (δ) are reported in parts per million (ppm) relative to the residual solvent signals. The multiplicities are reported as followed: singlet (s), broad signal (br), multiplet (m). The coupling constants (*J*) are reported in Hz. The crystallographic data for compounds **[TTH]H$_2$** and **TTH** were collected on a Bruker D8 Venture Photon II single-crystal diffractometer working with monochromatic Mo-K_α radiation and equipped with an area detector. The structures were solved and refined against F^2 with SHELXL-2018/3 with anisotropic thermal parameters for all non-hydrogen atoms.[3] Idealized geometries were assigned to the hydrogen atoms. For **TTH** the calculated molar mass, density and absorption coefficient include one disordered dichloromethane molecule per cell which does not appear in the final files because of the refinements carried out with data subjected to SQUEEZE. Crystallographic data were deposited with the Cambridge Crystallographic Data Centre as supplementary publication. Copy of the data (CCDC Deposition Number2466108 and 2466109) can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 223 336033; e-mail, deposit@ccdc.cam.ac.uk). Crystal data and refinement parameters are reported in **Table S01** and **Table S02**.

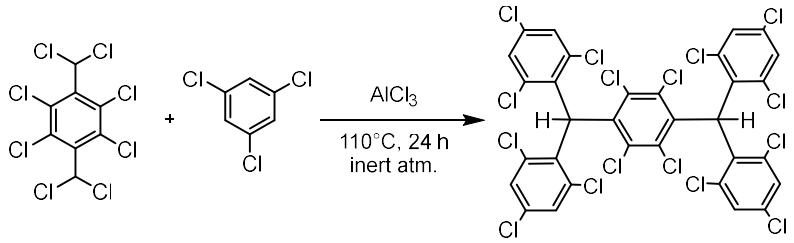
1.1 Synthesis of 1,2,4,5-tetrachloro-3,6-bis(dichloromethyl)benzene



The present molecule has been synthetized according to a modified literature procedure.[1] A mixture of 1,2,4,5-tetrachlorobenzene (1.0 g, 4.5 mmol) and aluminum chloride (3.0 g, 22.6 mmol) in anhydrous chloroform (12 mL) was refluxed under inert atmosphere for 72 h. The reaction mixture was cooled to room temperature, diluted with $CHCl_3$ (40 mL) and poured into a mixture of aqueous hydrochloric acid 1 M (50 mL) and ice-water (50 mL). The organic layer was separated, dried over sodium sulfate and concentrated to give a beige solid. The solid was washed with 5 mL of *n*-pentane and dried under *vacuum*, affording 1.36 g (80 % yield) of the desired product as beige solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (br, 2H).

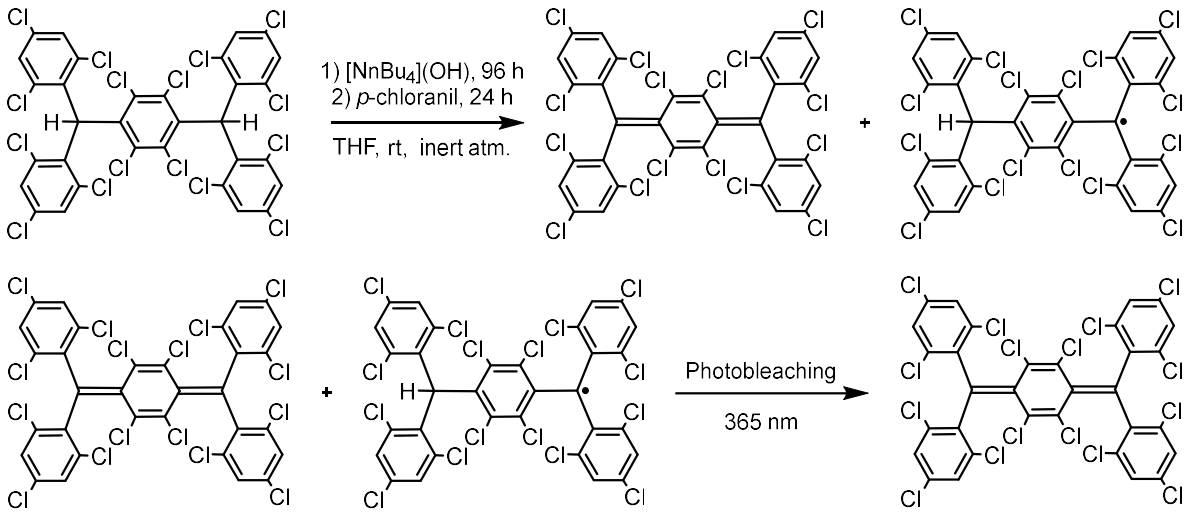
1.2 Synthesis of 2,2',2'',2'''-((perchloro-1,4-phenylene)bis(methanetriyl))tetrakis(1,3,5-trichlorobenzene) ***[TTH]H₂***



The present molecule has been synthetized according to a modified literature procedure.[1] In a pressure tube equipped with a magnetic stirrer, 200 mg of 1,2,4,5-tetrachloro-3,6-bis(dichloromethyl)benzene (0.50 mmol), 2.0 g of 1,3,5-trichlorobenzene (11 mmol) and 553 mg of aluminum chloride (4.20 mmol) were introduced. The mixture was heated under stirring at 110 °C for 24 hours. After this time, the mixture was cooled down to room temperature and poured in 50 mL of aqueous hydrochloric acid (1 M) and ice-water (50 mL). Subsequently, the crude product was extracted with $CHCl_3$ (3 x 50 mL). The organic phases were collected, dried over Na_2SO_4 and concentrated under *vacuum*, affording a brownish solid. The solid was dispersed in 70 mL of CH_3CN and sonicated for 5 minutes. The solid was filtered, washed with 50 mL of CH_3CN and dried under *vacuum*, affording 409 mg (82 % yield) of **[TTH]H₂** as brownish powder. Crystals suitable for SCXRD were obtained from slow evaporation of DCM solution of **[TTH]H₂**.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.40 (m, 4H), δ 7.28 (m, 4H), δ 6.82 (m, 2H).

1.3 Synthesis of 2,2',2'',2'''-((perchlorocyclohexa-2,5-diene-1,4-diylidene)bis(methanediylylidene))tetrakis-(1,3,5-trichlorobenzene) ***TTH***



The present molecule has been synthetized according to a modified literature procedure.[1] In a two-neck round-bottom flask (100 mL) equipped with a magnetic stirrer, 186 mg of **[TTH]H$_2$** (0.20 mmol) were dissolved in 40 mL of freshly distilled THF at room temperature and under inert atmosphere. Subsequently, 1.45 mL of a solution of tetrabutylammonium hydroxide (55% w/w) (3.10 mmol) was added dropwise, affording a purple solution. The apparatus was protected from light using aluminum foil and the mixture was left under stirring for 96 h. After this time, the mixture presented a blue color. Hence, 1.03 g of *p*-chloranil (3.70 mmol) were added under inert atmosphere and the mixture was left under stirring for additional 24 h. After this time, the solvent was removed under *vacuum*, affording a blue solid. The crude product was extracted with 40 mL of Hex:$CHCl_3$ (85:15) and the mixture filtrated. The filtrate was concentrated under *vacuum* and the remaining red solid purified through column chromatography, using Hex:$CHCl_3$ (85:15) as eluent, affording 56 mg of red solid. The solid was dissolved in $CHCl_3$ and analyzed by UV-Vis spectroscopy. The analysis highlighted the presence of mono-radical impurity (band centered at 381 nm). Therefore, the solid was dissolved in 45 mL of $CHCl_3$ and irradiated with a TLC lamp (365 nm, 6 W) for 11 h, monitoring the photobleatching process by UV-Vis spectroscopy (**Figure S04**). After this time, the solvent was removed under *vacuum* and the solid purified through column chromatography, using Hex:$CHCl_3$ (85:15) as eluent, affording a red solid. The solid was washed with 2 mL of *n*-pentane and dried under *vacuum*, providing 20 mg (11 % yield) of **TTH** as red powder. Crystals suitable for SCXRD were obtained from slow evaporation of DCM solution of **TTH**.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.38 (s, 4H), δ 7.30 (s, 4H).

UV-Vis (DCM, 5.2 × 10^{-6} M): 322 nm (11849 $M^{-1}cm^{-1}$), 500 nm (42497 $M^{-1}cm^{-1}$).

ESI-MS (*m/z*): 958.42 ($[M-H]^+$, 958.54 expected for $C_{32}H_8Cl_{16}$).

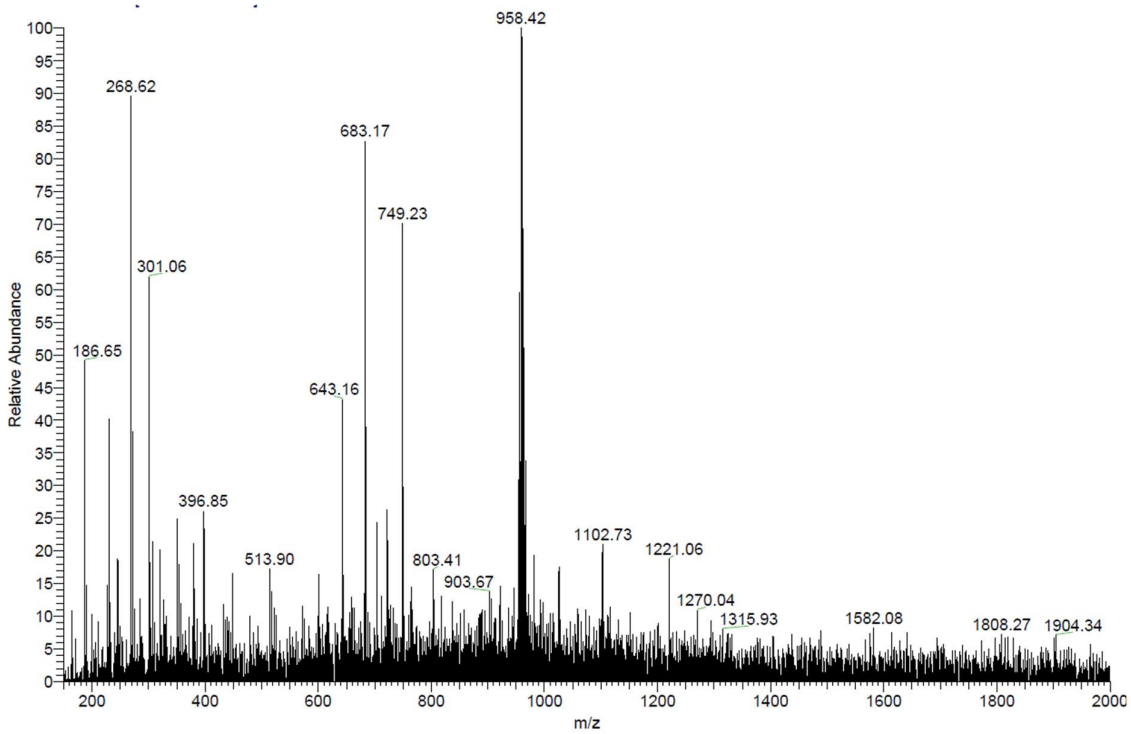


Figure S01: ESI-MS analysis of **TTH** dissolved in THF.

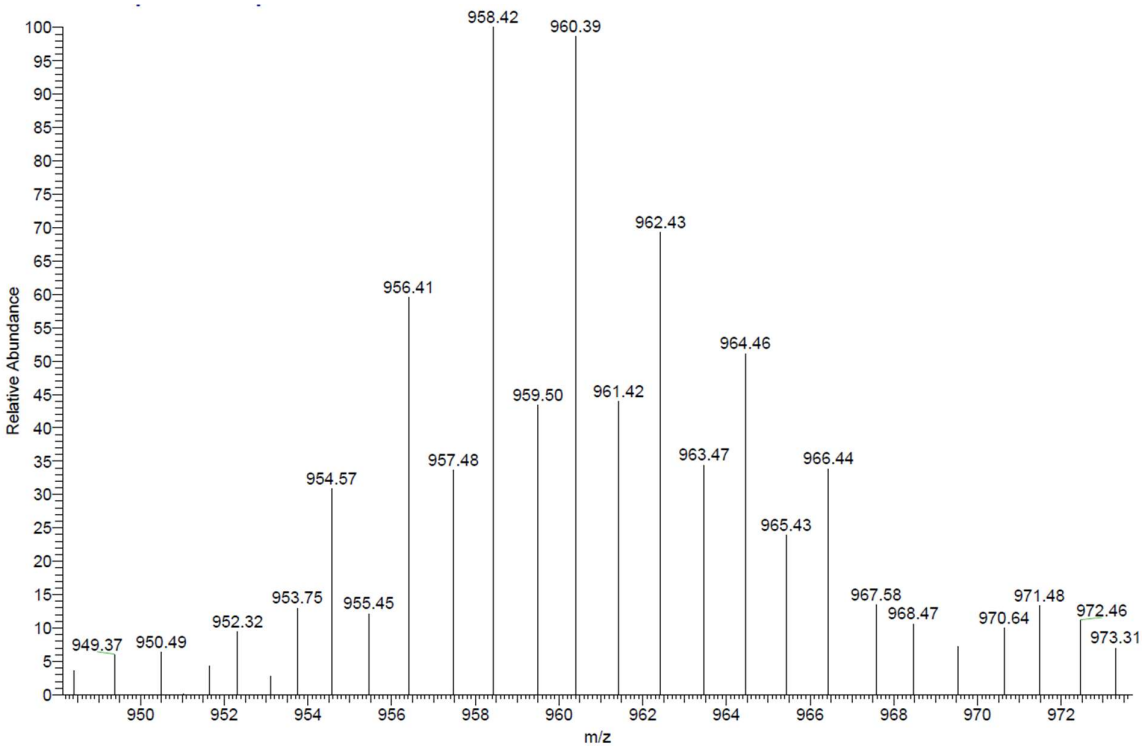


Figure S02: zoomed ESI-MS signal of **TTH** dissolved in THF.

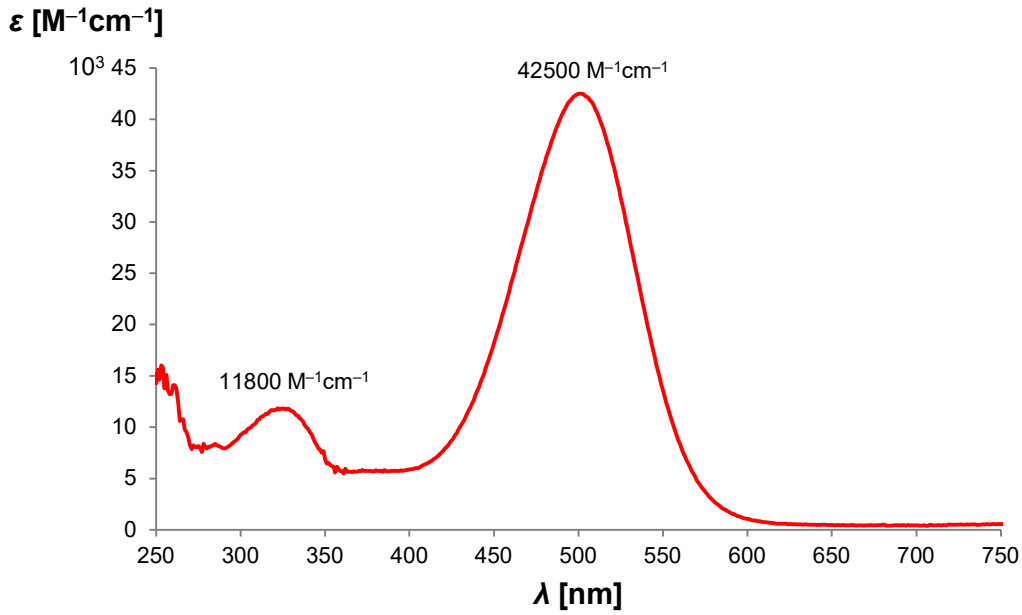


Figure S03: UV-Vis spectrum of **TTH** dissolved in DCM. [C]: 5.2×10^{-6} M.

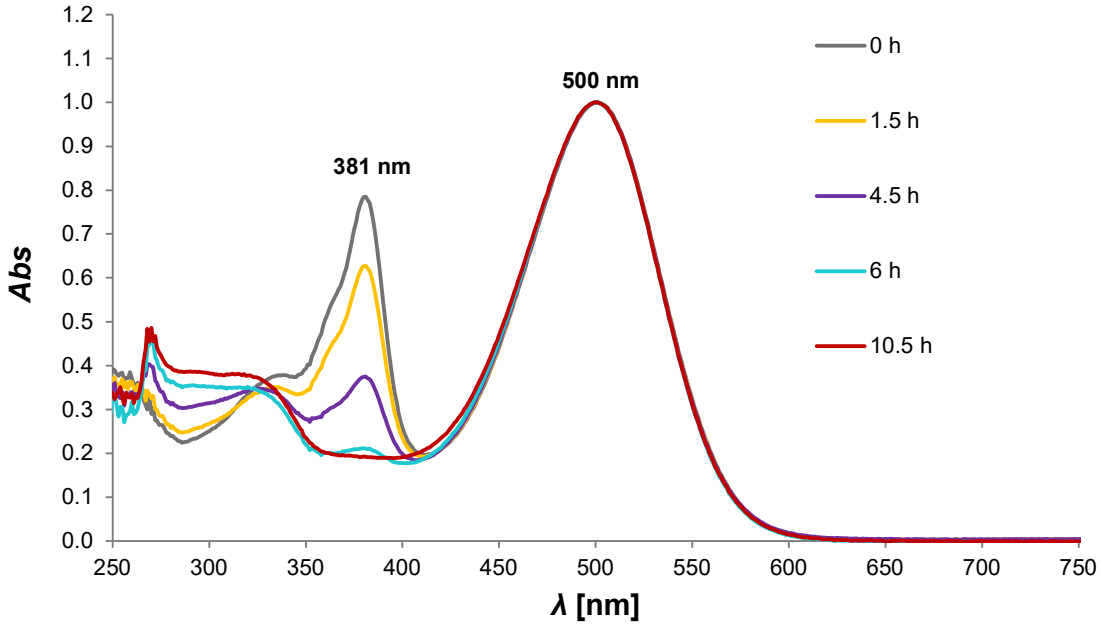
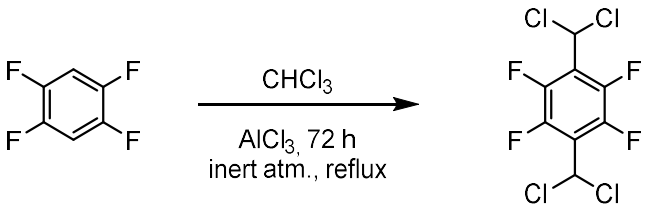


Figure S04: Normalized UV-Vis spectra of photobleaching process of **TTH** dissolved in $CHCl_3$. The mono-radical impurity (381 nm) disappears after 10.5 h of irradiation at 365 nm.

1.4 Synthesis of 1,2,4,5-tetrafluoro-3,6-bis(dichloromethyl)benzene

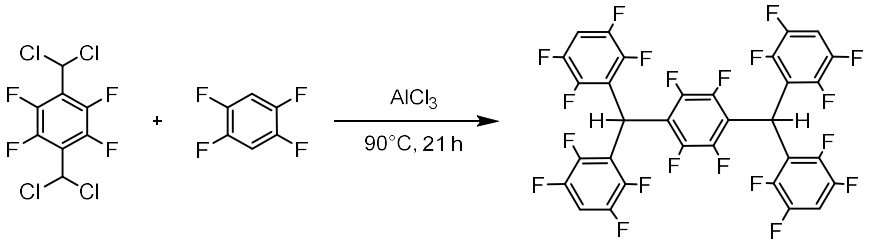


The present molecule has been synthetized according to a modified literature procedure.[2] A mixture of 1,2,4,5-tetrafluorobenzene (1.0 g, 6.7 mmol) and aluminum chloride (5.0 g, 32.5 mmol) in anhydrous chloroform (25 mL) was refluxed under inert atmosphere for 72 h. The reaction mixture was cooled to room temperature, diluted with chloroform (100 mL) and poured into a mixture of aqueous hydrochloric acid 1 M (100 mL) and ice-water (100 mL). The organic layer was separated, dried over sodium sulfate and concentrated to give a brown sticky solid. The solid was dispersed in 15 mL of *n*-pentane and the mixture filtrated on celite. The filtrate was concentrated under *vacuum*, affording 1.1 g (52 %) of crude product as sticky yellowish solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.96 (br, 2H).

^{19}F NMR (200 MHz, $CDCl_3$): δ –139.49 (s, 4F).

1.5 Synthesis of 2,2',2'',2'''-((perfluoro-1,4-phenylene)bis(methanetriyl))tetrakis(1,3,5-trifluorobenzene) ***[TFH]H₂***

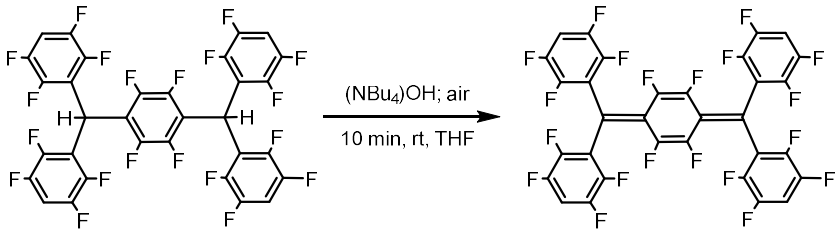


The present molecule has been synthetized according to a modified literature procedure.[2] In a high-pressure vessel (15 mL) equipped with a magnetic stirrer, were introduced 304 mg of 1,2,4,5-tetrafluoro-3,6-bis(dichloromethyl)benzene (0.96 mmol), 1.30 g of 1,2,4,5-tetrafluorobenzene (8.40 mmol) and 850 mg of aluminum chloride (6.4 mmol). The mixture was heated at 90 °C for 21 h. After this time, the hot mixture was poured into a mixture of aqueous hydrochloric acid 1 M (50 mL) and ice-water (50 mL). and extracted with $CHCl_3$ (3 x 100 mL). The organic phase was collected, dried over Na_2SO_4 and concentrated under *vacuum*, obtaining a brownish solid. The solid was dispersed in *n*-pentane, decanted and dried, affording 270 mg (36 % yield) of **[TFH]H₂** as brownish solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (m, 4H), δ 6.33 (s, 2H).

^{19}F NMR (200 MHz, $CDCl_3$): δ –138.57 (m, 8F), δ –142.15 (m, 12F).

1.6 Synthesis of 2,2',2'',2'''-((perfluorocyclohexa-2,5-diene-1,4-diylidene)bis(methanediylylidene))tetrakis-(1,2,4,5-tetrafluorobenzene) ***TFH***



The present molecule has been synthetized according to a modified literature procedure.[2] In a one-neck round-bottom flask (250 mL) equipped with a magnetic stirrer, 270 mg of **[TFH]H₂** (0.15 mmol) were dissolved in 30 mL of freshly distilled THF at room temperature. 1.55 mL of a solution of tetrabutylammonium hydroxide (55% w/w) (1.50 mmol) was added dropwise, affording a purple solution. After 10 minutes, the solvent was removed under *vacuum*, affording a yellow solid. The solid residue was dispersed in 100 mL of Hex:DCM (1:1) and purified through a flash column chromatography, collecting the yellow colored fractions (R_f: 0.1-0.3 in *n*-hexane), affording a yellow solid. The solution was concentrated under *vacuum* until a yellow solid precipitated. The solid was decanted, washed with MeOH (3 mL) and *n*-pentane (2 mL). The remaining solid was dried, affording 53 mg (20% yield) of **TFH** as a yellow solid. Despite several attempts, it was not possible to isolate the product with higher purity.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (m, 4H).

^{19}F NMR (200 MHz, $CDCl_3$): δ –138.69 (m, 8F), δ –140.44 (m, 8F), δ –140.95 (s, 4F).

UV-Vis (DCM, 1.5×10^{-5} M): 270 nm (15000 $Mol^{-1}cm^{-1}$), 389 nm (40300 $Mol^{-1}cm^{-1}$).

ESI-MS (*m/z*): undetectable *m/z* peaks due to low ionization of **TFH** during the mass analysis.

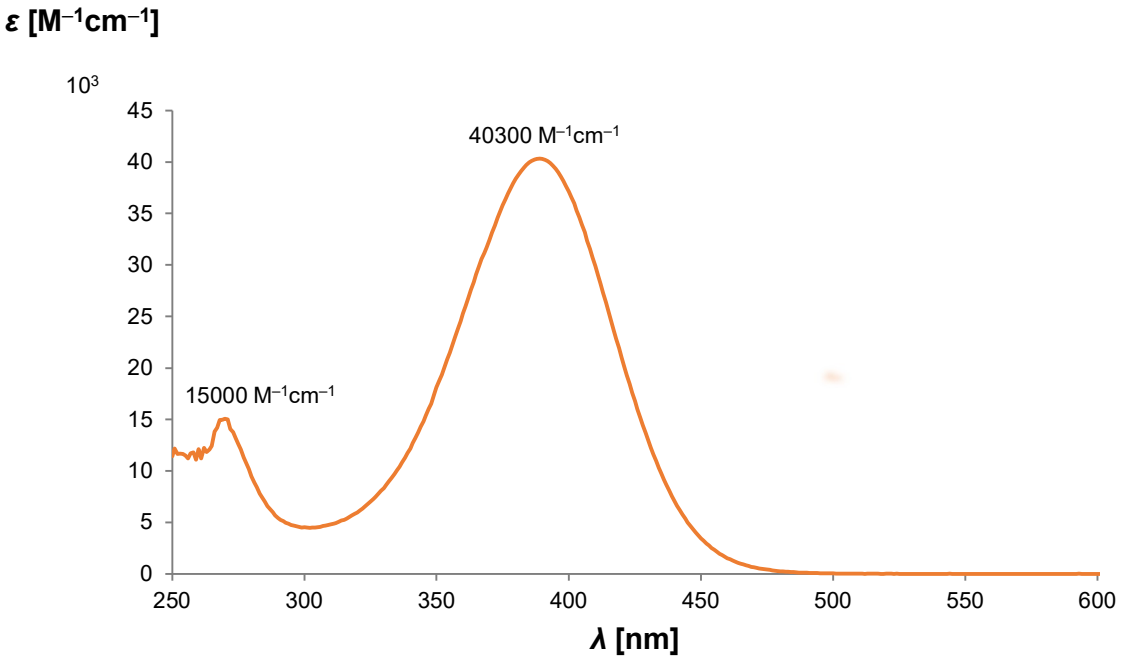


Figure S05: UV-vis spectrum of **TFH** dissolved in DCM. [C]: 1.5 × 10^{-5} M.

2. NMR spectra

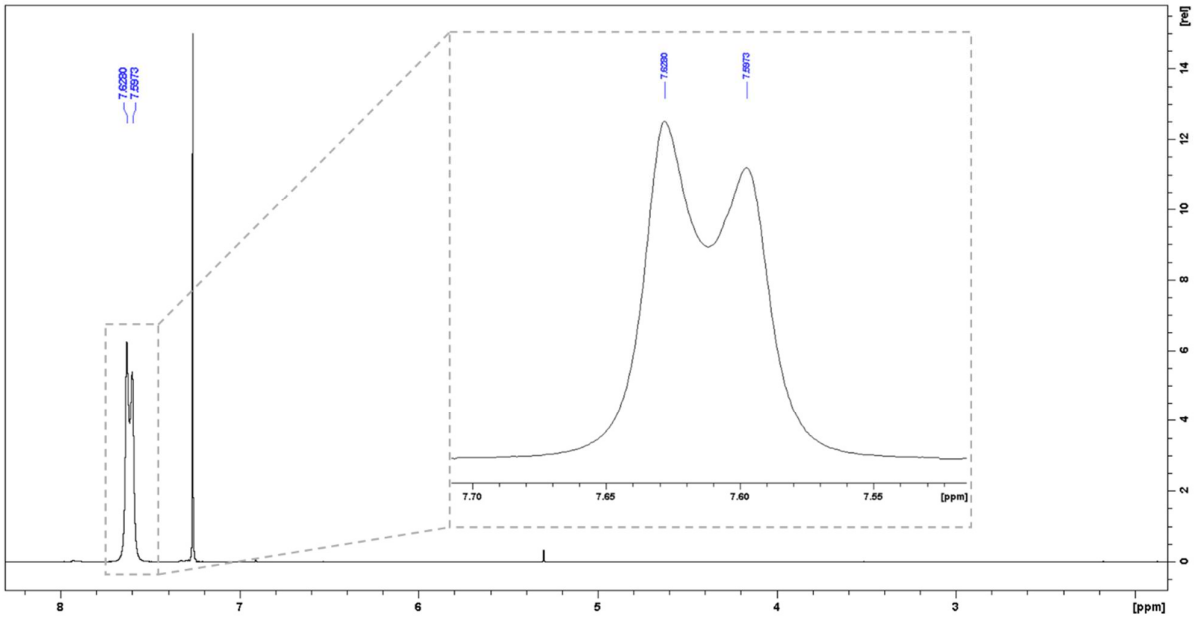


Figure S06: ^{1}H NMR (400 MHz, $CDCl_3$) of 1,2,4,5-tetrachloro-3,6-bis(dichloromethyl)benzene.

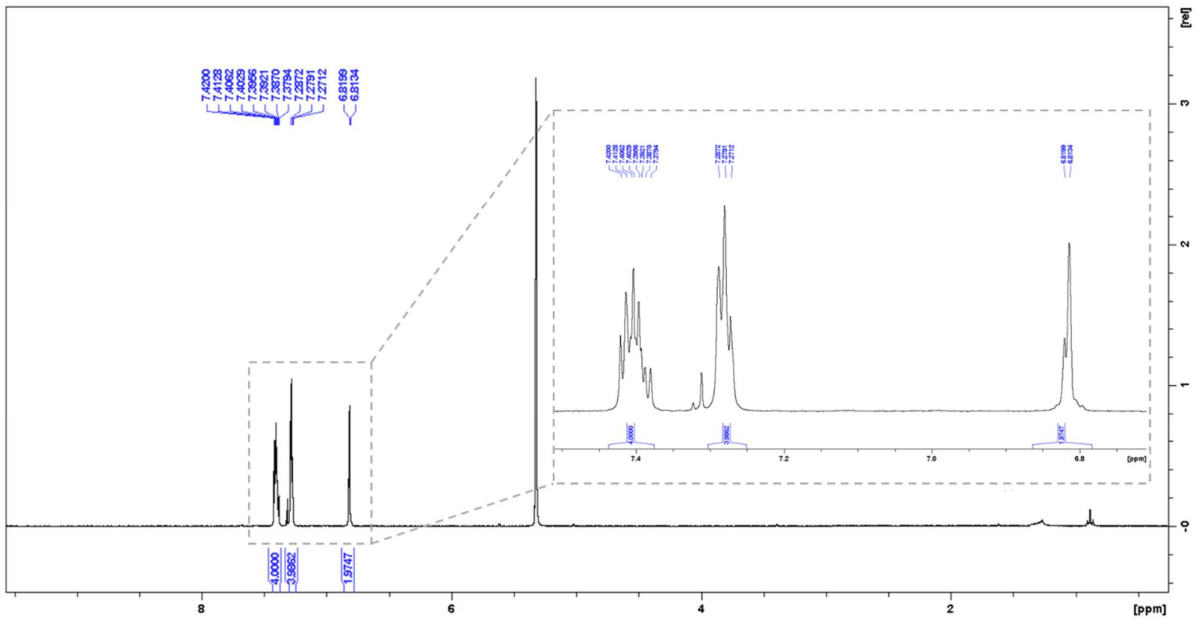


Figure S07: ^{1}H NMR (400 MHz, CD_2Cl_2) of **[TTH]H_2**.

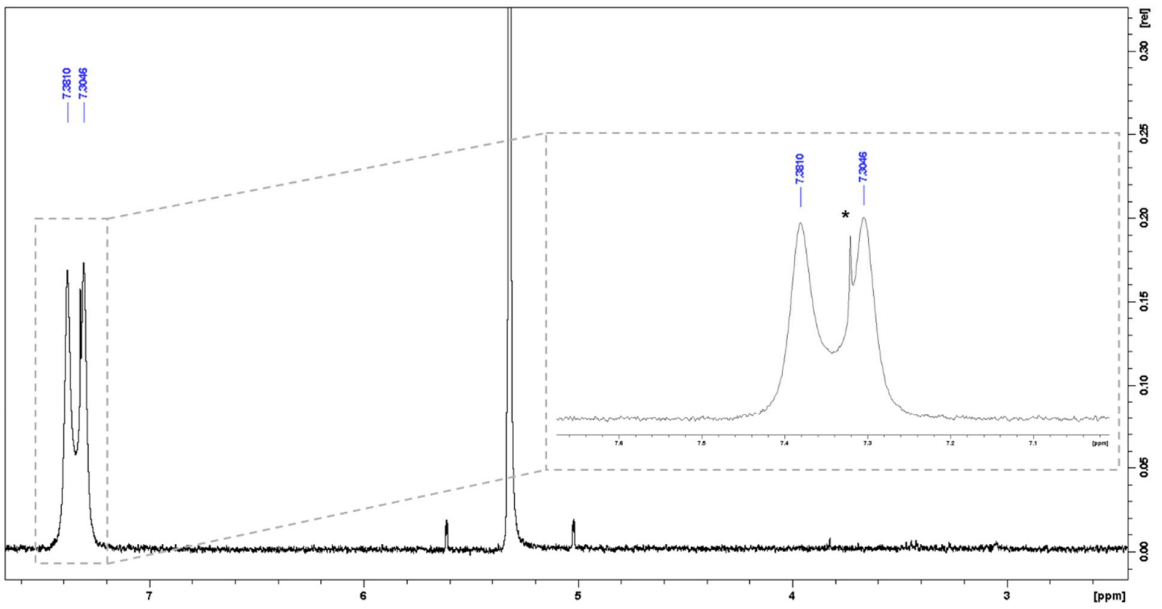


Figure S08: ^{1}H NMR (400 MHz, CD_2Cl_2) of **TTH** ($CHCl_3$ impurity highlighted with *).

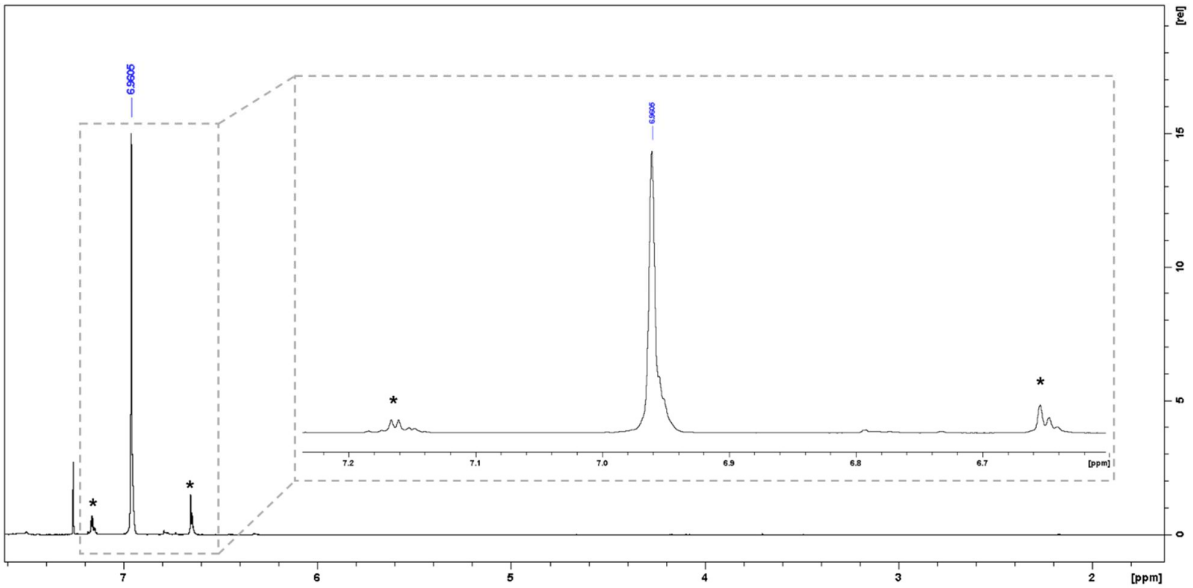


Figure S09: ^{1}H NMR (400 MHz, $CDCl_3$) of 1,2,4,5-tetrafluoro-3,6-bis(dichloromethyl)benzene. Unknown impurities are highlighted with *****.

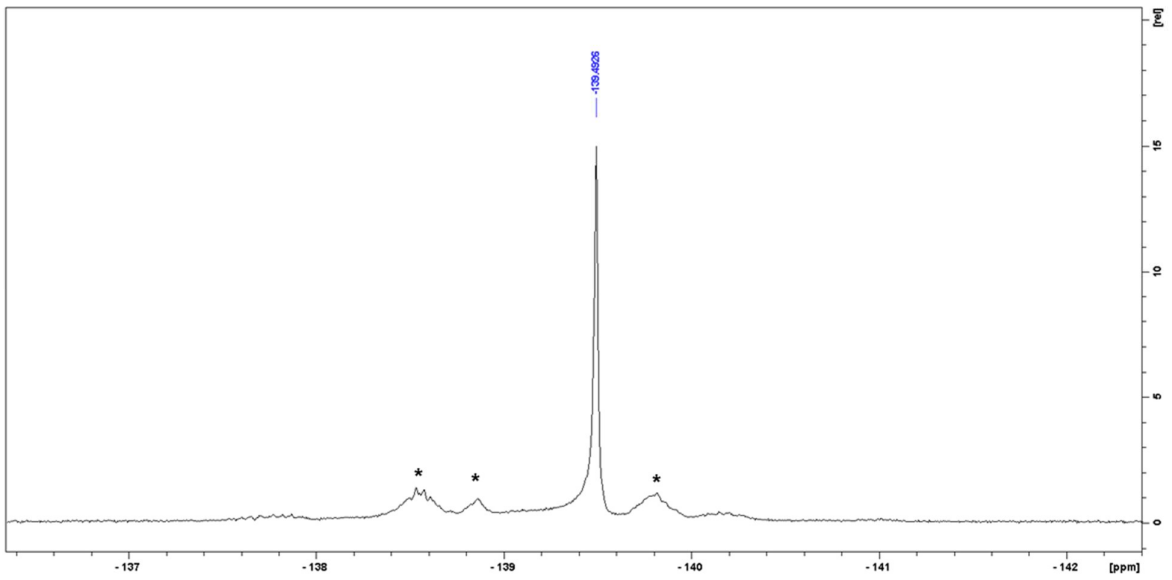


Figure S10: ^{19}F NMR (200 MHz, $CDCl_3$) of 1,2,4,5-tetrafluoro-3,6-bis(dichloromethyl)benzene. Unknown impurities are highlighted with *****.

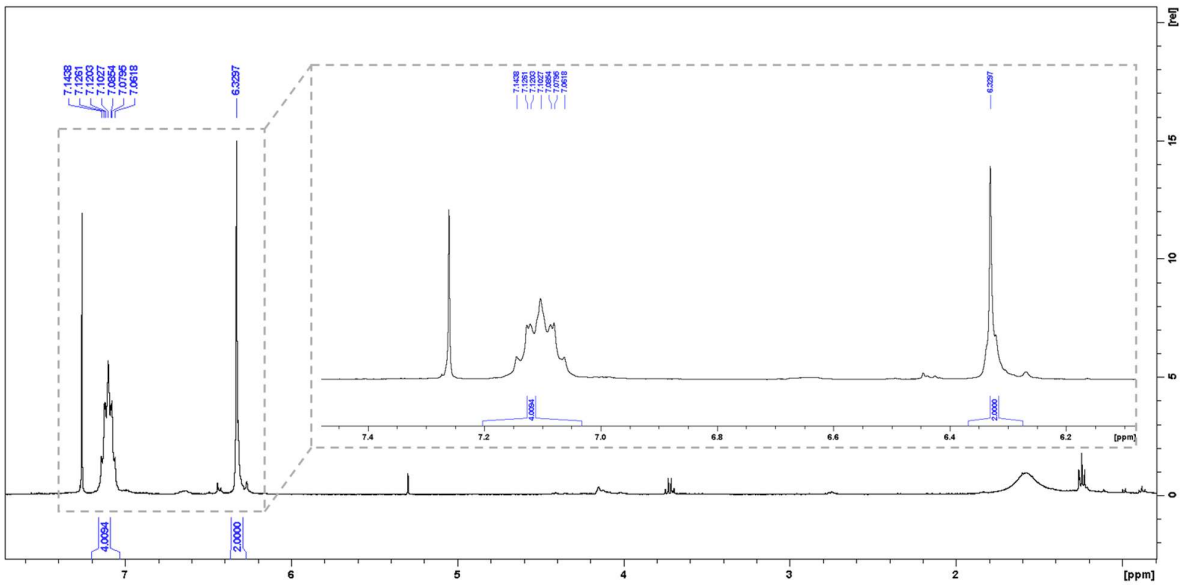


Figure S11: ^1H NMR (400 MHz, $CDCl_3$) of **[TFH]H_2**.

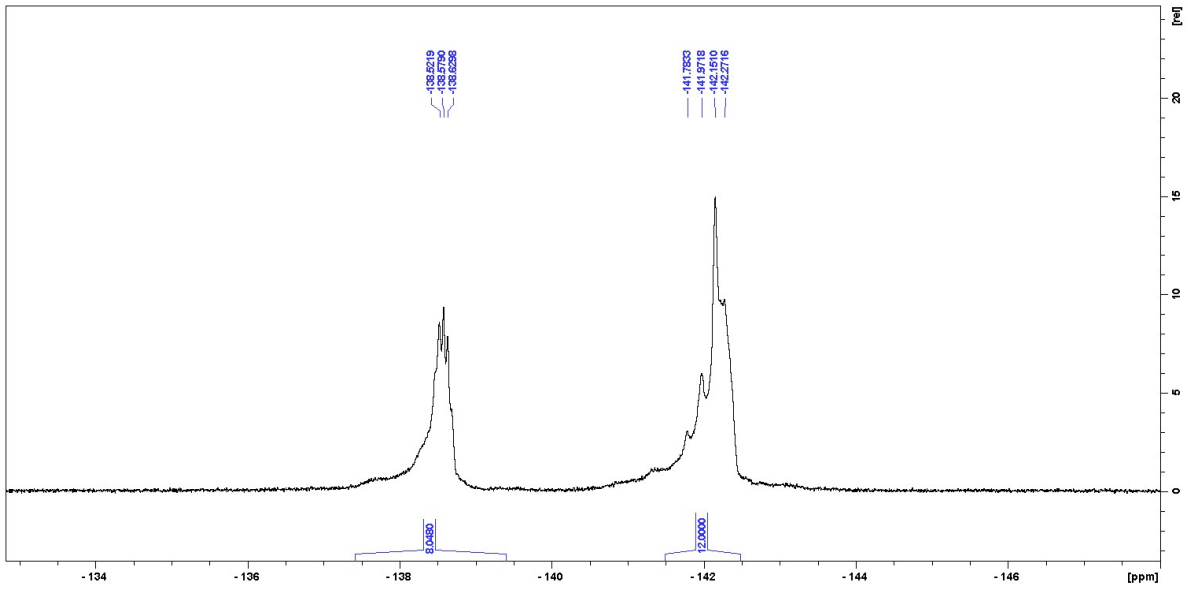


Figure S12: ^{19}F NMR (200 MHz, $CDCl_3$) of **[TFH]H$_2$**.

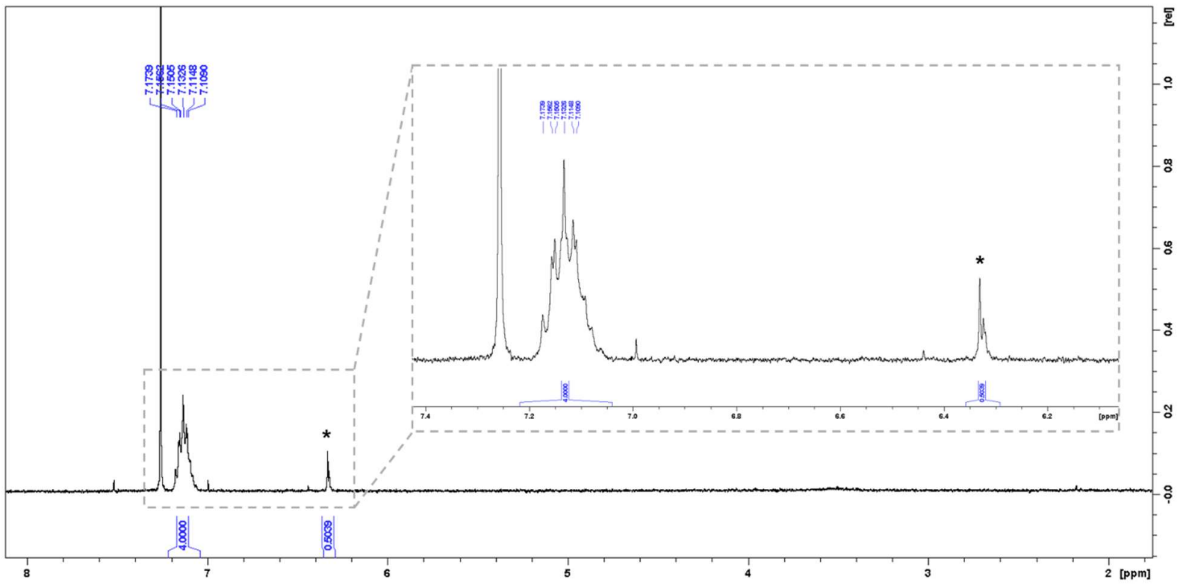


Figure S13: ^{1}H NMR (400 MHz, $CDCl_3$) of **TFH** (impurity of **[TFH]H$_2$** is highlighted with *).

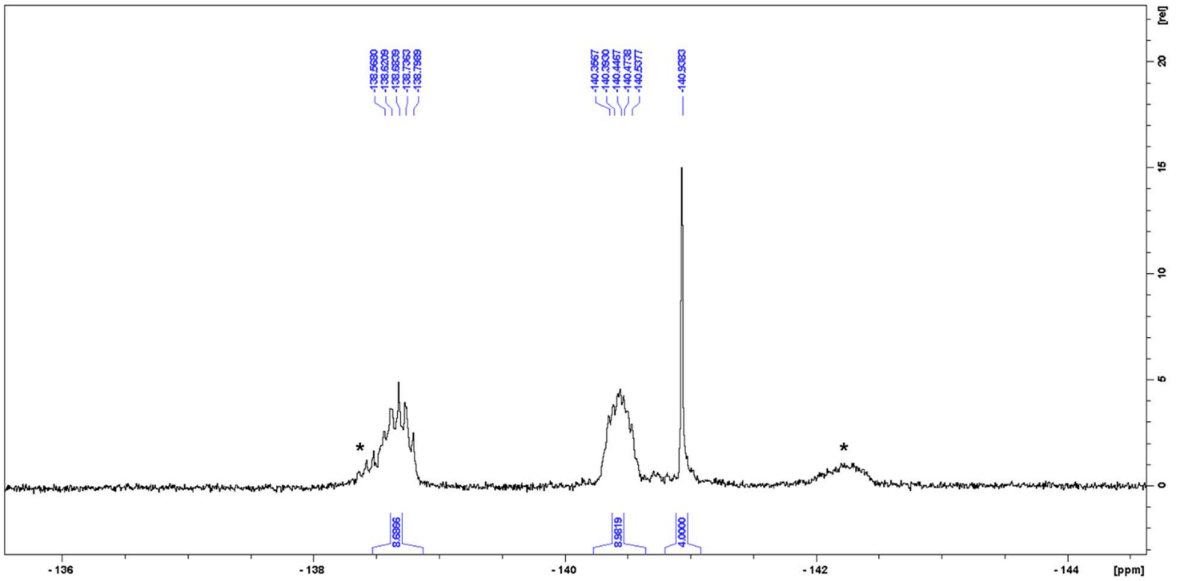


Figure S14: ^{19}F NMR (200 MHz, $CDCl_3$) of **TFH** (impurity of **[TFH]H$_2$** is highlighted with *).

3. SCXRD data

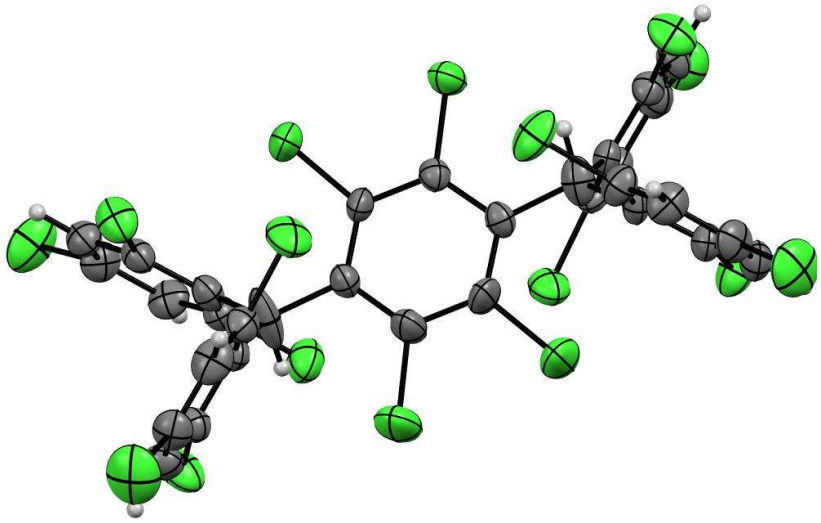


Figure S15: Molecular structure of **[TTH]H_2** in solid state. Solvent molecules are omitted for clarity. Thermal ellipsoids are displayed at 50% probability. Color code: green (Cl), gray (C), white (H).

Table S01: crystallographic data for **[TTH]H_2.**

Empirical formula	$C_{33}H_{12}Cl_{18}$
Formula weight	1046.53
Temperature/K	200(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.375(2)
b/Å	22.677(11)
c/Å	20.846(10)
α/°	90
β/°	93.666(11)
γ/°	90
Volume/Å^3	3951(3)
Z	4
ρ_{calc}g/cm^3	1.759
μ/mm^{-1}	1.275
F(000)	2064.0
Crystal size/mm^3	0.10 × 0.11 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.916 to 52.826
Index ranges	-10 ≤ h ≤ 10, -28 ≤ k ≤ 26, -26 ≤ l ≤ 25
Reflections collected	39417
Independent reflections	7887 [R_{int} = 0.1250, R_{sigma} = 0.1063]
Data/restraints/parameters	7887/0/460
Goodness-of-fit on F^2	1.017
Final R indexes [I>=2σ (I)]	R_1 = 0.0966, wR_2 = 0.2107
Final R indexes [all data]	R_1 = 0.1525, wR_2 = 0.2400
Largest diff. peak/hole / e Å^{-3}	1.15/-0.91

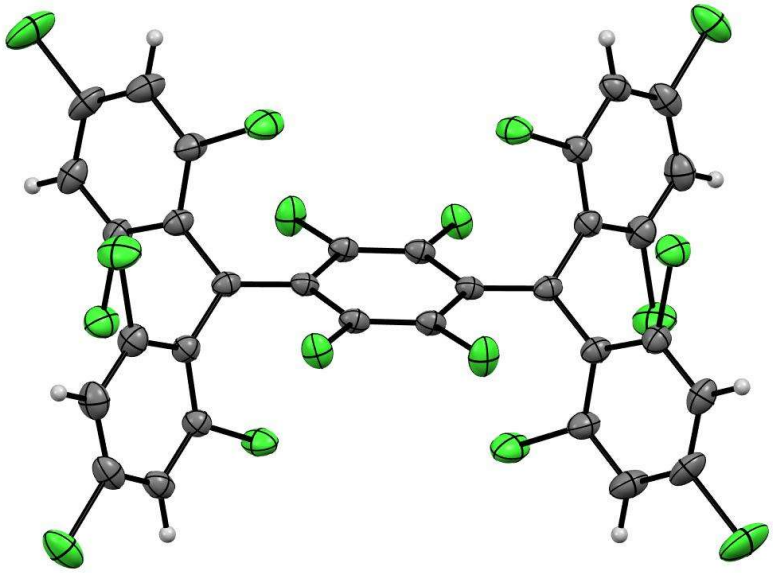


Figure S16: Molecular structure of **TTH** in solid state. Solvent molecules are omitted for clarity. Thermal ellipsoids are displayed at 50% probability. Color code: green (Cl), gray (C), white (H).

Table S02: crystallographic data for **TTH**.

Empirical formula	$C_{33}H_{10}Cl_{18}$
Formula weight	1044.51
Temperature/K	200.0
Crystal system	monoclinic
Space group	C2/c
a/Å	26.9772(11)
b/Å	8.5953(3)
c/Å	17.3226(7)
α/°	90
β/°	91.111(2)
γ/°	90
Volume/Å^3	4016.0(3)
Z	4
ρ_{calc}g/cm^3	1.728
μ/mm^{-1}	1.254
F(000)	2056.0
Crystal size/mm^3	0.07 × 0.11 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.352 to 29.58
Index ranges	-37 ≤ h ≤ 36, -11 ≤ k ≤ 11, -23 ≤ l ≤ 24
Reflections collected	70236
Independent reflections	5622 [R_{int} = 0.0838, R_{sigma} = 0.0428]
Data/restraints/parameters	5622/0/217
Goodness-of-fit on F^2	1.016
Final R indexes [I>=2σ (I)]	R_1 = 0.0395, wR_2 = 0.0880
Final R indexes [all data]	R_1 = 0.0534, wR_2 = 0.0975
Largest diff. peak/hole / e Å^{-3}	0.581/-0.36

*4. **F**ilm thickness and absorption*

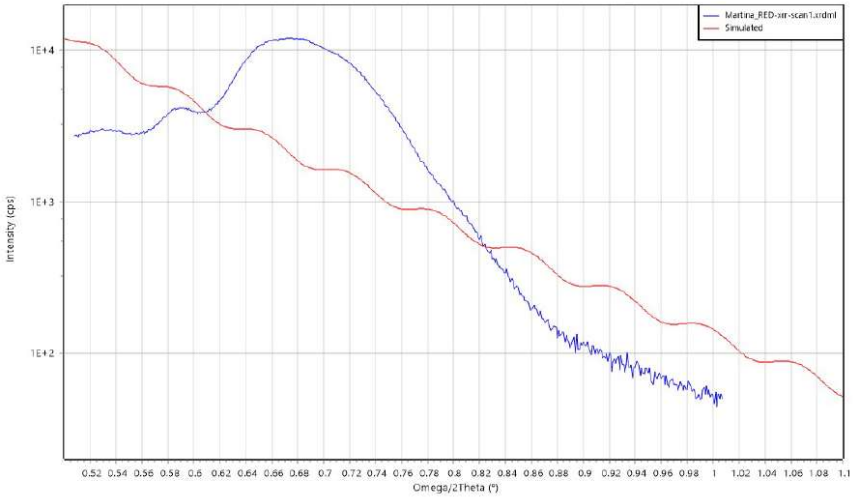


Figure S17: X-ray reflectivity (XRR) measurement analyzed using Malvern Panalytical's advanced materials analysis and simulation software, illustrating precise determination of thin film thickness of **TTH** of 65 (5) nm. he simulation deviates from the experimental trace due to significant surface roughness, which reduces the quality of the interference fringes and limits the accuracy of optical modeling. To validate the thickness independently, we performed profilometer measurements using a KLA Tencor profilometer on the same sample, confirming a thickness of approximately 70 nm. **TFH** deposition was performed with the same conditons used for **TTH**. For the TFH film for UV-VIS measurements, profilometry confirmed a thickness of approximately 250 nm.

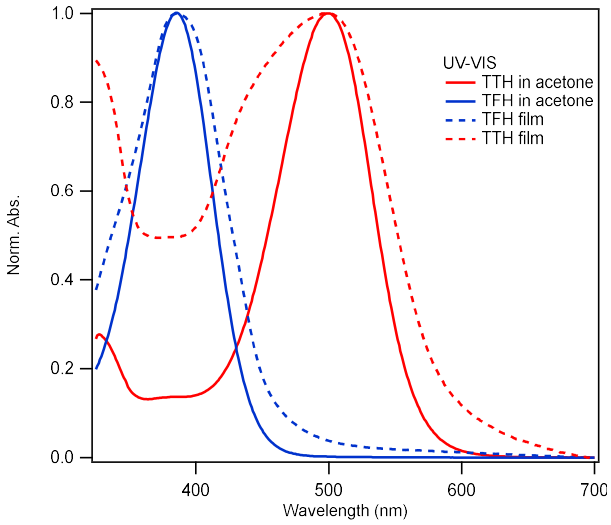


Figure S18: UV-Vis absorption spectra of TFH and TTH thin films measured in transmission mode. The spectra show broadened absorption features compared to solution (also reported), consistent with intermolecular coupling in the solid state.

*5. Evolution of **TTH** film under X-ray illumination*

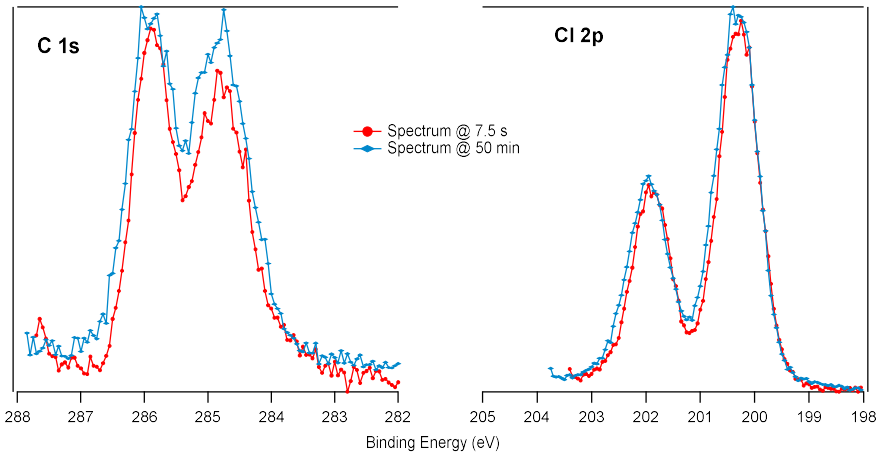


Figure S19: XPS C 1s and Cl 2p spectra of **TTH** in solid state after 7.5 s (fresh) and 50 min X-ray exposure. The strong asymmetry in the Cl 2p indicates a new clorine species on the surface.

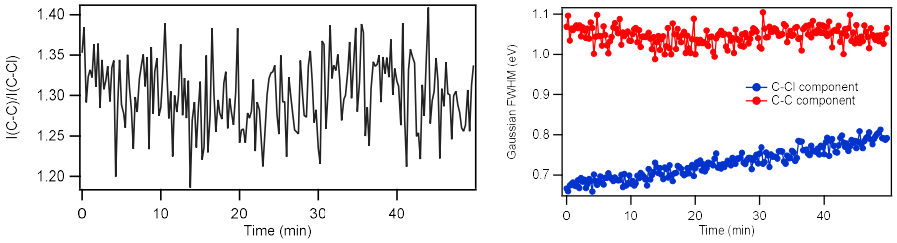


Figure S20: The peak ratio in the C1s core level in **TTH** remains constant under X-ray illumination, i.e. no material is lost. The width of the C-Cl component is strongly modified, supporting the X-ray evolution of the C-Cl bond.

6. Dynamics of the excited states from Glotaran fit

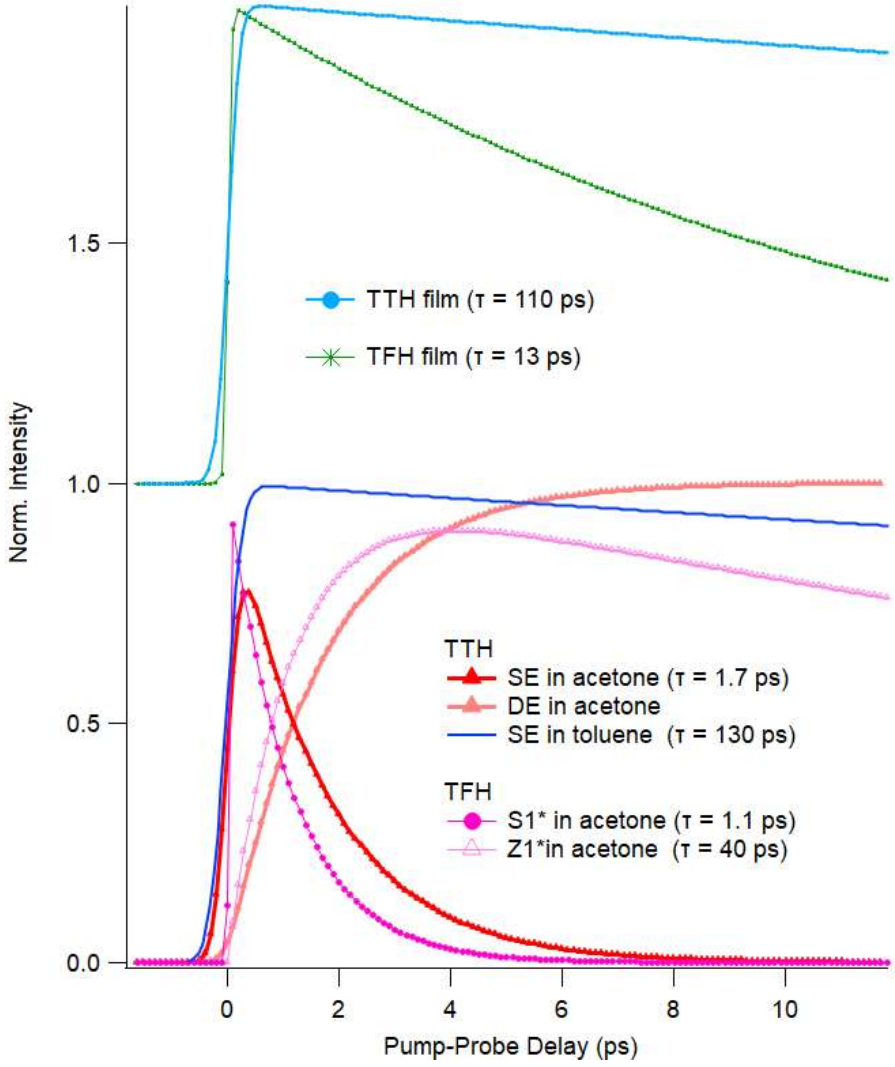


Figure S21: Dynamics of the states extracted from the global fit analysis with sequetial model in Glotaran software.

7. fs-TAS of TFH in PVA matrix

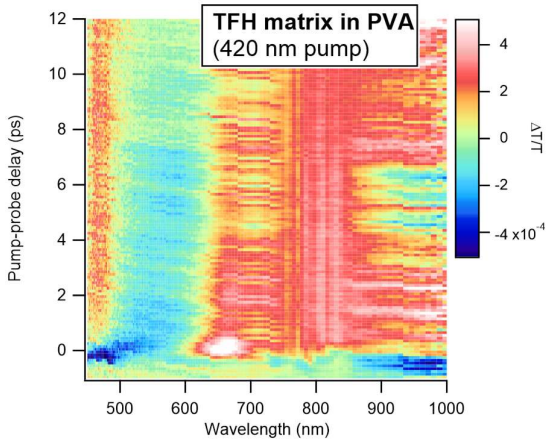


Figure S22: Femtosecond transient absorption (fs-TAS) spectra of TFH embedded in a poly(vinyl alcohol) (PVA) matrix, measured in transmission mode. Despite the reduced molecular density and minimized intermolecular interactions in the matrix, the spectral and kinetic features closely match those observed in the pure thin film

8. References

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[2] C.-H. Liu, Z. He, C. Ruchlin, Y. Che, K. Somers, D. F. Perepichka, *J. Am. Chem. Soc.* **2023**, *145*, 15702–15707.
[3] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.* **2015**, *71*, 3−8.