Synthesis and Characterization of Tetraphenylethene AIEgen-Based Push-Pull Chromophores for Photothermal Applications: Do the Cycloaddition – Retroelectrocyclization Click Reaction Could Make any Molecule Photothermally Active?

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I. Materials

1. Solvents

Dry tetrahydrofuran (THF), dichloromethane (DCM) and diethyl ether (Et_2O) were obtained by using a solvent purification system Puresolve MD5 from Inert. Anhydrous N,N-dimethylformamide (DMF) (Acros, 99.8%), dichlorobenzene (TCI, 99%), anhydrous acetonitrile (Alfa Aesar, 99.8%) and absolute ethanol (VWR) were used as received.

2. Reagents

Triphenylphosphine (Fluorochem, 99%), *n*-tetrabutylammonium fluoride (Sigma-Aldrich, 1M in THF), 1,1,2,2-tetraphenylethene (**TPE**) (Fluorochem, 95%), bromine (Sigma-Aldrich, 99%), copper iodide (Alfa Aesar, 99.998%), 4-ethynyl-N,N-dimethylaniline (Aldrich, 97%), diisopropylamine (Aldrich, 99.5%), 4-iodoaniline (Alfa Aesar, 98%), 1-bromododecane (ABCR, 99%), trimethylsilylacetylene (Fluorochem, 99%), 4,4'-dibromobenzophenone (Fluorochem, 98%), titanium (IV) chloride (Merck, 97%), zinc dust (Aldrich, 98%), pyridine (Aldrich, 99.8%), tetracyanoethylene (**TCNE**) (Aldrich, 96%), 7,7,8,8-Tetracyanoquinodimethane (**TCNQ**) (Alfa Aesar, 98%), 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (**F_4-TCNQ**) (Fluorochem, 95%) were used as received. Tetrakis(triphenylphosphine)-palladium (0) [$Pd(PPh_3)_4$], was prepared according to literature procedures.[1] **Ph-I-N-C_{12}**, **Ph-$SiMe_3$-N-C_{12}** and **Ph-alkyne** were synthesized according to procedures described in the litterature. [1]

3. Chromatography

Reactions were monitored by thin-layer chromatography (TLC) using Merck© TLC Silica gel 60 F254 plates. Flash chromatography was carried out using a Biotage® Isolera™ System (UV-Vis 200 nm – 800 nm detector) over silica cartridges (SNAP Ultra or Sfär HC D).

II. Methods

Unless otherwise stated, measurements were done on the equipment available at the Plateforme d'Analyse et Caractérisation (PAC) of the Balard Institute, CNRS, University of Montpellier, France.

1. Infrared spectroscopy

IR spectra were carried out on a Perkin Elmer Spectrum 2 FT-IR instrument using the attenuated total reflectance (ATR) measurement mode (diamond crystal). The wavenumber range analyzed was 500-4000 cm^{-1} and the optical resolution of the instrument was 4 cm^{-1}.

2. Solution NMR spectroscopy

^1H NMR spectra were recorded at 273 K or 298 K on a Bruker Avance III 400 MHz NMR spectrometer using a BBFO probe or a Bruker Avance III 500 MHz NMR spectrometer using a Prodigy

BBO Z-gradient CryoProbe or a Bruker Avance III 600 MHz NMR spectrometer using a Prodigy TCI Z-gradient CryoProbe and calibrated to TMS on the basis of the relative chemical shift of the residual non-deuterated solvent as an internal standard (CD_2Cl_2: δ = 5.32 ppm, $CDCl_3$: δ = 7.26 ppm, DMSO-d_6: δ = 2.50 ppm, THF-d_8: δ = 3.58 ppm).

$^{13}C\{^1H\}$ NMR spectra were recorded at 298 K on a Bruker Avance III 500 MHz NMR spectrometer using a Prodigy BBO Z-gradient CryoProbe or a Bruker Avance III 600 MHz NMR spectrometer using a Prodigy TCI Z-gradient CryoProbe and calibrated to TMS on the basis of the relative chemical shift of the residual non-deuterated solvent as an internal standard (CD_2Cl_2: δ = 53.84 ppm, $CDCl_3$: δ = 77.16 ppm, DMSO-d_6: δ = 39.52 ppm, THF-d_8: δ = 67.21 ppm).

^{19}F NMR spectra were recorded at 298 K on a Bruker Avance III 400 MHz NMR spectrometer using a BBFO probe.

3. Mass spectrometry

The MS (MALDI) spectra were recorded on a Rapiflex (Bruker) with Matrix-Assisted Laser Desorption Ionization (MALDI) source and a TOF analyzer. The mass spectra were recorded in positive mode between 500 and 15000 Da in reflector mode for TPE-adduct. Samples were incorporated in a DCTB matrix.

Mass accuracy measurement were done at UMONS, Organic Synthesis and Mass Spectrometry Laboratory (S2MOs, Mons, Belgium), by using a Waters QToF Premier mass spectrometer equipped with Matrix-Assisted Laser Desorption/Ionization source. A Nd-YAG laser of 355 nm with a maximum pulse energy of 65 µJ delivered to the sample at 50 Hz repeating rate is used. Time-of-flight mass analyses were performed in the reflection mode at a resolution of about 10k (m/z 569). Trans-2-(3-(4-tert-butyl-phenyl)-2-methyl-2-propenylidene)malononitrile (DCTB) was used as the matrix and was prepared as a 40 mg/ml solution in chloroform. The matrix solution (1 µL) was applied to a stainless-steel target and air-dried. Samples were dissolved in chloroform to obtain 1 mg/mL solutions. 1 µL aliquots of these solutions were applied onto the target area (already bearing the matrix crystals) and air-dried. Exact mass was determined by using poly(ethylene glycol) as internal reference.

4. UV-Visible absorption spectroscopy

The UV-Visible absorption spectra were recorded on a JASCO V-650 spectrophotometer in 10 mm quartz cells (Hellma). The molar extinction coefficients (ε) were determined by the plot of absorbance *vs*. concentration by preparing solutions at different concentrations in THF. The concentration range was chosen to remain in the linear range of the Beer–Lambert relationship (A *ca.* 0.2–0.8).

$$A = \varepsilon l C$$

A: Absorbance

ε: Molar extinction coefficient

l: path length

C: concentration

The onset wavelength of the absorption spectra was determined by the intersection of the straight line fitted to the right-hand side of the maximum with the baseline of the absorption.

Thin film were realized by deposition of *ca.* 10^{-5} mol.l^{-1} THF solutions on a quartz plate followed by the evaporation of the solvent. The operation was repeated until an absorbance of *ca.* 0.25 was measured at the maximum of the Intramolecular Charge Transfer (ICT) band.

5. Photoluminescence spectroscopy

The emission spectra in powder and in solution for **TPE-TCNE**, **TPE-TCNQ** and **TPE-F_4-TCNQ** adducts were recorded in the Laboratoire de Chimie de l'ENS Lyon recorded on a fluorescence spectrofluorimeter (Fluorolog-3, Horiba-Jobin Yvon) equipped with R2658 photomultiplier tube (Hamamatsu, water cooling) or Synapse InGaAs/Symphony II (Horiba, nitrogen cooling) as detectors. The steady-state luminescence was excited by non-polarized light from a 450 W xenon CW lamp.

6. Electrochemical studies

Measurements were performed in the Institut des Sciences Chimiques de Rennes –France (ISCR). For **TPE-adducts**, CVs were carried out on a 10^{-3} mol.L^{-1} solution of sample in CH_2Cl_2/[NBu_4][PF_6] 0.1 mol.l^{-1}. CVs were recorded on a Biologic SP-50 instrument at 0.1 V s^{-1} on a platinum\u0002 disk electrode. Potentials were measured versus a KCl saturated calomel electrode (SCE).

7. Electron Spin Resonance (ESR)

ESR spectra were recorded on a Bruker Elexsys E500 CW continuous wave, X band (9.8 GHz) spectrometer equipped with ER4122 SHQ cavity at room temperature. Sample was diluted in THF and introduced in a quartz tube. The window was 10mT (100G) centered around g = 2 with 2 G of amplitude modulation, 100 kHz of frequency modulation, 10 dB of micro-wave power and 70 dB of gain.

8. Thermal analysis

Thermogravimetric analyses (TGA) were carried out on a STA 449 F1 Jupiter Netzsch analyzer under dry nitrogen at a heating rate of 10 °C.min^{-1}.

9. Photothermal measurements and simulations.

Photothermal measurements were realized on samples of **TPE-TCNE** and **TPE-F_4-TCNQ**. Two different deposits were realized with both samples. First bulk materials (powders) were placed on a quartz surface. Secondly, thin films of both samples were deposited on quartz slide from diluted THF solutions (*ca.* 1.10^{-4} mol.L^{-1}). Then, we used a 808 nm laser (Kamax society, Limoges, France) with an adjustable power from 0 to 2.58 W/cm^2. The laser spot surface was 0.32 cm^2. The temperature of the surface was measured using an OPTRIS PI 450 thermal camera (Media Mesures, Bouc Bel Air, France). The samples were deposited on a polystyrene surface in contact with air to limit heat transfer with the support.

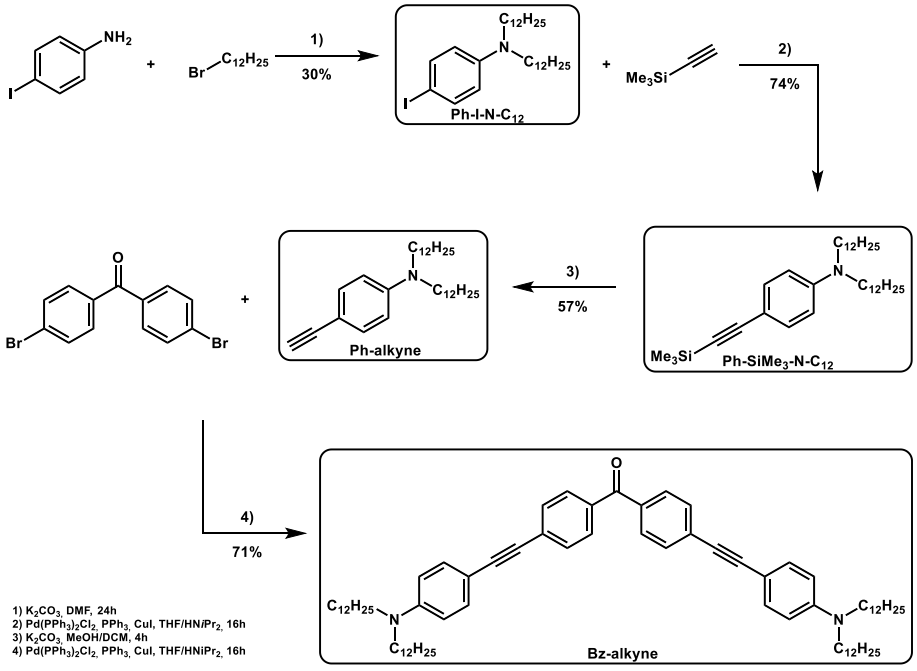
Photothermal simulations were realized using the COMSOL software.[2] The heat equation was solved simultaneously with the simplified Navier–Stokes equation to take into account the heat propagation and the convection terms present for the air. The model consisted of a quartz substrate, with a surface heat source to simulate the heat produced by the laser absorption of the **TPE-TCNQ** or **TPE-F_4-TCNQ** sample layer, deposited on a polystyrene support.

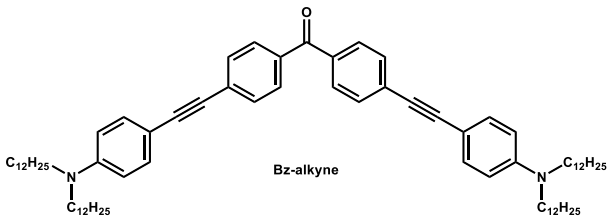
10. Calculations details

The ground-state geometry of the molecules has been first optimized without any symmetry constraint in the gas phase and the electronic properties of the optimized structures have been next determined in gas phase, in THF and in DCM used in the CV measurements. The vibrational frequencies associated to the optimized structures were also calculated to verify that they correspond to local minima on the energy surface. The absorption spectra and the vertical electronic transitions have been next computed at the TD-DFT level and compared to the corresponding experimental data. All calculations have been carried out using the long-range hybrid Cam-B3LYP functional [3] and a 6-311G (d,p) basis set within Revision D.01 of the Gaussian 09 program package.[4] The solvent effects in THF, used for the spectroscopic measurements, were simulated by means of the polarizable continuum model (PCM).[5]

III. Procedures

1. **Bz-alkyne** synthesis

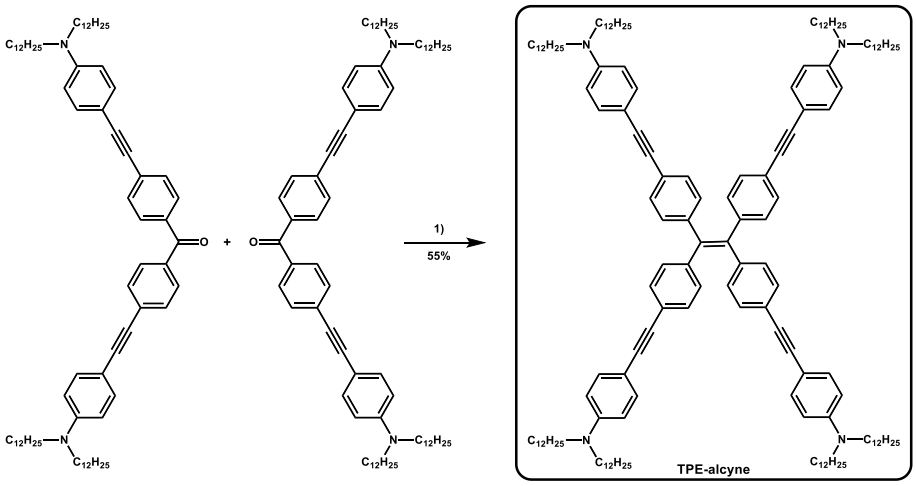




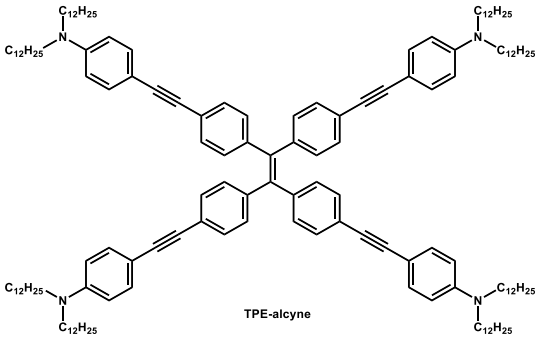
Synthesis of Bz-alkyne. 4,4'-dibromobenzophenone (0.90 g, 2.66 mmol) was introduced into a 100 mL two neck round-bottom flask under argon atmosphere with 30 mL of anhydrous THF. Copper (I) iodide (20 mg, 0.11 mmol, 4 mol%), bis(triphenylphosphine)palladium (II) chloride (77 mg, 0.11 mmol, 4 mol%) and triphenylphosphine (13 mg, 0.05 mmol, 2 mol%) were then added (solution 1). In parallel, **Ph-alkyne** (2.90 g, 6.38 mmol, 2.4 eq) was introduced into a Schlenk tube under argon atmosphere with 10 mL of anhydrous THF and 20 mL of diisopropylamine (solution 2). Once prepared, solution 2 was transferred into solution 1 through cannula. The mixture was then heated to 65 °C overnight. Once judged complete, the solvent was removed under reduced pressure. The crude mixture was first filtrated on a silica gel column chromatography with cyclohexane before being purified by column chromatography on silica gel using gradient elution (100% cyclohexane to 70% cyclohexane / 30% dichloromethane). The fraction corresponding to the product was concentrated and then, diluted with a mixture of dichloromethane (5 mL) and acetone (50 mL). The solution was cooled. The resulting precipitate was filtered leading to **Bz-alkyne** as a yellow-orange powder.

Yield 73% (2.10 g, 1.93 mmol). FTIR-ATR (cm^{-1}): 2202 (νC≡C), 1651 (νC=O). ^{1}H NMR (500 MHz, CD_2Cl_2, δ): 7.75 (d, 4H, $^{3}J_{H-H}$ = 8.5 Hz), 7.58 (d, 4H, $^{3}J_{H-H}$ = 8.5 Hz), 7.37 (d, 4H, $^{3}J_{H-H}$ = 9.0 Hz), 6.60 (d, 4H, $^{3}J_{H-H}$ = 9.0 Hz), 3.29 (t, 8H, $^{3}J_{H-H}$ = 7.7 Hz), 1.63-1.55 (m, 8H), 1.37-1.21 (m, 72H), 0.88 (t, 12H, $^{3}J_{H-H}$ = 7.0 Hz) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, δ): 195.3, 148.9, 136.3, 133.5, 131.2, 130.5, 129.2, 111.6, 108.0, 95.2, 87.2, 51.4, 32.5, 30.2, 30.2, 30.1, 30.0, 29.9, 27.6, 27.6, 23.2, 14.4 ppm. HRMS (Maldi, DCTB): m/z $[M]^{\bullet+}$ calc for $[C_{77}H_{116}N_2O]^{\bullet+}$: 1084.9088; found: 1084.9081 (δ = 0.6 ppm).

2. **TPE-alkyne** synthesis by McMurry coupling



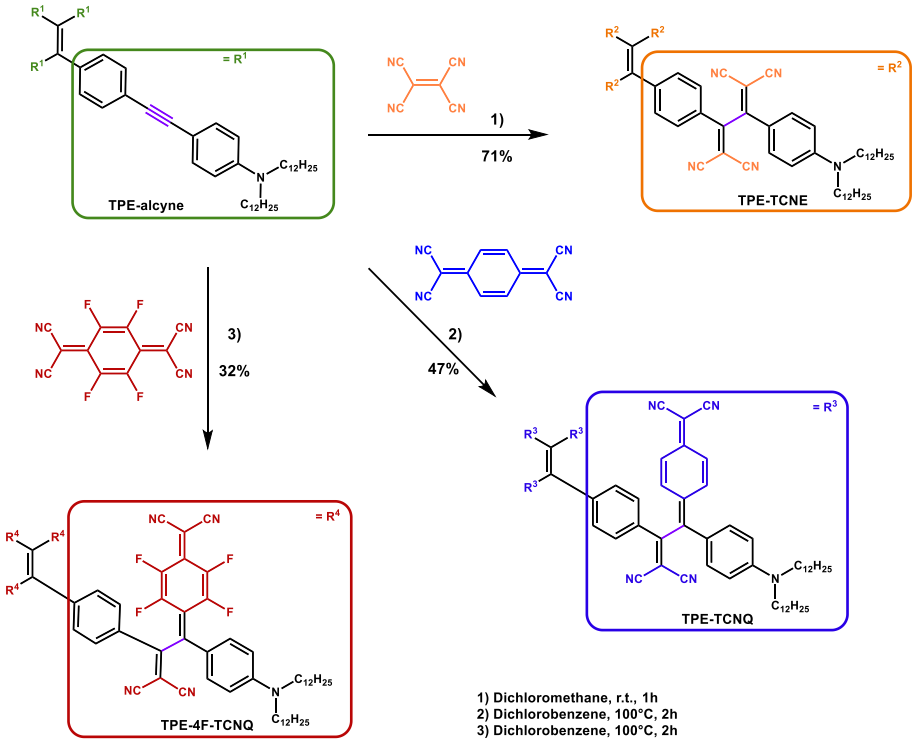
1)$TiCl_4$, pyridine, THF, 16h

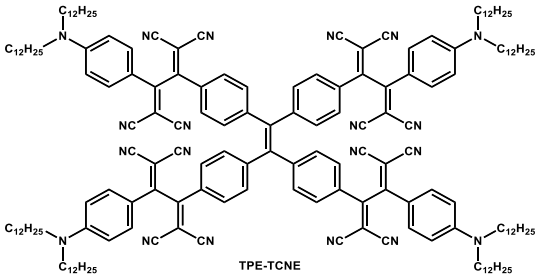


Synthesis of TPE-alkyne. Bz-alkyne (600 mg, 0.55 mmol) and zinc dust (111 mg, 1.70 mmol, 3 eq) were dissolved in anhydrous THF (30 mL) into a 100 mL three neck round bottom flask under argon atmosphere. Titanium (IV) chloride (120 µL, 1.11 mmol, 2 eq) was added dropwise at -78 °C. After return at room temperature, pyridine (20 µL, 0.44 mmol, 0.4 eq / $TiCl_4$) was added and the solution was stirred during 30 minutes at room temperature. The mixture was then heated at 65 °C overnight. The progress of the reaction was followed by TLC using *n*-hexane 96% / 4% dichloromethane as eluent. When judged complete, the mixture was cooled at room temperature and then, quenched with of a 10% aqueous solution of K_2CO_3 (60 mL). The aqueous layer was extracted with dichloromethane (5 x 50 mL). The organic layer was then dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel using isocratic elution (90% *n*-hexane / 9% dichloromethane / 1% triethylamine). The product was isolated as an orange oil.

Yield: 312 mg (0.15 mmol, 53%). FTIR-ATR (cm^{-1}): 2208 (νC≡C). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.33 (d, 8H, $^3J_{H\text{-}H}$ = 8.4 Hz), 7.25 (d, 8H, $^3J_{H\text{-}H}$ = 8.4 Hz), 6.98 (d, 8H, $^3J_{H\text{-}H}$ = 7.8 Hz), 6.55 (d, 8H, $^3J_{H\text{-}H}$ = 7.8 Hz), 3.25 (t, 16H, $^3J_{H\text{-}H}$ = 7.4 Hz), 1.62-1.54 (m, 16H), 1.36-1.22 (m, 160H), 1.36-1.22 (t, 24H, $^3J_{H\text{-}H}$ = 7.0 Hz) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, δ): 148.0, 142.6, 140.8, 133.0, 131.6, 130.9, 122.7, 111.3, 108.9, 91.6, 87.3, 51.1, 32,1, 29.8, 29.8, 29.7, 29.5, 27.4, 27.3, 22.9, 14.3 ppm. HRMS (Maldi, DCTB) m/z: $[M]^{\bullet+}$ calc for $[C_{154}H_{232}N_4]^{\bullet+}$: 2137.8277; found: 2137.8262 (δ = -0.7 ppm). UV-Vis (THF): λ (ε, $L.mol^{-1}.cm^{-1}$) = 359 (143 400), 294 (82 400) nm.

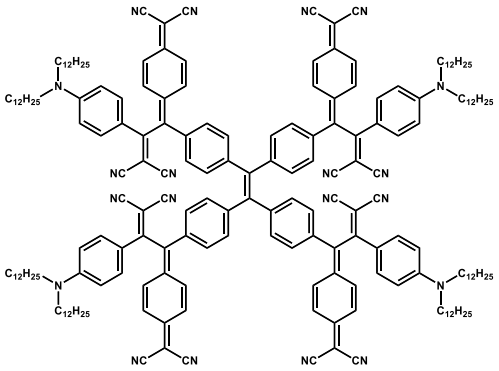
3. Synthesis of CARE adducts.





Synthesis of TPE-TCNE. TPE-alkyne (74 mg, 35.0 µmol) was introduced into a Schlenk tube under argon atmosphere. 10 mL of anhydrous dichloromethane as well as tetracyanoethylene (TCNE, 27 mg, 0.21 mmol, 6 eq) were added. The solution was stirred at room temperature during 1h. The progress of the reaction was followed by TLC using *n*-hexane/CH_2Cl_2 (90/10 v/v) as eluent. When judged complete, the solvent was removed under vacuum. The product was then purified by column chromatography on silica gel using a gradient elution (90% *n*-hexane / 10% dichloromethane to 80% *n*-hexane / 20% dichloromethane). **TPE-TCNE** was isolated as a dark red film-forming solid.

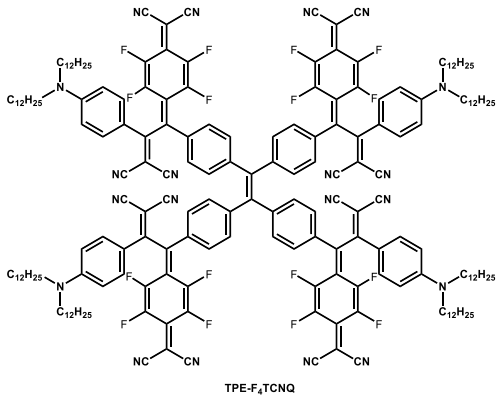
Yield: 65 mg (24 µmol, 70%). FTIR-ATR (cm^{-1}): 2213 (νC≡N). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.76 (d, 8H, $^3J_{H\text{-}H}$ = 9.0 Hz), 7.54 (d, 8H, $^3J_{H\text{-}H}$ = 8.5 Hz), 7.14 (d, 8H, $^3J_{H\text{-}H}$ = 8.5 Hz), 6.70 (d, 8H, $^3J_{H\text{-}H}$ = 9.0 Hz), 3.40 (t, 16H, $^3J_{H\text{-}H}$ =7.6 Hz), 1.64 (q, 16H, $^3J_{H\text{-}H}$ = 6.2 Hz), 1.38 – 1.22 (m, 144H), 0.88 (t, 24H, $^3J_{H\text{-}H}$ =6.8 Hz). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, δ): 168.8, 162.0, 153.5, 146.6, 142.8, 133.1, 132.3, 132.0, 129.9, 117.6, 114.9, 114.1, 112.6, 112.2, 111.3, 87.7, 51.7, 32.1, 29.8, 29.7, 29.6, 29.5, 27.5, 27.2, 22.8, 14.3 ppm. HRMS (Maldi, DCTB) m/z: $[M]^{\bullet+}$ calc for $[C_{178}H_{232}N_{20}]^{\bullet+}$: 2649,8769; found: 2649.8757 (δ = -0.5 ppm). UV-Vis (THF): λ (ε, $L.mol^{-1}.cm^{-1}$) = 469 (113 400), 307 (45 600) nm. Mp: 124-127°C



TPE-TCNQ

Synthesis of TPE-TCNQ. TPE-alkyne (100 mg, 47.0 µmol, 1 eq) was introduced into a Schlenk tube under argon atmosphere with dichlorobenzene (10 mL). 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ, 57.6 mg, 0.28 mmol, 6 eq) was added. The solution was stirred at 100°C during 1h. The progress of the reaction was followed by TLC using *n*-hexane/CH_2Cl_2 (90/10 v/v) as eluent. The solvent was removed under vacuum. The residue was purified by column chromatography on silica gel with a gradient elution (90% *n*-hexane / 10% dichloromethane to 80% *n*-hexane / 20% dichloromethane). TPE-TCNQ was isolated as a dark film-forming solid.

Yield: 66 mg (22.0 µmol, 47%). FTIR-ATR (cm^{-1}): 2201 (νC≡N). ^{1}H NMR (600 MHz, 273K, CD_2Cl_2, δ): 7.46 (d, 4H, $^3J_{H\text{-}H}$ = 8.0 Hz), 7.43 (d, 8H, $^3J_{H\text{-}H}$ = 8.6 Hz), 7.28 (d, 8H, $^3J_{H\text{-}H}$ = 9.1 Hz), 7.20 (d, 4H, $^3J_{H\text{-}H}$ = 8.1 Hz), 7.04 (d, 12H, $^3J_{H\text{-}H}$ = 8.6 Hz), 6.93 – 6.81 (m, 4H), 6.71 (d, 8H, $^3J_{H\text{-}H}$ = 9.1 Hz), 3.38 (t, 16H, $^3J_{H\text{-}H}$ = 7.7 Hz,), 1.65 – 1.60 (m, 16H), 1.38 – 1.18 (m, 144H), 0.88 (t, 24H, $^3J_{H\text{-}H}$ = 6.9 Hz) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, 273K, CD_2Cl_2, δ): 172.5, 154.1, 152.2, 152.1, 146.3, 142.7, 136.4, 135.7, 135.1, 132.3, 131.0, 129.8, 124.7, 124.0, 115.9, 115.8, 113.6, 112.9, 112.5, 88.8, 51.7, 32.3, 30.0, 30.0, 30.0, 29.8, 27.6, 27.2, 23.1, 14.4 ppm. HRMS (Maldi, DCTB) m/z: $[M]^{\bullet+}$ calc for $[C_{202}H_{248}N_{20}]^{\bullet+}$: 2954.0021; found: 2953.9946 (δ = -2.5 ppm). UV-Vis (THF) λ (ε, $L.mol^{-1}.cm^{-1}$) = 688 (155 000), 468 (78 500), 337 (113 900) nm. Mp: 115-119°C



TPE-F_4TCNQ

Synthesis of TPE-F_4-TCNQ. TPE-alkyne (100 mg, 47.0 µmol) was introduced into a Schlenk tube under argon atmosphere with dichlorobenzene (10 mL). 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4-TCNQ, 77.9 mg, 0.28 mmol, 6 eq) was added. The solution was stirred at 100°C during 1h. The progress of the reaction was followed by TLC using 20% n-hexane / 80% dichloromethane as eluent. The solvent was removed under vacuum. The product was purified by column chromatography on silica gel with a gradient elution (20% n-hexane / 80% dichloromethane to 100% dichloromethane). **TPE-F_4TCNQ** was isolated as a dark film-forming solid.

Yield: 55 mg (22.0 µmol, 36%). FTIR-ATR (cm^{-1}): 2196 (νC≡N). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.51 – 7.29 (m, 16H), 7.15 – 6.99 (m, 8H), 6.90 (d, 8H, $^3J_{H\text{-}H}$ = 8.1 Hz), 3.74 – 3.50 (m, 16H), 1.83 – 1.70 (m, 16H), 1,35 – 1.19 (m, 144H), 0.88 (t, 24H, $^3J_{H\text{-}H}$ = 6.8 Hz) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 172.0, 156.5, 146.6, 146.1, 145.6, 143.5, 142.8, 140.5, 138.8, 138.5, 134.4, 133.7, 132.0, 130.1, 117.5, 116.3, 113.3, 113.1, 112.1, 107.3, 89.4, 53.5, 53,4, 32.0, 29.8, 29.7, 29.7, 29.6, 29.4, 28.5, 27.1, 22.8, 14.3 ppm. ^{19}F NMR (376 MHz, $CDCl_3$, δ): -134.1, -134.4, -143.1, 143.4 ppm. HRMS (Maldi, DCTB) m/z: $[M]^{\bullet+}$ calc for $[C_{202}H_{232}F_{16}N_{20}]^{\bullet+}$: 3241.8513; found: 3241.8586 (δ = 2.3 ppm). UV-Vis (THF) λ (ε, $L.mol^{-1}.cm^{-1}$) = 849 (163 400), 497 (73 600), 348 (97 500) nm. Mp: 160-164°C

IV. IR, NMR and MS spectroscopies

1. Bz-alkyne

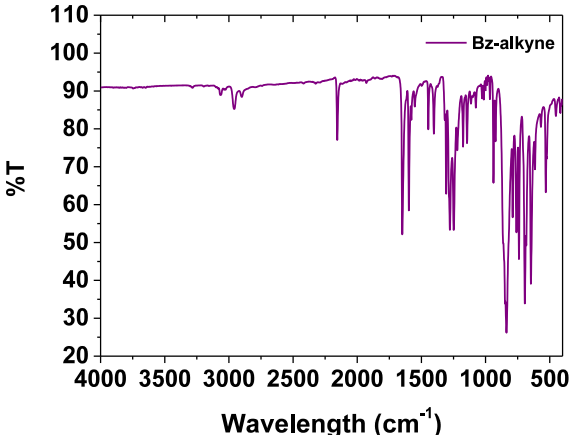


*Figure S 1. FTIR-ATR spectrum of **Bz-alkyne.***

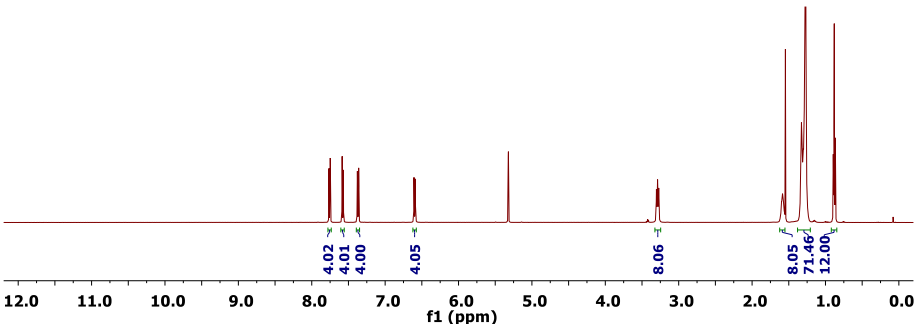


*Figure S 2: ^{1}H NMR spectrum (500 MHz, CD_2Cl_2, 298K) of **Bz-alkyne**.*

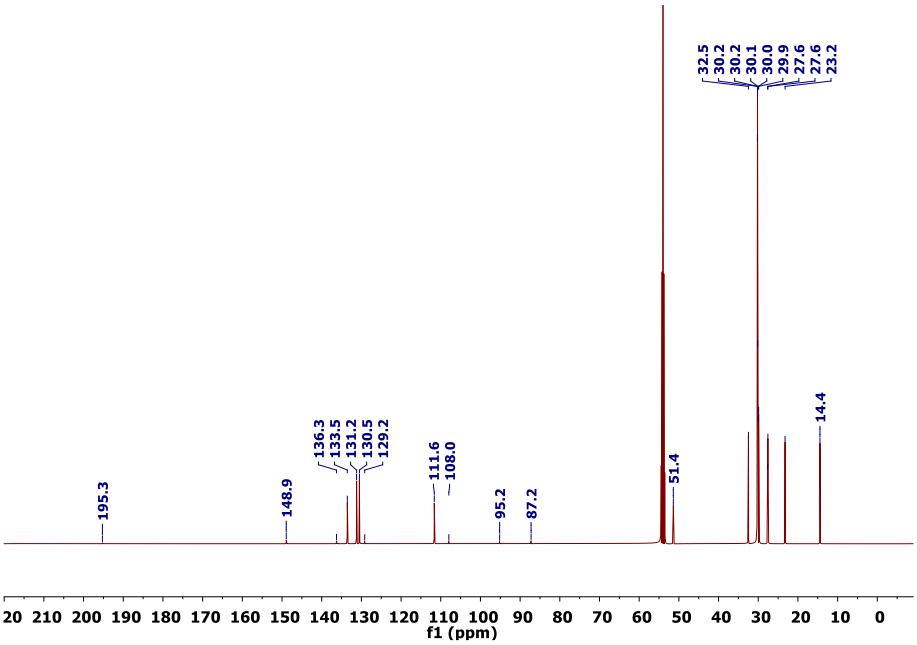
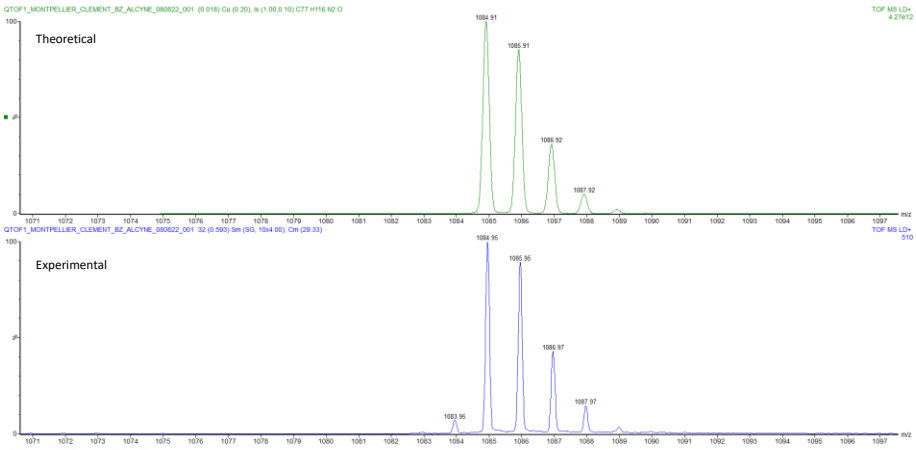


Figure S 3. $^{13}C\{^1H\}$ *NMR spectrum (126 MHz, CD_2Cl_2, 298K) of* ***Bz-alkyne****.*



Elemental Composition Report

Single Mass Analysis
Tolerance = 25.0 PPM / DBE: min = -1.5, max = 200.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
249 formula(e) evaluated with 9 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 20-250 H: 0-250 N: 2-2 O: 0-20

Minimum:				-1.5				
Maximum:			5.0	25.0	200.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
1084.9081	1084.9088	-0.7	-0.6	21.0	87.6	0.088	91.53	C77 H116 N2 O
	1084.9053	2.8	2.6	-1.0	93.8	6.316	0.18	C59 H124 N2 O14
	1084.9146	-6.5	-6.0	12.0	91.3	3.754	2.34	C70 H120 N2 O6
	1084.8994	8.7	8.0	8.0	92.6	5.119	0.60	C66 H120 N2 O9
	1084.9205	-12.4	-11.4	3.0	93.8	6.324	0.18	C63 H124 N2 O11
	1084.9224	-14.3	-13.2	65.5	93.9	6.365	0.17	C64 H N2 O18
	1084.8935	14.6	13.5	17.0	90.9	3.419	3.27	C73 H116 N2 O4
	1084.9299	-21.8	-20.1	16.0	91.6	4.084	1.68	C74 H120 N2 O3
	1084.8841	24.0	22.1	4.0	95.5	8.040	0.03	C62 H120 N2 O12

*Figure S 4. High resolution MALDI-TOF spectrum of **Bz-alkyne** (matrix: DCTB/NaI).*

2. TPE-alkyne

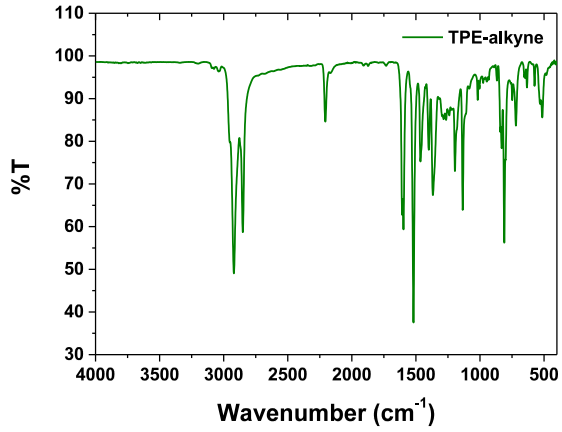


*Figure S 5. FTIR-ATR spectrum of **TPE-alkyne**.*

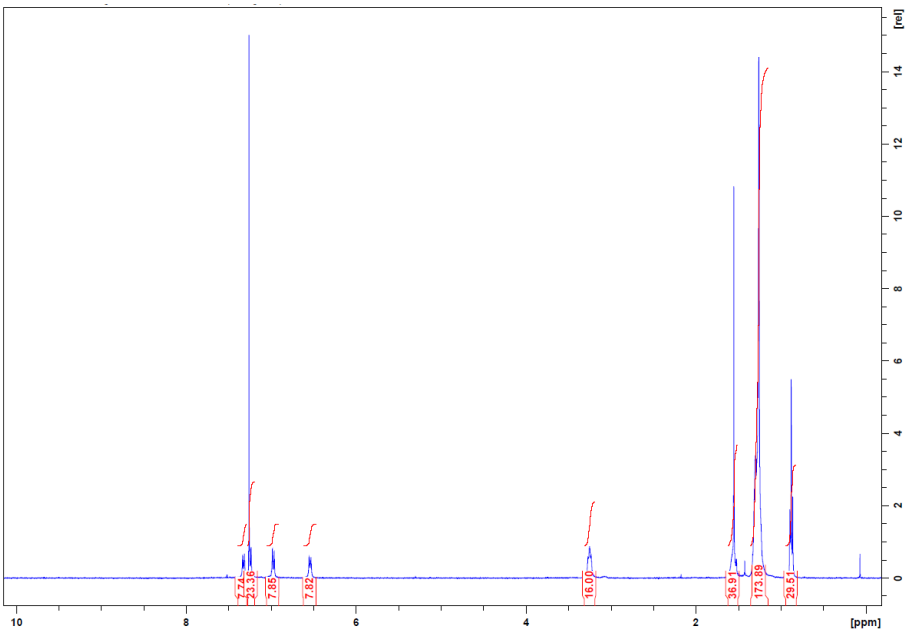


*Figure S 6. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **TPE-alkyne**.*

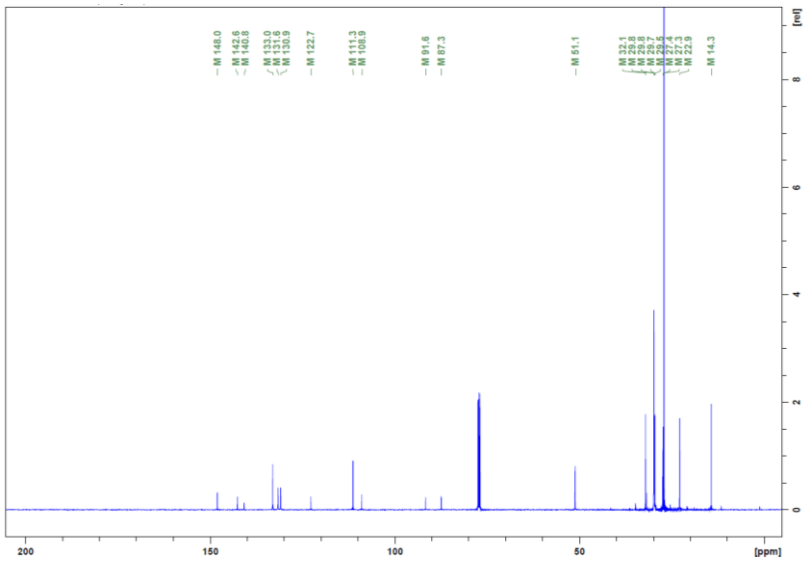
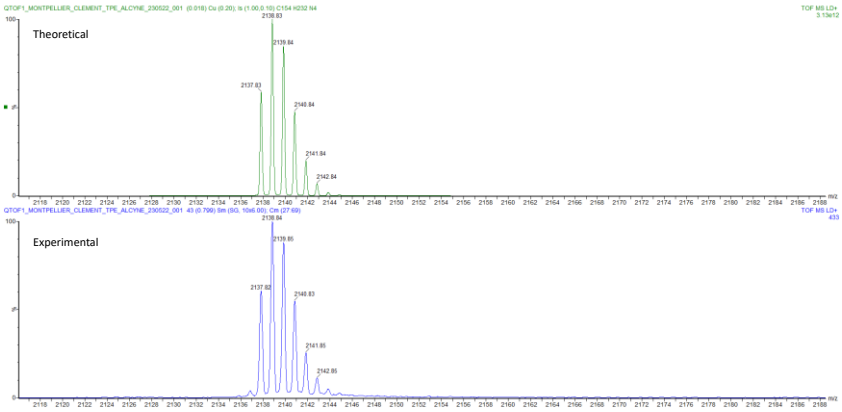


*Figure S 7. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$, 298K) of **TPE-alkyne**.*



Elemental Composition Report

Single Mass Analysis
Tolerance = 25.0 PPM / DBE: min = -1.5, max = 150.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
21 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 20-250 H: 0-250 N: 4-4

Minimum:				-1.5				
Maximum:			5.0	25.0	150.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
2137.8262	2137.8277	-1.5	-0.7	41.0	27.8	0.026	97.39	C154 H232 N4
	2137.8026	23.6	11.0	117.5	31.4	3.647	2.61	C165 H101 N4

*Figure S 8. High Resolution MALDI-TOF mass spectrum of **TPE-alkyne** (matrix: DCTB/NaI).*

3. TPE-TCNE

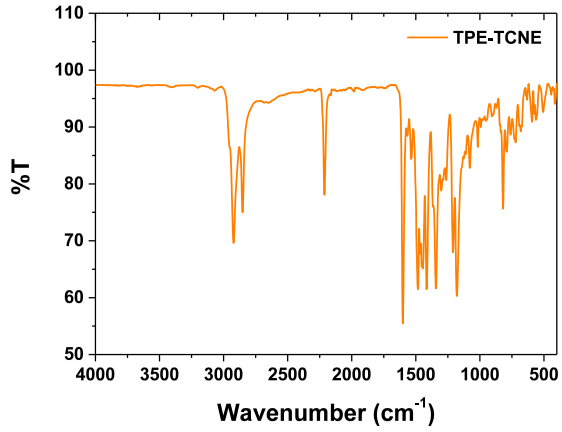


*Figure S 9. FTIR-ATR spectrum of **TPE-TCNE**.*

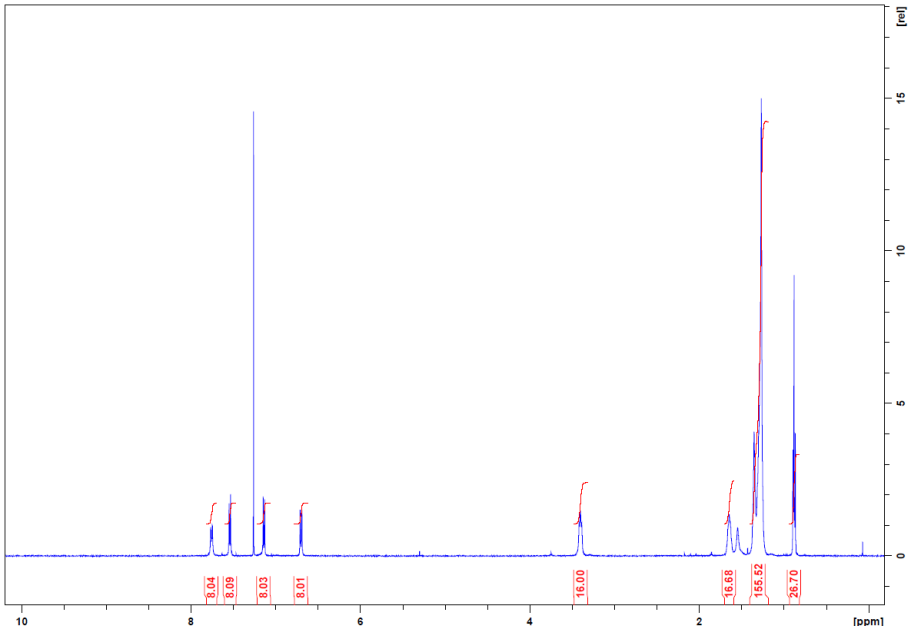


*Figure S 10. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298K) of **TPE-TCNE**.*

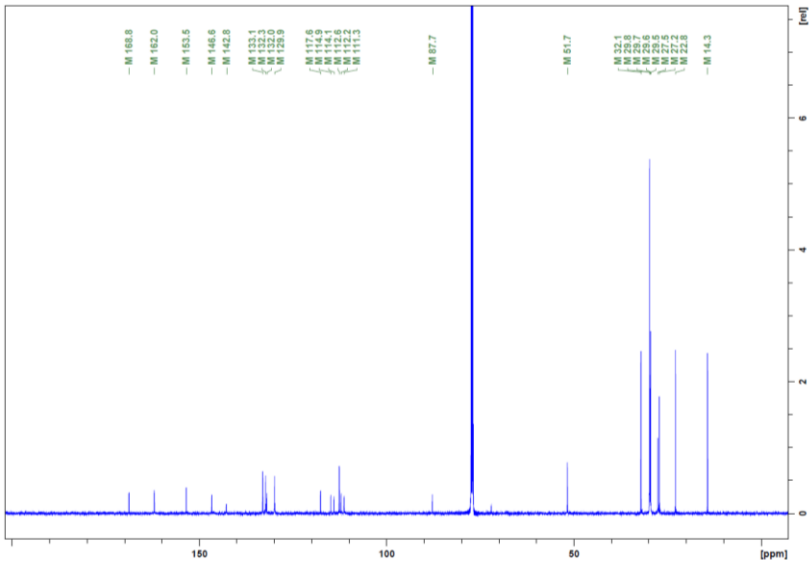
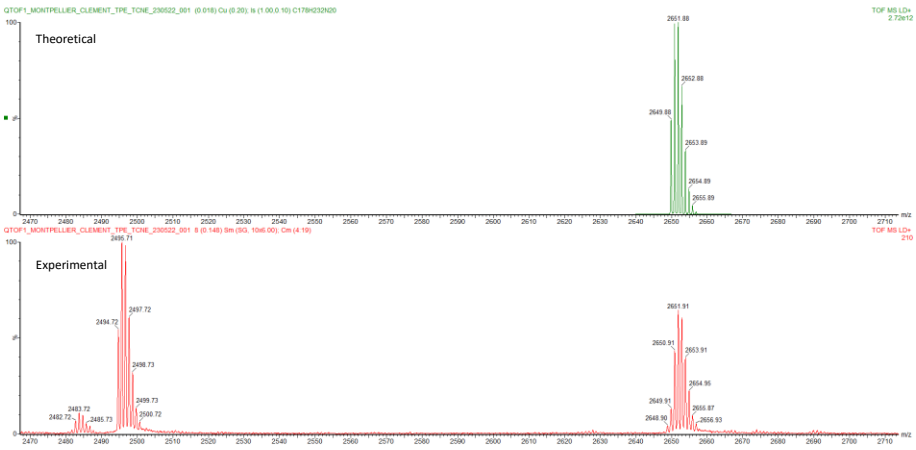


*Figure S 11. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$, 298K) of **TPE-TCNE**.*



Elemental Composition Report

Single Mass Analysis
Tolerance = 25.0 PPM / DBE: min = -1.5, max = 200.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
21 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 20-250 H: 0-250 N: 20-20

Minimum:				-1.5				
Maximum:			5.0	25.0	200.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
2649.8757	2649.8769	-1.2	-0.5	73.0	20.8	0.586	55.63	C178 H232 N20
	2649.8518	23.9	9.0	149.5	21.0	0.813	44.37	C189 H101 N20

*Figure S 12. High resolution MALDI-TOF mass spectrum of **TPE-TCNE** (matrix: DCTB/NaI).*

4. TPE-TCNQ

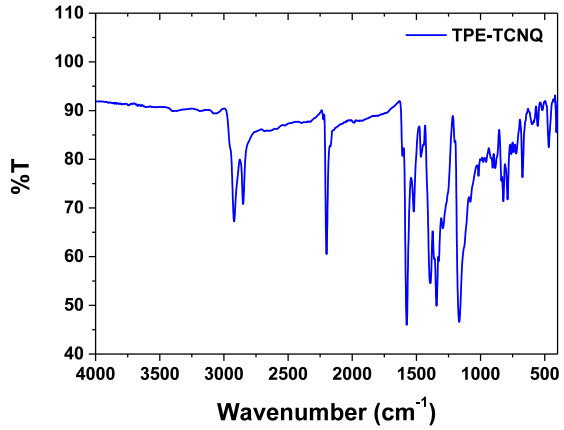


*Figure S 13. FTIR-ATR spectrum of **TPE-TCNQ**.*

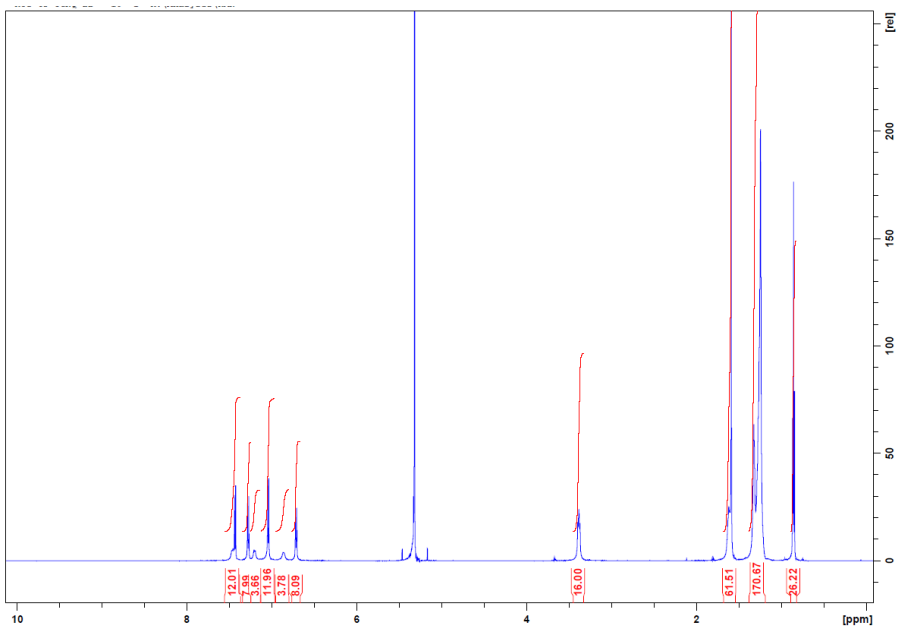


*Figure S 14. ^{1}H NMR spectrum (600 MHz, CD_2Cl_2, 273K) of **TPE-TCNQ**.*

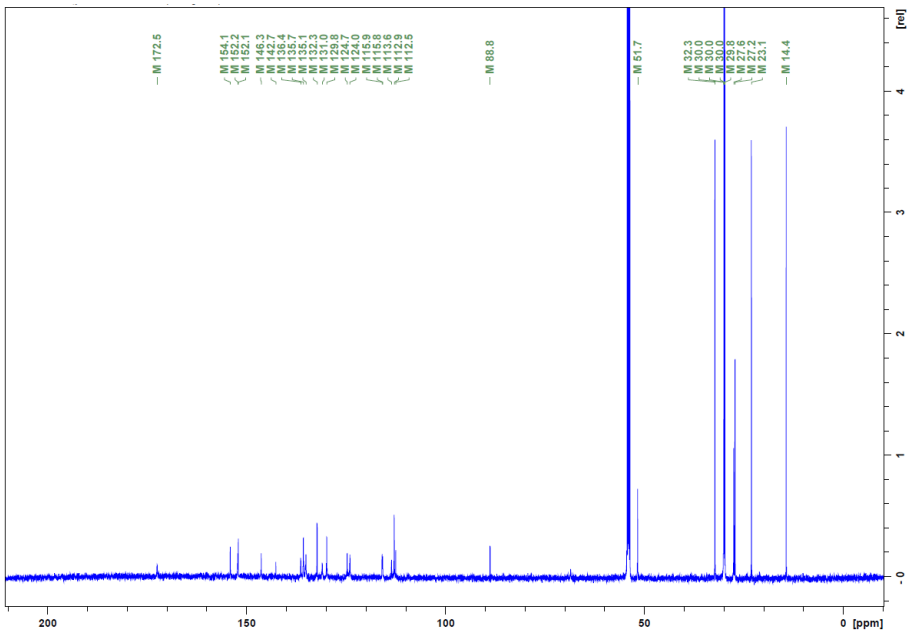


*Figure S 15. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, CD_2Cl_2, 273K) of **TPE-TCNQ**.*

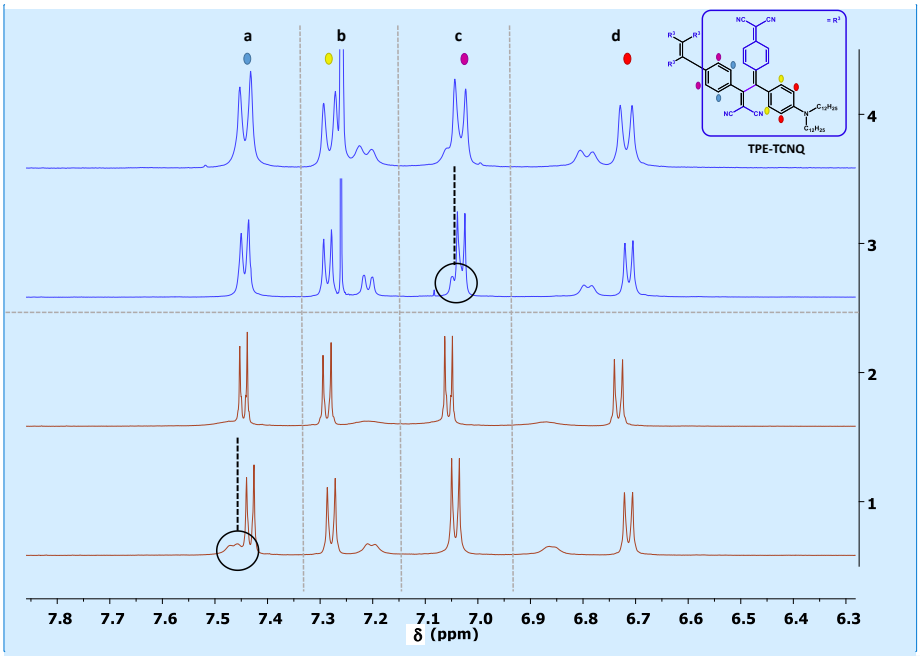
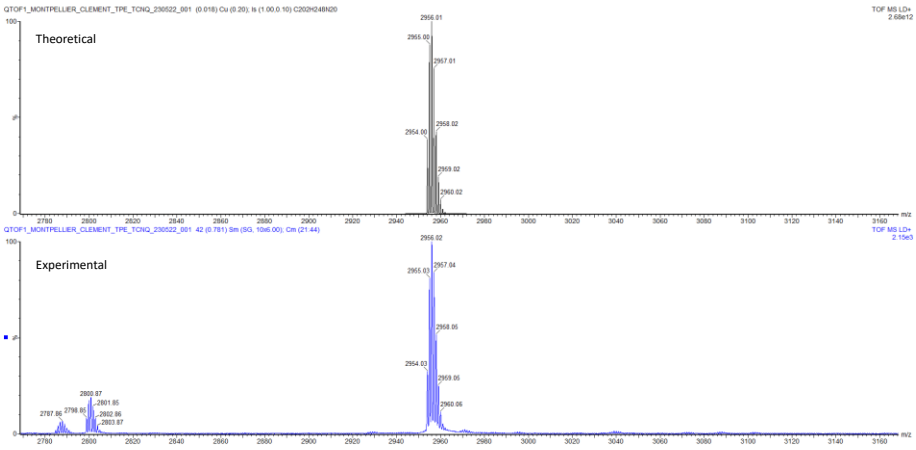


*Figure S 16. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, blue, 4 and 3) and ^{1}H NMR spectrum (600 MHz, $CDCl_3$, red, 2 and 1) of **TPE-TCNQ** at 298 K and 278 K.*

Commenté [SC1]: Je ne comprends pas la légende de ces spectres…Pkoi quatre spectres pour deux températures ?



Elemental Composition Report

Single Mass Analysis
Tolerance = 25.0 PPM / DBE: min = -1.5, max = 200.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
21 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 20-250 H: 0-250 N: 20-20

Minimum:				-1.5				
Maximum:			5.0	25.0	200.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
2953.9946	2954.0021	-7.5	-2.5	89.0	26.3	2.890	5.56	C202 H248 N20
	2953.9770	17.6	6.0	165.5	23.5	0.057	94.44	C213 H117 N20

*Figure S 17. High resolution MALDI-TOF mass spectrum of **TPE-TCNQ** (matrix: DCTB/NaI).*

5. TPE-F_4-TCNQ

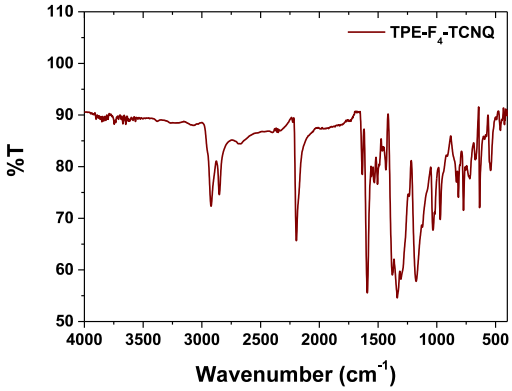


*Figure S 18. FTIR-ATR spectrum of **TPE-F_4-TCNQ**.*

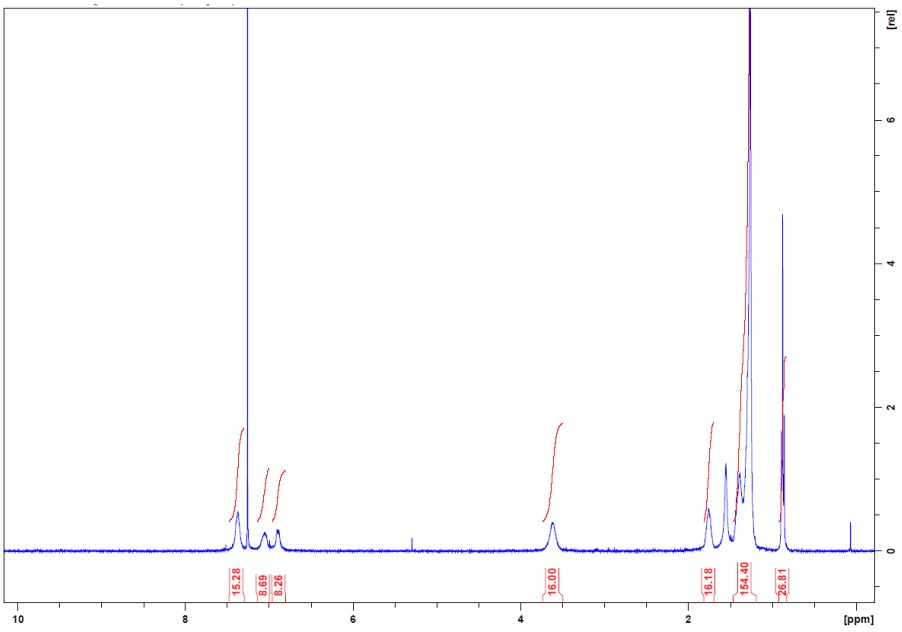


*Figure S 19. ^{1}H NMR (400 MHz, $CDCl_3$, 298K) of **TPE-F_4-TCNQ**.*

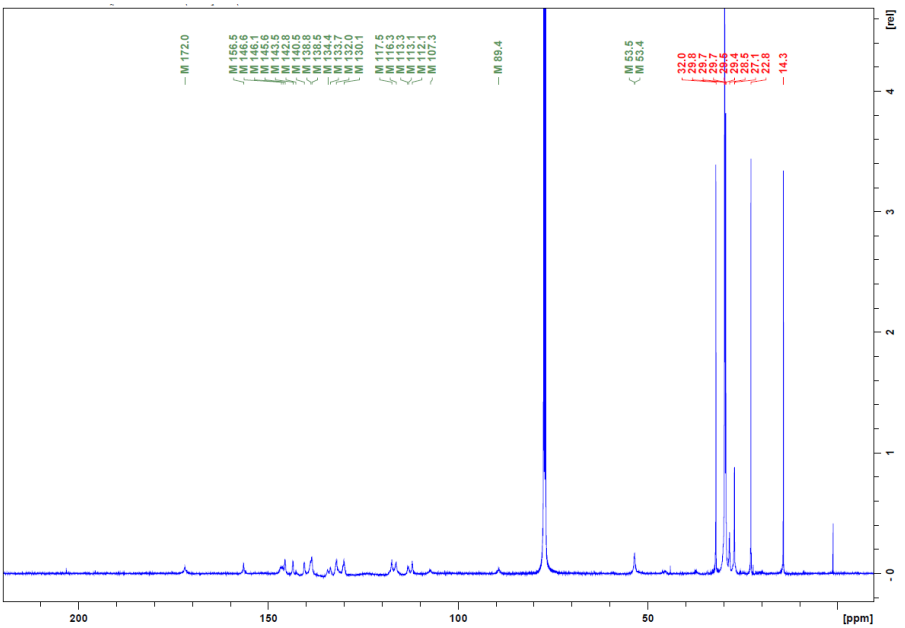


*Figure S 20. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$, 298K) of **TPE-F_4-TCNQ**.*

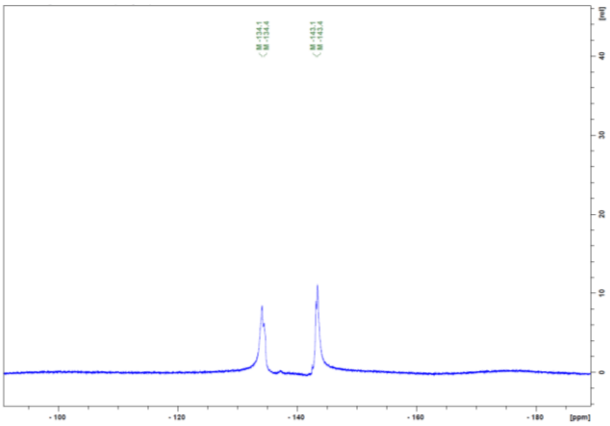
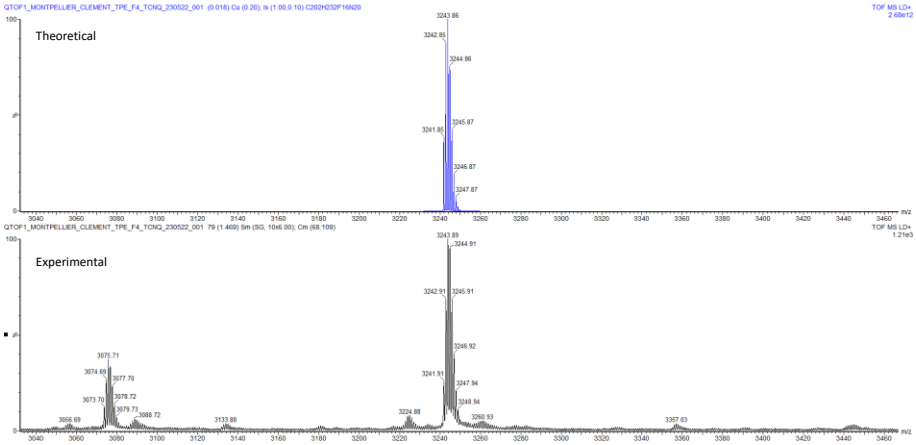


*Figure S 21. $^{19}F\{^{1}H\}$ NMR spectrum (376 MHz, $CDCl_3$, 298K) of **TPE- F_4-TCNQ**.*



Elemental Composition Report

Single Mass Analysis
Tolerance = 25.0 PPM / DBE: min = -1.5, max = 200.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
21 formula(e) evaluated with 3 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 20-250 H: 0-250 N: 20-20 F: 16-16

Minimum:				-1.5				
Maximum:			5.0	25.0	200.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
3241.8586	3241.8513	7.3	2.3	89.0	21.5	1.084	33.83	C202 H232 N20 F16
	3241.8263	32.3	10.0	165.5	21.0	0.556	57.33	C213 H101 N20 F16
	3241.9202	-61.6	-19.0	158.5	22.9	2.426	8.84	C212 H113 N20 F16

*Figure S 22. High resolution MALDI-TOF mass spectrum of **TPE-F_4-TCNQ** (matrix: DCTB/NaI).*

V. Absorption and fluorescence spectroscopies

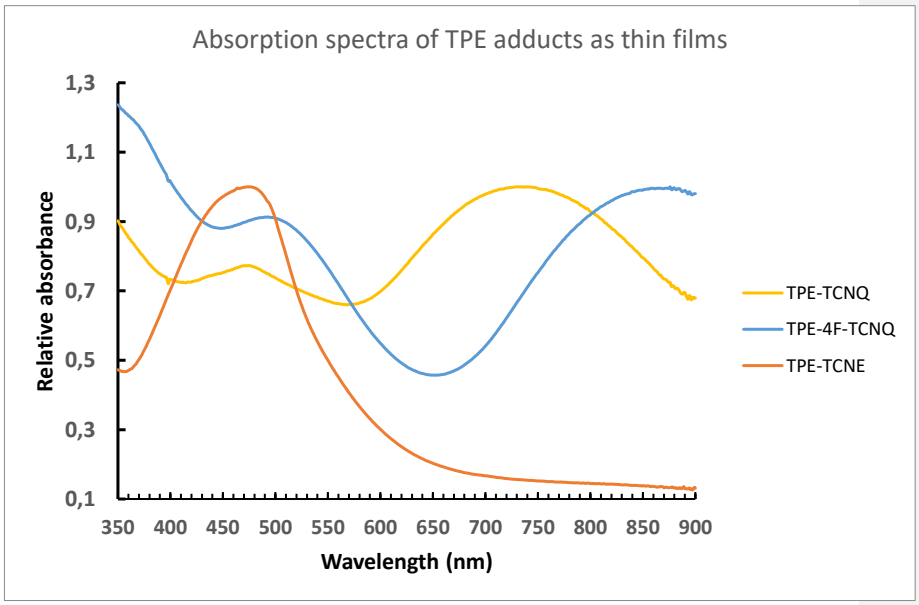


Figure S 23. Absorption spectra of TPE adducts as thin films on quartz substrate.

VI. Study of AIE behavior

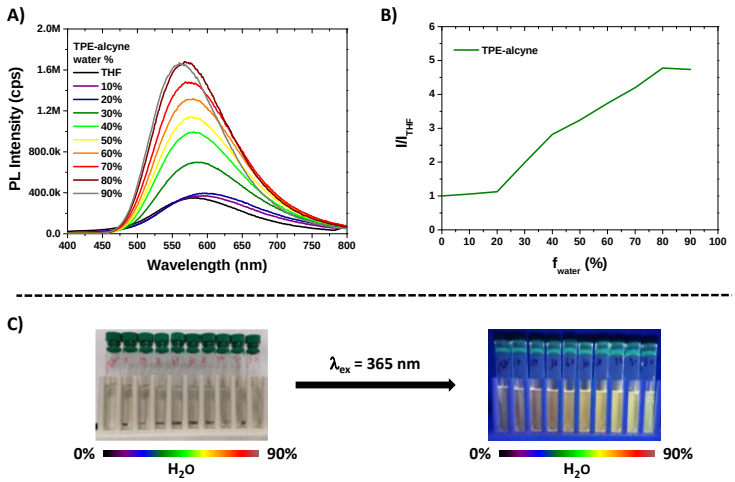


*Figure S 24. iA) emission spectra ($\lambda_{exc.}$ = 360 nm) of **TPE-Alkyne** in various THF / water mixtures (C = 6.10^{-6} mol.L^{-1}). ; B) variation of the relative emission intensity vs. water fraction (I_{THF}: Intensity of the fluorescence of **TPE-alkyne** at the*

maximum emission in THF and I: Intensity of the fluorescence of TPE-alkyne at the maximum emission in various THF /water mixtures) and C) photographs of the corresponding mixtures under natural (left) and UV (left, 365 nm) light illumination.

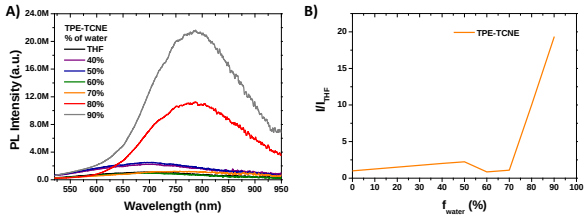


*Figure S 25. A) emission spectra ($\lambda_{exc.}$ = 480 nm) of **TPE-TCNE** in various THF / water mixtures (C = 5.3.10^{-5} mol.L^{-1}) ; B) variation of the relative emission intensity vs. water fraction.*

VII. pH-dependent emission studies

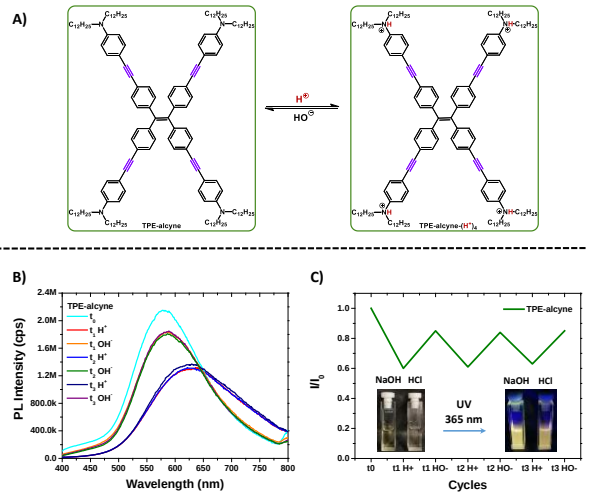


*Figure S 26. A) Reversible proposed acidification scheme for **TPE-alkyne** in THF/water solution ; B) variation of the emission spectra as a function of the pH (H$^+$: addition of an aqueous HCl solution and OH$^-$: addition of an aqueous NaOH solution) (C = 1.10^{-5} mol.L^{-1}, $\lambda_{exc.}$ = 360 nm) and C) drawing of the relative emission intensity variation upon pH cycling and corresponding images under natural and UV (365 nm) light illumination.*

Commenté [SC2]: Concentration ?

Commenté [SC3]: Concentration ?

VIII. Electrochemistry

1. TPE-TCNE

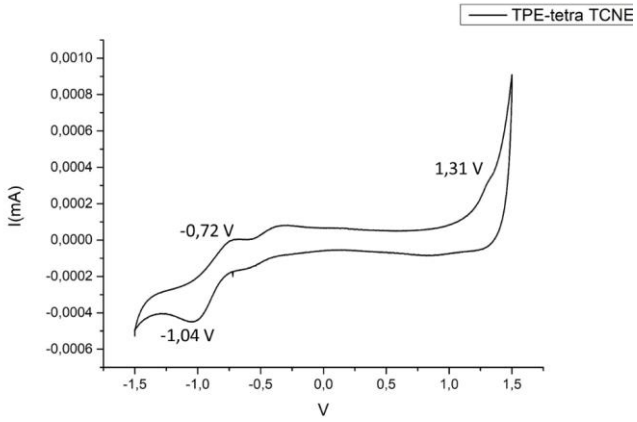


*Figure S 27. Cyclic voltammogram of **TPE-TCNE** in 0.2 M solution of Bu_4NPF_6 in CH_2Cl_2. (scan rate: 100 mV.s^{-1}; . electrode potential vs. SCE (saturated calomel electrode)).*

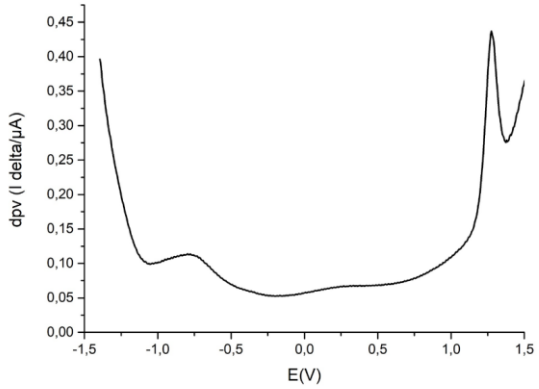


*Figure S 28. Differential pulse voltammetry (DPV) of **TPE-TCNE** in 0.2 M solution of Bu_4NPF_6 in CH_2Cl_2 (scan rate: 100 mV.s^{-1}; . electrode potential vs. SCE)..*

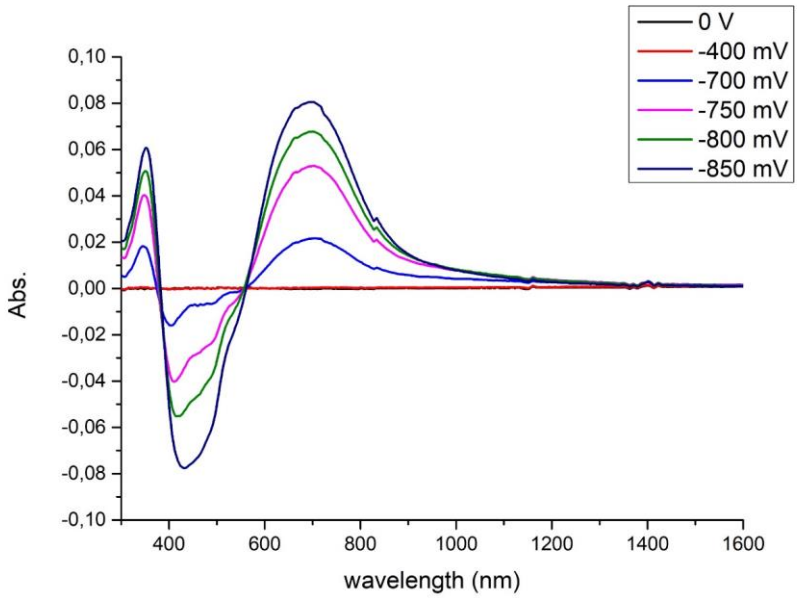


*Figure S 29. Differential absorption spectra obtained during the reduction of **TPE-TCNE** in 0.2 M solution of Bu_4NPF_6 in CH_2Cl_2 (scan rate: 100 mV.s^{-1}; . electrode potential vs. SCE).*

2. TPE-TCNQ

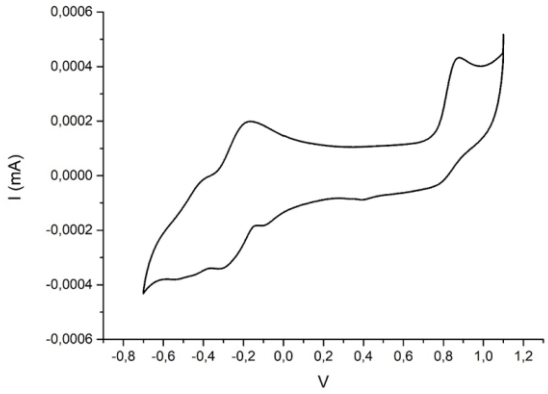


*Figure S 30. Cyclic voltammogram of **TPE-TCNQ** in 0.2 M solution of Bu_4NPF_6 in CH_2Cl_2 (scan rate: 100 mV.s^{-1}; . electrode potential vs. SCE).*

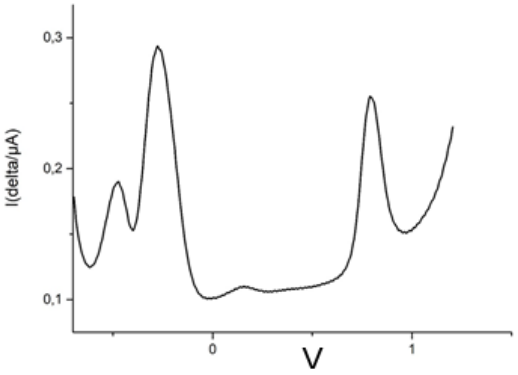


*Figure S 31. Differential pulse voltammetry (DPV) of **TPE-TCNQ** in 0.2 M solution of Bu_4NPF_6 in CH_2Cl_2 (scan rate: 100 $mV.s^{-1}$; . electrode potential vs. SCE).*

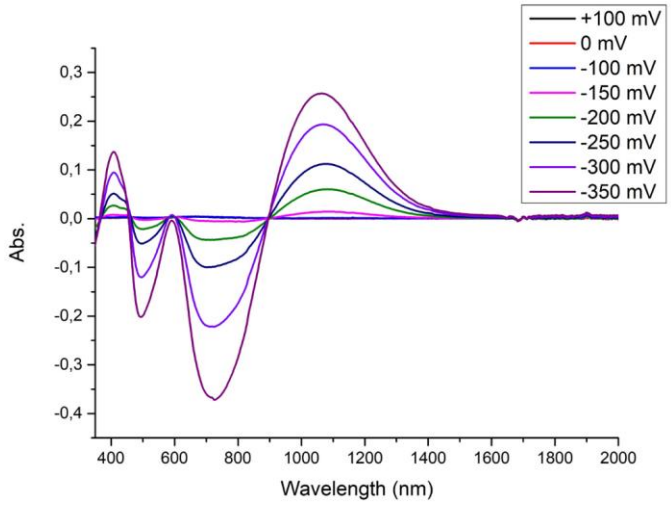


*Figure S 32. Differential absorption spectra obtained during the reduction of **TPE-TCNQ** in 0.2 M solution of Bu_4NPF_6 in CH_2Cl_2.*

3. TPE-F_4-TCNQ

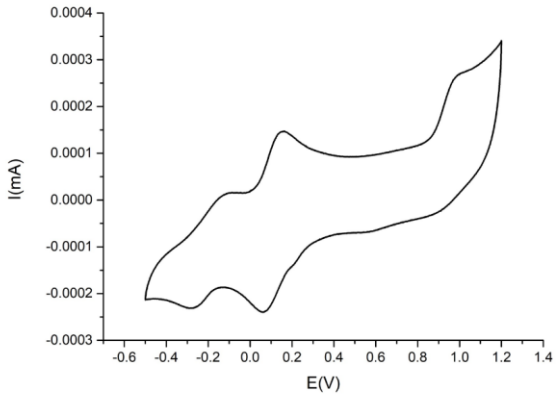
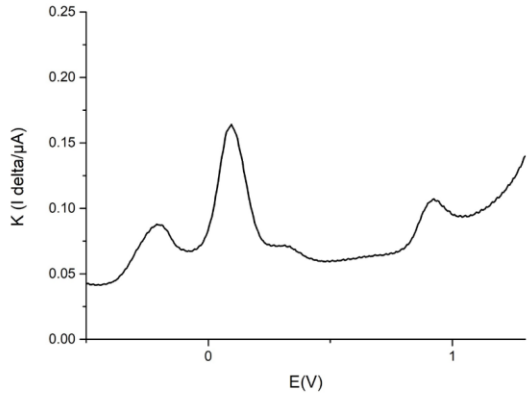


*Figure S 33. Cyclic voltammogram of **TPE-F_4-TCNE** in 0.2 M solution of Bu_4NPF_6 in CH_2Cl_2 (scan rate: 100 mV.s^{-1}; .*



electrode potential vs. SCE).

*Figure S 34. Differential pulse voltammetry (DPV) of **TPE-F$_4$-TCNQ** in 0.2 M solution of Bu_4NPF_6 in CH_2Cl_2 (scan rate: 100 mV.s^{-1}; . electrode potential vs. SCE).*

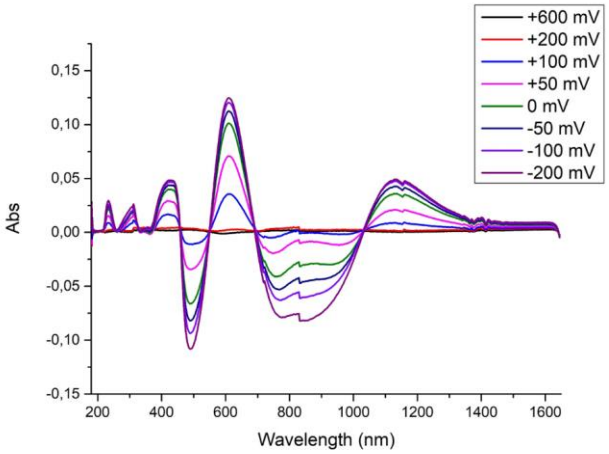


*Figure S 35. Differential absorption spectra obtained during the reduction of **TPE-F$_4$-TCNE** in 0.2 M solution of Bu_4NPF_6 in CH_2Cl_2.*

IX. Thermal and photothermal studies

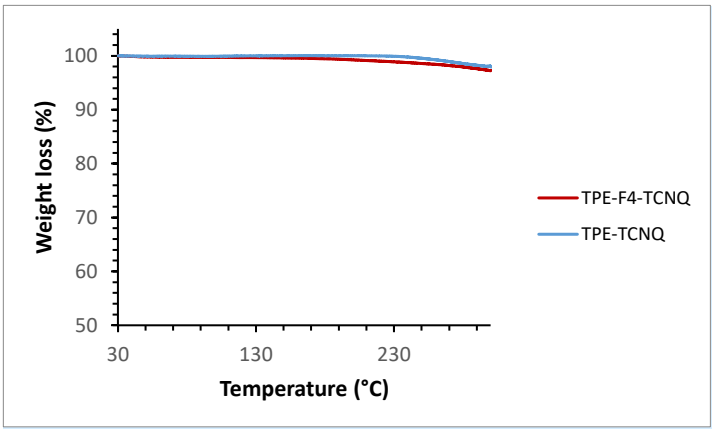


*Figure S 36. Thermogravimetric analysis (TGA) of **TPE-TCNQ** (blue) and **TPE-F$_4$-TCNQ** (red) under N_2 flow.*

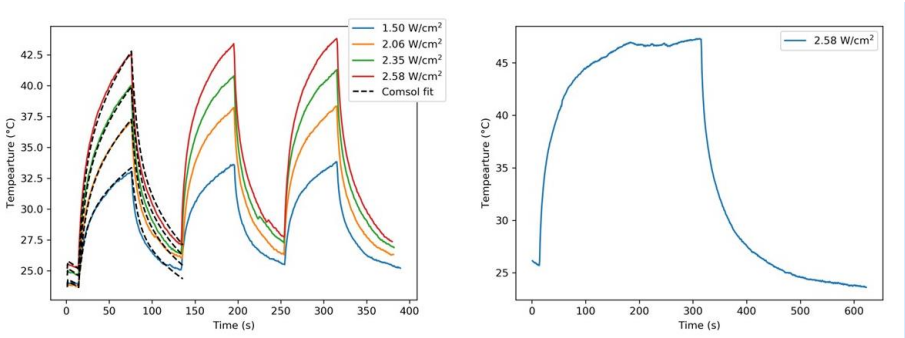


*Figure S 37. Photothermal conversion behavior of **TPE-TCNQ** as a thin film under 808 nm laser irradiation at different laser powers (1.50, 2.06, 2.35, and 2.58 cm^{-2}) vs. Comsol fits.*

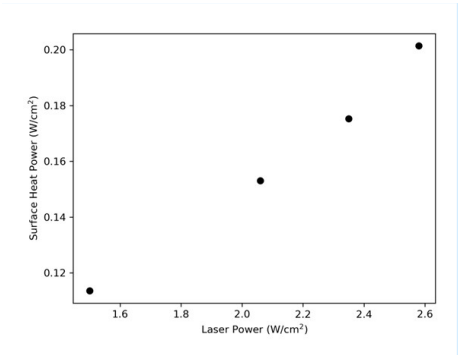


*Figure S 38. Surface heat power vs. laser power at 808 nm for **TPE-TCNQ** as a thin film.*

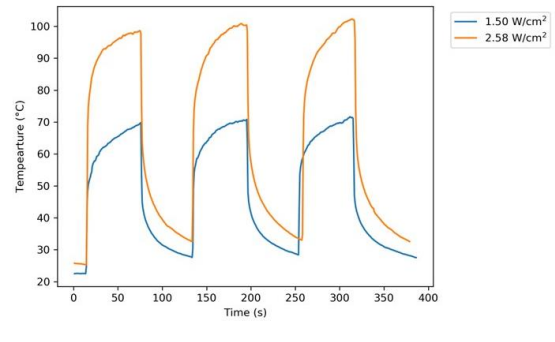


*Figure S 39. Photothermal conversion behavior of **TPE-TCNQ** as a powder under 808 nm laser irradiation at laser powers of 1.50 and 2.58 cm^{-2}.*

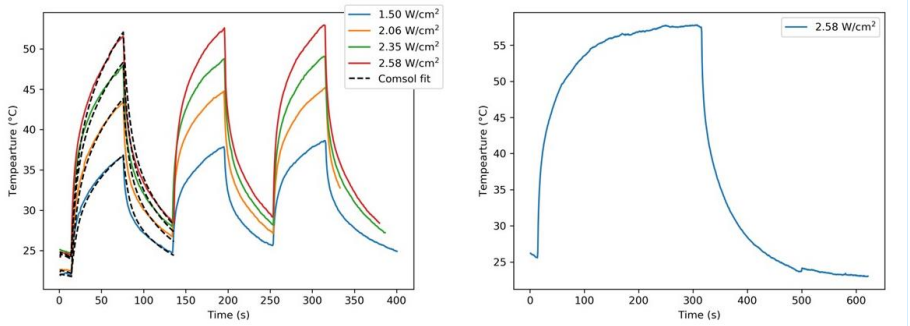


*Figure S 40. Photothermal conversion behavior of **TPE-F$_4$-TCNQ** as a thin film under 808 nm laser irradiation at different laser powers (1.50, 2.06, 2.35, and 2.58 cm^{-2}) vs. Comsol fits.*

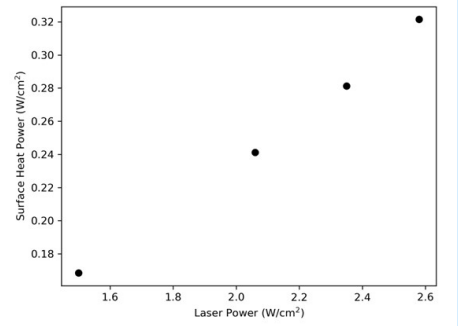


*Figure S 41. Surface heat power vs. laser power at 808 nm for **TPE-TCNQ** as a thin film.*

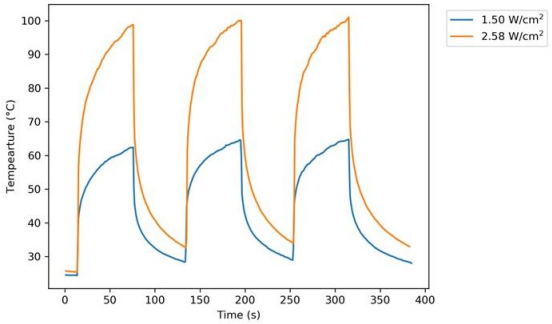


*Figure S 42. Photothermal conversion behavior of **TPE-F$_4$-TCNQ** as a powder under 808 nm laser irradiation at laser powers of 1.50 and 2.58 cm^{-2}.*

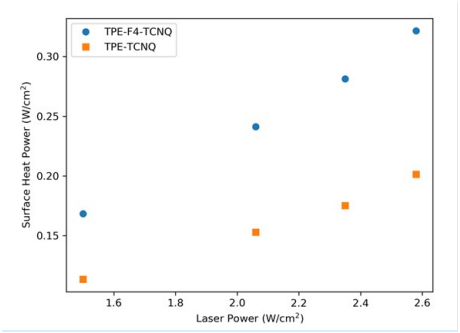


*Figure S 43. Comparison of the surface heat power vs. laser power at 808 nm for **TPE-TCNQ** (orange) and **TPE-F4-TCNQ** as thin films.*

Commenté [SC4]: Mettre après les calculs

X. Calculations

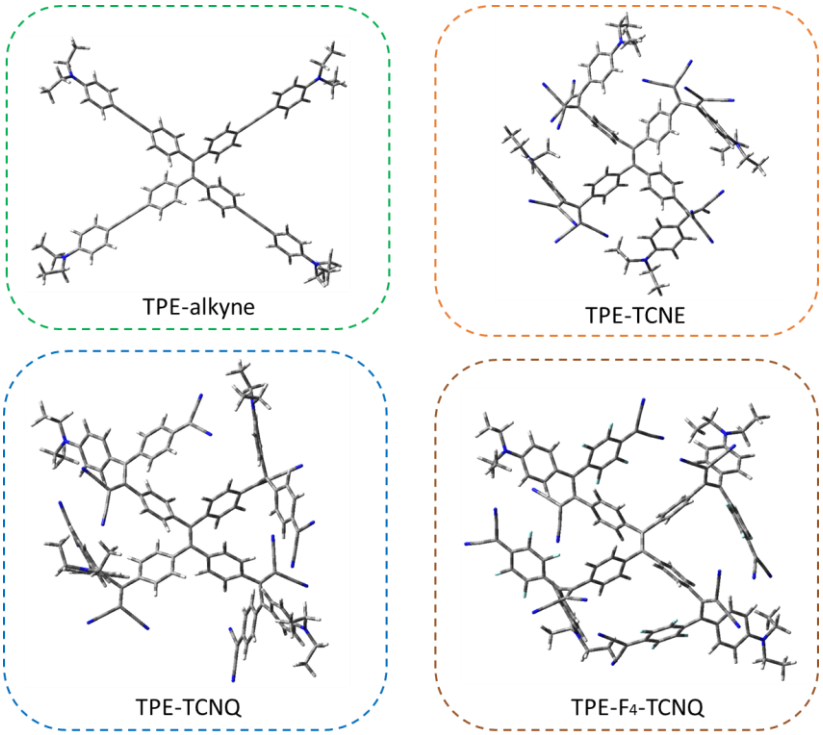


Figure S 44. Optimized geometry of the investigated compounds computed at DFT-Cam-B3LYP/6-311G(d,p) theory level.

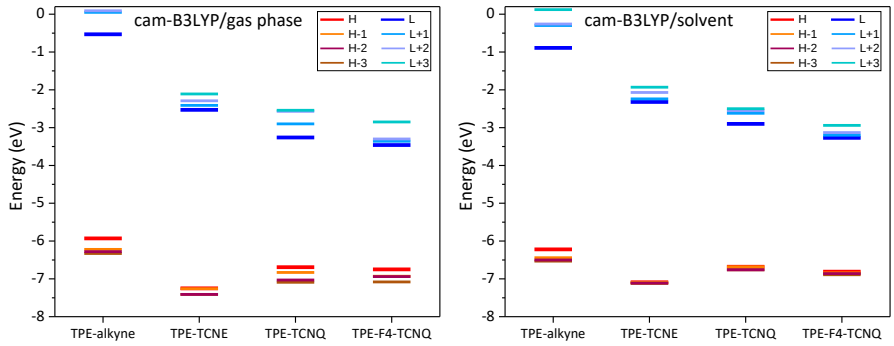


Figure S 45. Energy alignment of the four frontier occupied and virtual molecular orbitals for the investigated systems in both gas phase and in THF/DCM solution, as calculated at CAM-B3LYP/6- 311G (d,p) level.

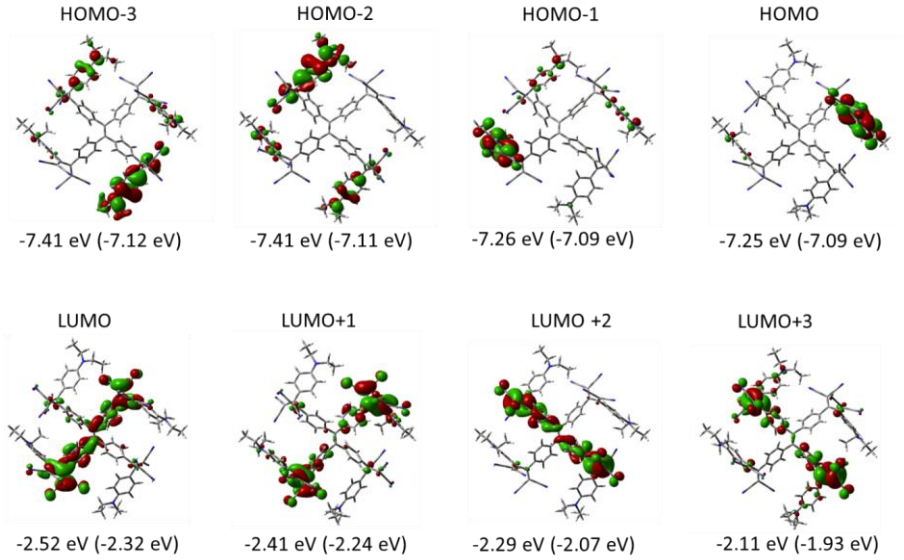


*Figure S 46. Shape of the four occupied and virtual molecular orbitals for **TPE-TCNE** in the gas phase. Energies are computed at the CAM-B3LYP/6-311G(d,p) level of theory in gas phase and in THF solution. Isovalues are set to 0.02 e/au^3.*

***Table S1**: Assignment of electronic excitations for the investigated compounds, as obtained at the TD-DFT/Cam-B3LYP level [a].*

Transition number	Computed transition energy λ, nm (eV)	Oscillator strength	Main contributions
		TPE-alkyne	
1	367 (3.38)	2.02	H->L (67%), H-4->L (12%)
3	330 (3.76)	4.82	H->L+1 (33%), H-2->L (30%), H-3->L+2 (10%)
5	287 (4.32)	0.54	H-4->L (22%), H-2->L+1 (22%), H-1->L+2 (13%)
		TPE-TCNE	
1	443 (2.80)	0.20	H-1->L+1 (35%), H-1->L (33%), H->L (15%)
2	443 (2.80)	0.28	H->L+1 (46%), H->L (25%), H-1->L (15%)
3	401 (3.09)	0.24	H-2->L+5 (26%), H-2->L+3 (25%), H-3->L+4
4	399 (3.11)	0.95	H-3->L+4 (28%), H-3->L+3 (24%), H-2->L+4
		TPE-TCNQ	
1	625 (1.98)	0.87	H→L (87%)
2	549 (2.26)	0.39	H-2->L+1 (31%), H-1->L+2 (31%), H-3->L+1
3	545 (2.27)	1.75	H-1->L+2 (50%), H-2->L+1 (18%), H-3->L+1
4	518 (2.39)	1.29	H-3->L+3 (38%), H-2->L+3 (37%), H-1->L+2
		TPE-F_4-TCNQ	
1	675 (1.84)	0.10	H->L (46%), H-1->L (20%), H-2->L+1 (12%)
2	642 (1.93)	2.16	H-2->L+1 (62%), H->L (16%)
3	606 (2.04)	1.81	H-3->L+2 (73%), H-2->L+1 (12%)
4	585 (2.12)	0.69	H-1->L+3 (50%), HOMO->L+3 (30%)

[a] Only excitations with a significant oscillator strength around the main peak of the lowest absorption band are included. H stands for HOMO and L for LUMO

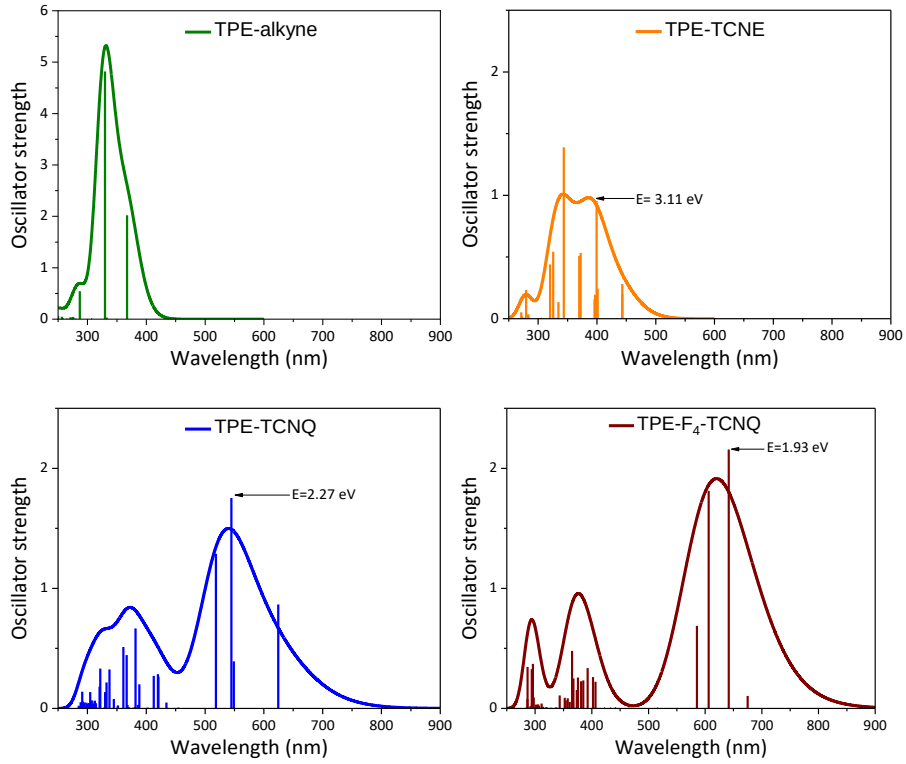


Figure S 47. Simulated UV-Vis absorption spectra of the investigated compounds in THF solution at the TDDFT/Cam-B3LYP level with all transition peaks. The main transition energy of the CT absorption band for TPE adducts is also pointed with an arrow.

XI. References

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