# Electronic Supplementary Information

## Doping-induced decomposition of organic semiconductors: a caveat to the use of Lewis acid *p*-dopants†

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† G.C.V. and P.E.K. dedicate this paper to Emeritus Prof. Dr G. J. Karabatsos (Michigan State University and University of Crete) on the occasion of his 90th birthday.

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## Experimental

**Materials:** $B(C_6F_5)_3$, diF-TES-ADT, $NOBF_4$ and atactic poly(styrene) (a-PS) were purchased from Sigma Aldrich, whereas PTAA from Flexink. All materials were used as received.

**Solution preparation:** PTAA:$B(C_6F_5)_3$ and diF-TES-ADT:$B(C_6F_5)_3$ dilute solutions with variable mol% $B(C_6F_5)_3$ content were prepared in toluene and in chloroform. Additional solutions of the diF-TES-ADT:$B(C_6F_5)_3$ system were prepared in chlorobenzene. The mol% $B(C_6F_5)_3$ content of the PTAA:$B(C_6F_5)_3$ system was determined based on the number of moles of PTAA repeat unit. For the here studied dimethyl PTAA derivative the monomer molecular mass (MM= 291 amu) was used. Both types of PTAA:$B(C_6F_5)_3$ and diF-TES-ADT:$B(C_6F_5)_3$ systems that were prepared in toluene and chloroform solutions were with a 0.5 mg/ml concentration in respect to PTAA and diF-TES-ADT, respectively. For the diF-TES-ADT:$B(C_6F_5)_3$ system in chlorobenzene solutions the diF-TES-ADT concentration was kept to 0.25 mg/ml. A PTAA:$NOBF_4$ solution was prepared in a chloroform:toluene co-solvent (1:1) with a 0.25 mg/ml PTAA concentration and a 60 wt% $NOBF_4$ content.

**Thin film preparation:** PTAA:$B(C_6F_5)_3$ and diF-TES-ADT:$B(C_6F_5)_3$ thin films with variable mol% $B(C_6F_5)_3$ content were develeoped by spin-coating of solution mixtures on spectrosil B quartz substrates. Both types of PTAA:$B(C_6F_5)_3$ and diF-TES-ADT:$B(C_6F_5)_3$ films that were developed by toluene and chloroform solutions of a 5 mg/ml concentration in respect to PTAA and diF-TES-ADT, respectively. Additional solutions of diF-TES-ADT:$B(C_6F_5)_3$ were prepared in chlorobenzene with a concentration of 5 mg/ml versus diF-TES-ADT. For reference puproses, a solid-state $B(C_6F_5)_3$ film was also developed by dispersing $B(C_6F_5)_3$ in a-PS that served as a binder matrix. The a-PS:$B(C_6F_5)_3$ mixture was prepared in toluene by mixing equal volumes of a 10 mg/ml a-PS solution and a 5.1 mg/ml $B(C_6F_5)_3$ solution. Spin-coating of the solutions was performed in ambient at 1500 rpm for 60 s with a WS-650Mz-23NPPB spin-coater unit (Laurell Technologies Corporation).

**UV-Vis and photoluminescence characterization:** UV–vis absorption spectra of the fabricated films were recorded with UV-2700 Shimadzu spectrophotometer. Steady-state fluorescence measurements on the films were carried out on a Fluorolog iHR320

Horiba Jobin Yvon spectrometer system. The excitation of samples was achieved by a quasi-monochromatic beam produced by a combination of an $O_3$-free Xe lamp with a double monochromator. The lamp spot size was adjusted to be large enough to cover the whole surface of the studied films, providing an averaged representation of their emission properties. The fluorescence spectra were normalized to the absorptance (1-T) of the films at the excitation wavelength, to account for variations in thickness and concentration. All optical measurements were performed in ambient conditions.

**$^1$H-NMR:** Spectra were obtained with a Varian Mercury 200 MHz spectrometer.

**Fluorescence lamp results:** Initially 2 mg of diF-TES-ADT were dissolved in 0.2 ml $CHCl_3$ (10 mg/ml) and a photograph of the solution was obtained both under ambient light (t = 0). Next, 1 mg of $B(C_6F_5)_3$ was added in the solution and additional photographs were obtained in the course of time. A solution of diF-TES-ADT (2 mg, 0.0033 mmol, 16.5 mM) in $CHCl_3$ (200 μL) was added in $B(C_6F_5)_3$ (1 mg, 0.002 mmol, 9.8 mM). TLC analysis was performed at the indicated reaction times. A solution of PTAA (2 mg, 0.007 mmol, 34.7 mM) in $CHCl_3$ (200 μL) was prepared and next $B(C_6F_5)_3$ was added (1 mg, 0.002 mmol, 9.8 mM). TLC analysis was performed at the indicated reaction times.

**Thin Layer Chromatogrphy:** Silica gel 60 $F_{254}$ coated aluminium sheets (Merck) were used.

**Electrospray ionization mass spectroscopy:** Electrospray ionization mass spectra (ES-MS) were obtained in a Thermo Finnigan Surveyor MSQ Plus, employing HPLC grade MeOH or MeCN as solvents. The utilized spectrometer cannot measure substances with m/z>2000.

**Density functional theory calculations:** Density functional theory (DFT) calculations were performed with the code NWChem, [1] the B3LYP exchange-correlation functional [2, 3] and the DZVP orbital basis. [4] van der Waals interactions were included with the so-called DFT-D3 method. [5]

**Organic field effect transistors:** The organic field effect transistor (OTFT) devices were fabricated with top-gate, bottom-contact (TG-BC) architecture. The Al/Au (5 nm/35 nm) source and drain electrodes were vapor deposited using shadow mask on the glass substrate which were further treated with pentafluorothiophenol (PFBT). Three different $B(C_6F_5)_3$ doping concentrations (0.1 mol%, 0.5 mol% and 1 mol%) in diF-TES ADT were used to fabricate the OTFTs along with the pristine devices. For ageing experiment 0.5 mol% doping was used for both diF-TES-ADT and PTAA. The pristine and doped small molecule and polymer solutions (15 mg/ml in chlorobenzene) were spin coated on the glass substrates at a spin rate of 2000 rpm for 30 s and then annealed at 100 °C for 15 mins. ~900 nm CYTOP film was deposited on top of the semiconductor by spin coating at 2000 rpm spin rate followed by annealing at 50°C for 1 hr. The capacitance of the CYTOP dielectric was measured 2.1 nF/cm$^2$. 50 nm of Al were vapor deposited at the top as gate electrode. The current–voltage characteristics for the devices were measured using KEYSIGHT B2912A Precision Source/Measure Unit.

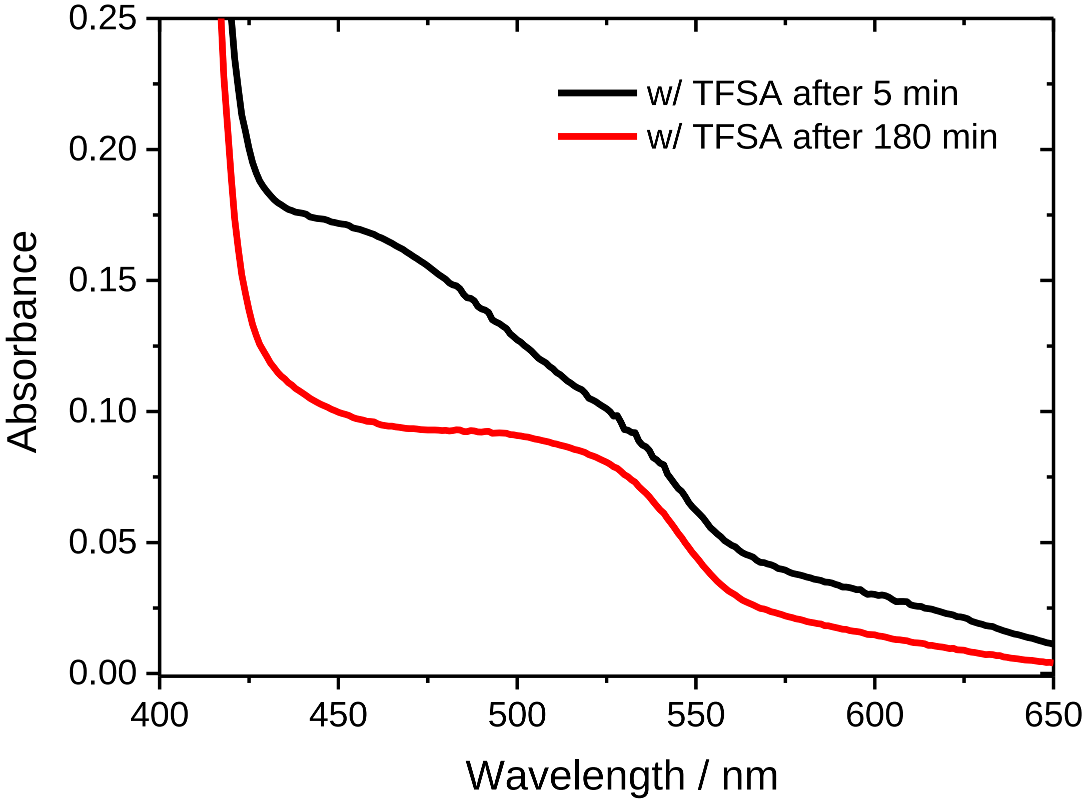

**Figure S1.** UV-Vis spectra of a 5 µg/ml PTAA solution in chlorobenzene with added trace amounts of trifluoromethanesulfonic acid (TFSA) as acquired a) 5 minutes and b) 180 minutes after adding TFSA. A 10 mm optical length quartz cuvette was used for registering both UV-Vis spectra.

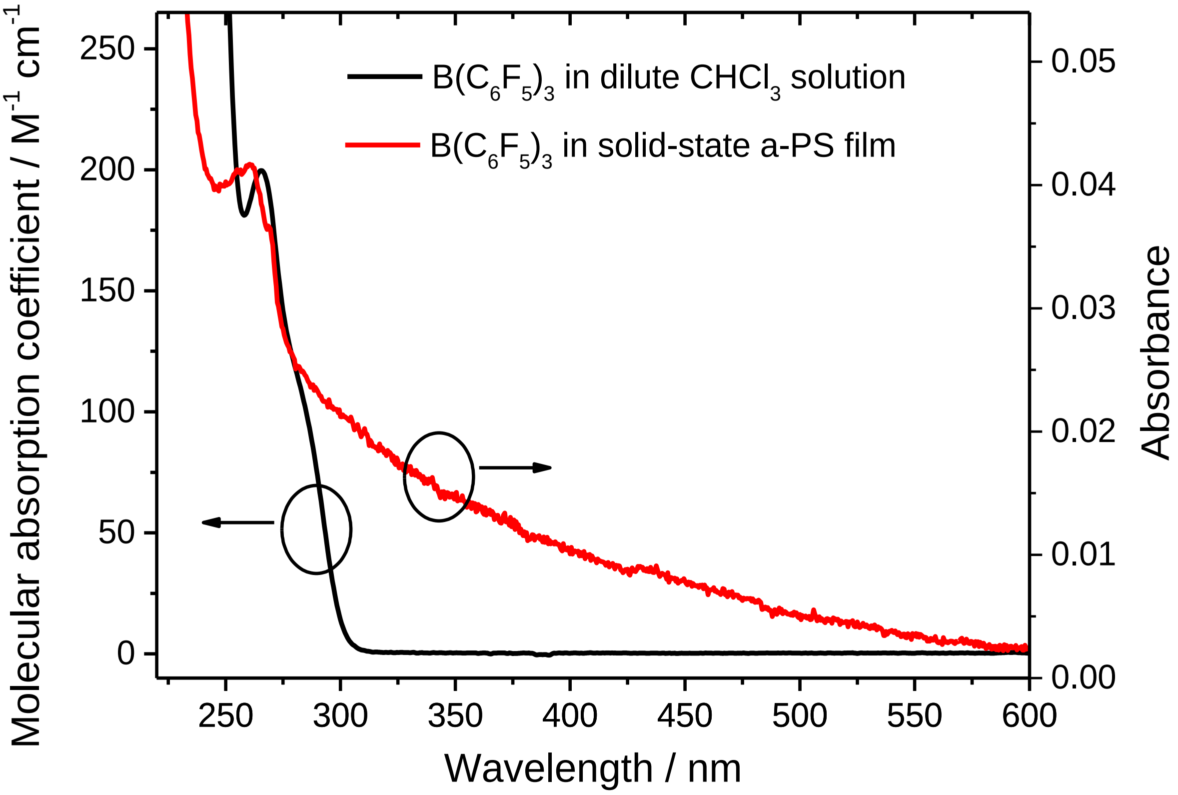

**Figure S2.** UV-Vis absorption spectra of $B(C_6F_5)_3$ solution in chloroform (black line), and of a-PS:$B(C_6F_5)_3$ 60 wt% film spin-coated from toluene.

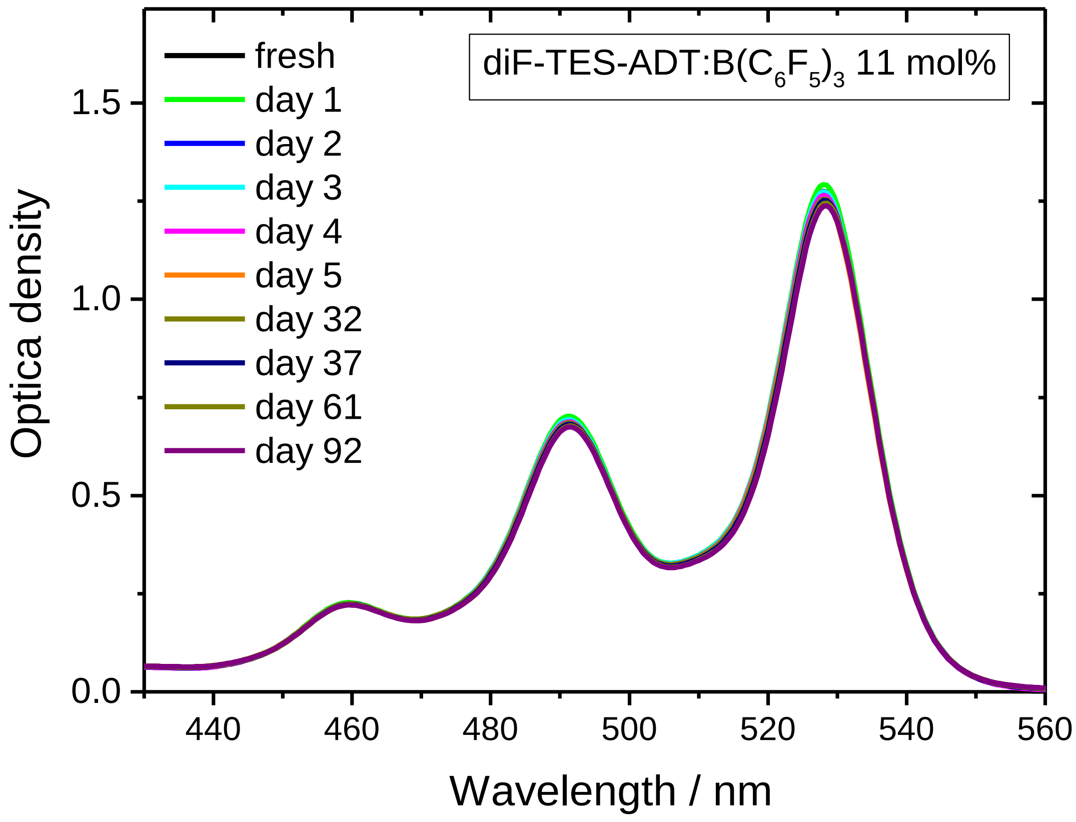

**Figure S3.** UV-Vis spectra of a 0.25 mg/ml diF-TES-ADT solution in chlorobenzene with 11% mol $B(C_6F_5)_3$ content, as recorded within a period of 92 days after solution preparation. All spectra were registered with a 1 mm optical length quartz cuvette.

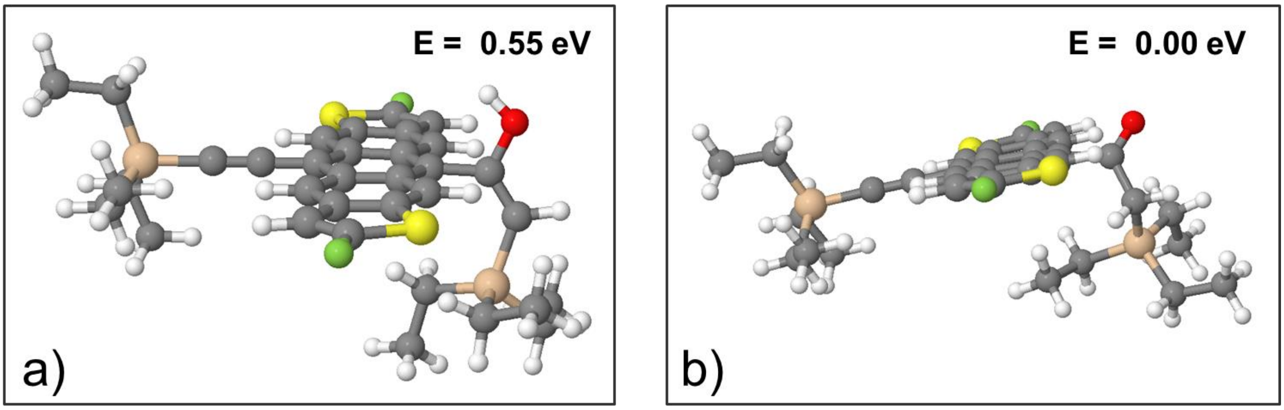

**Figure S4.** Enol – ketone tautomerization following the production of the hydrated diF-TES-ADT after reaction with $B(C_6F_5)_3$-$OH_2$. The energy (E) of the enol tautomer in a) is referenced with respect to that of the ketone tautomer in b). The sphere color-code for atoms is C: gray, O: red, Si: light orange, F: green, S: yellow, H: white.

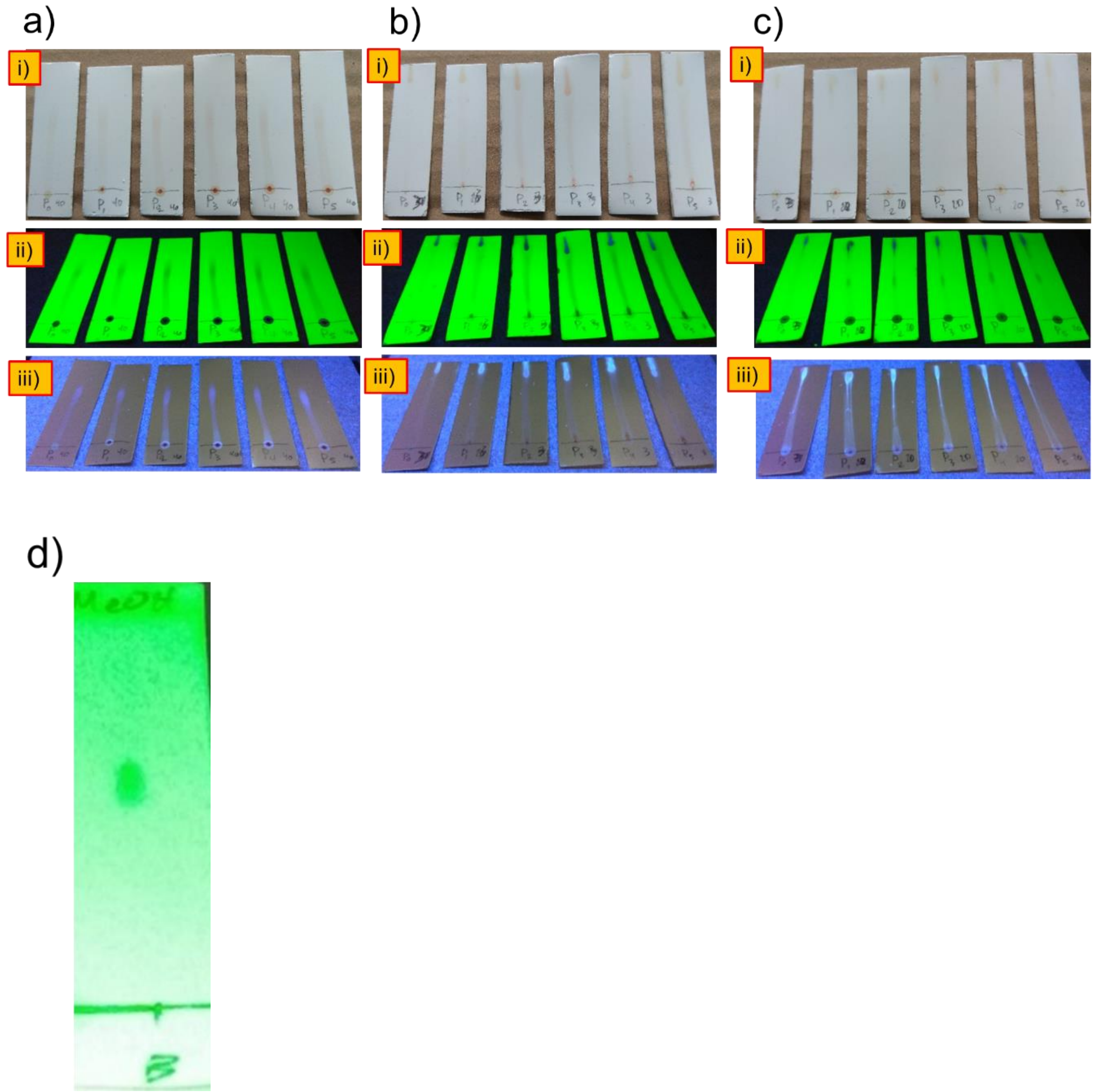

**Figure S5.** TLC analysis for PTAA:$B(C_6F_5)_3$ mixtures (1:1) at 0 – 2.5 h when various solvent systems are used as mobile phase: a) 40% DC/hexane, b) 3% MeOH/DCM, c) 20% MeOH/DCM at different reaction timεs (P0 – P5), d) TLC of $B(C_6F_5)_3$ alone (20% MeOH/DCM). Photos were taken under i) ambient, ii) 254 nm, and iii) 365 nm light. Photo in d) was taken under 254 nm light.

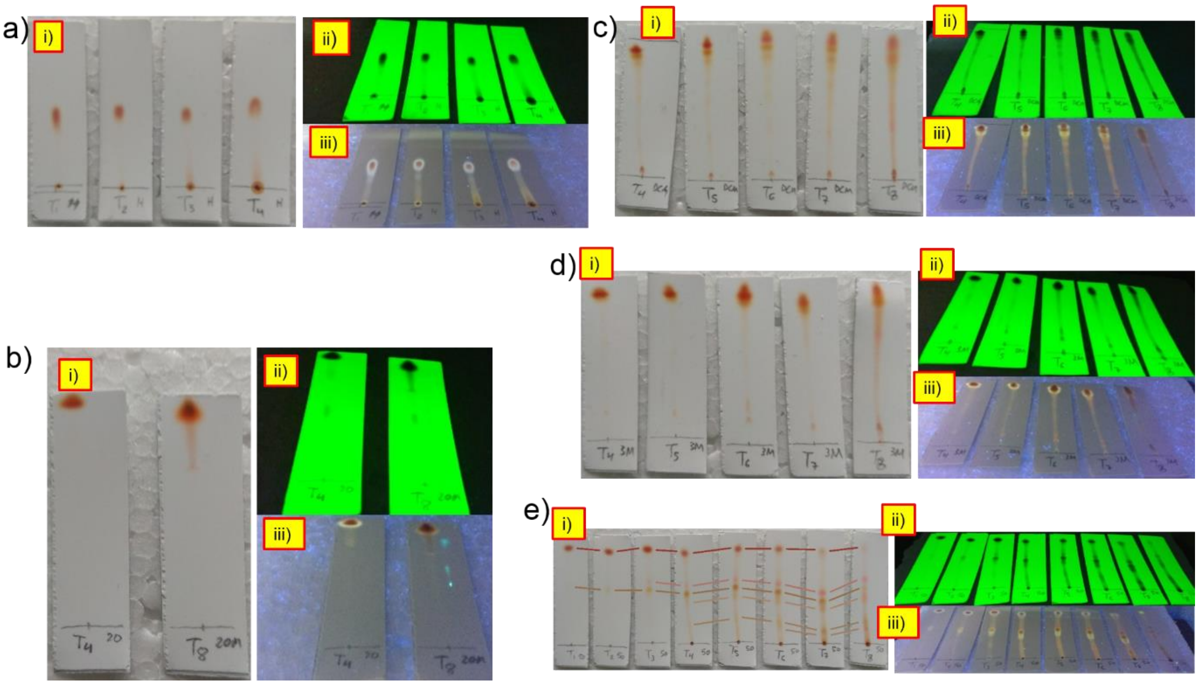

**Figure S6.** TLC analyses for diF-TES-ADT:B($C_6F_5$)$_3$ mixtures (1:1) when various solvent systems are used as mobile phase: a) hexane, b) 20% MeOH/DCM, c) DCM, d) 3% MeOH/DCM , and e) hexane/DCM 1:1. Photos were taken under i) ambient, ii) 254 nm, and iii) 365 nm light.

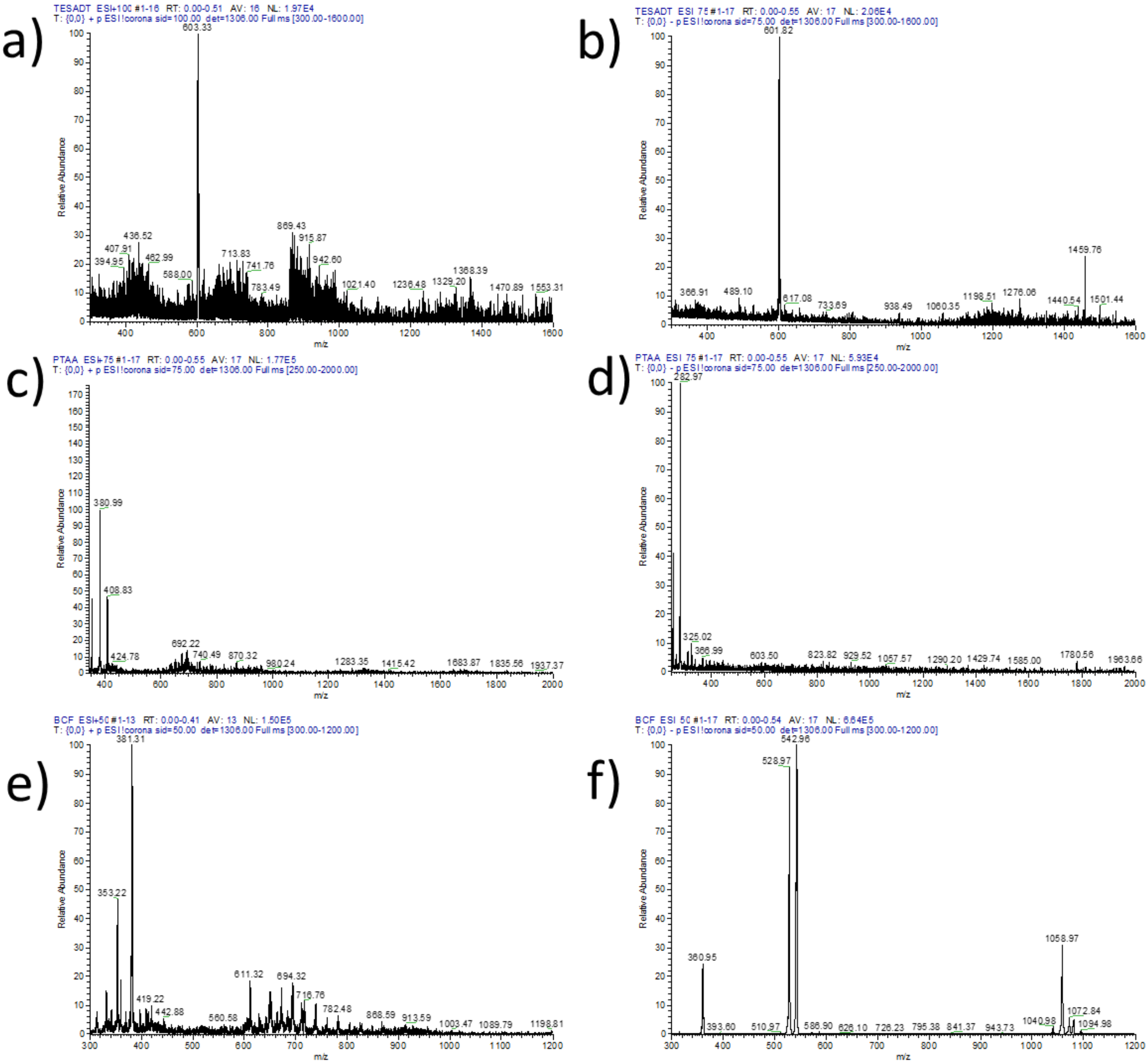

**Figure S7.** ES-MS spectra of: diF-TES-ADT, a) positive, b) negative mode; PTAA, c) positive, d) negative mode; B($C_6F_5$)$_3$, c) positive, d) negative mode.

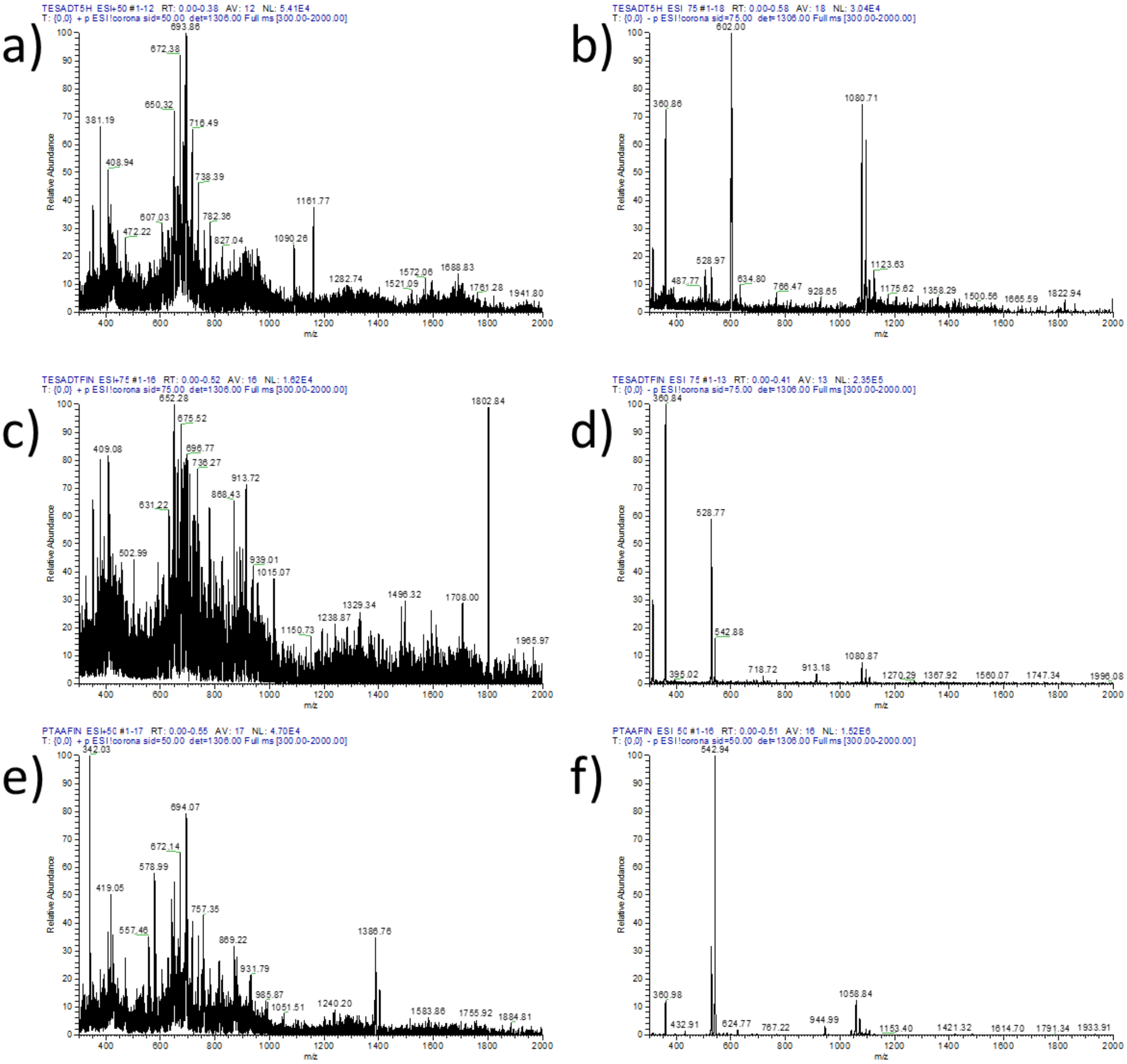

**Figure S8.** ES-MS spectra of: diF-TES-ADT:B($C_6F_5$)$_3$ reaction mixture at 5h (TES5): a) positive, b) negative mode; diF-TES-ADT:B($C_6F_5$)$_3$ reaction mixture at 5d (TES8): c) positive, d) negative mode; PTAA:B($C_6F_5$)$_3$ reaction mixture at 13d (PTAA11): e) positive, f) negative mode.

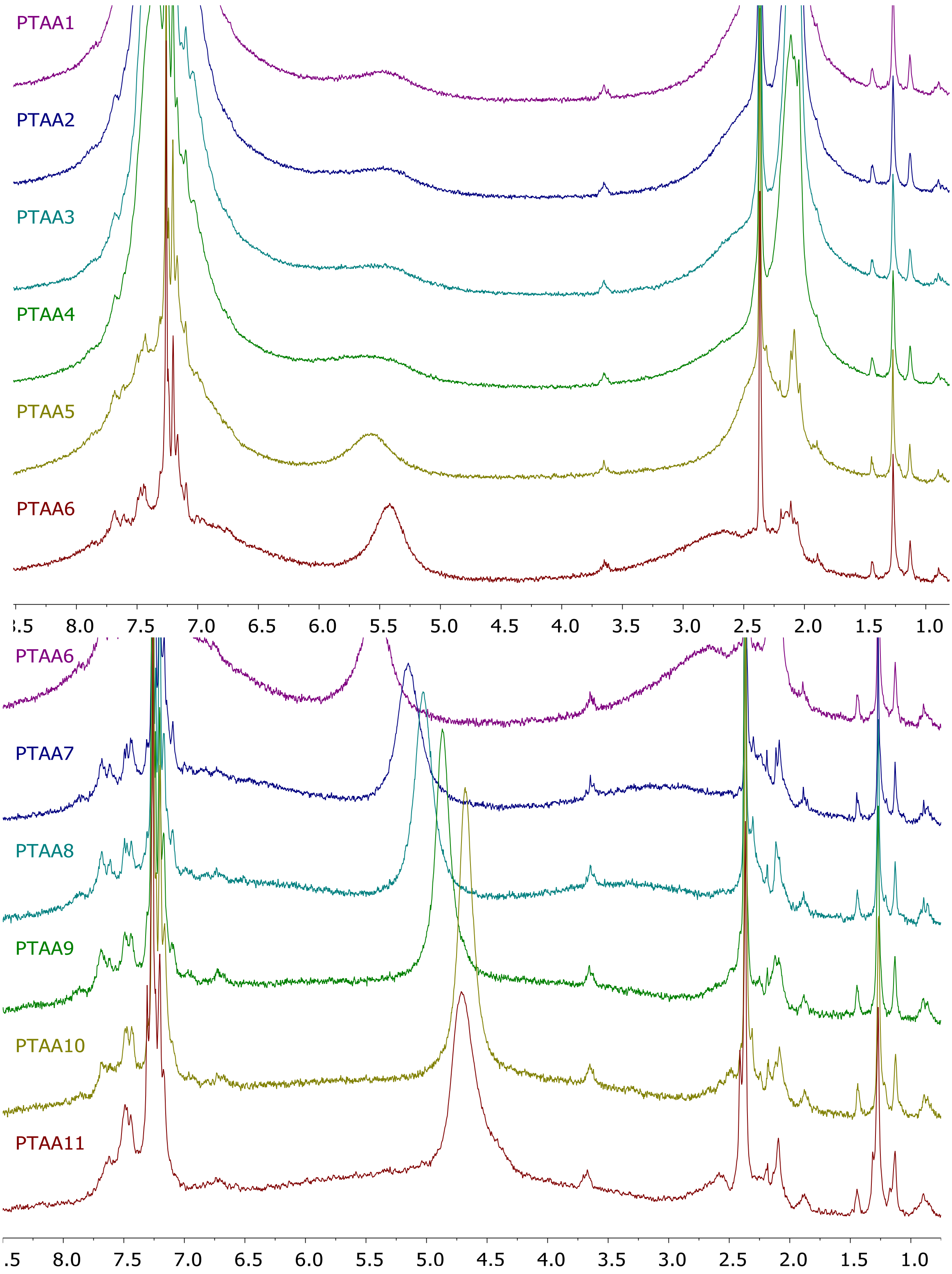

**Figure S9.** $^1$H-NMR ($CDCl_3$, 200 MHz) monitoring of PTAA:$B(C_6F_5)_3$ reaction.

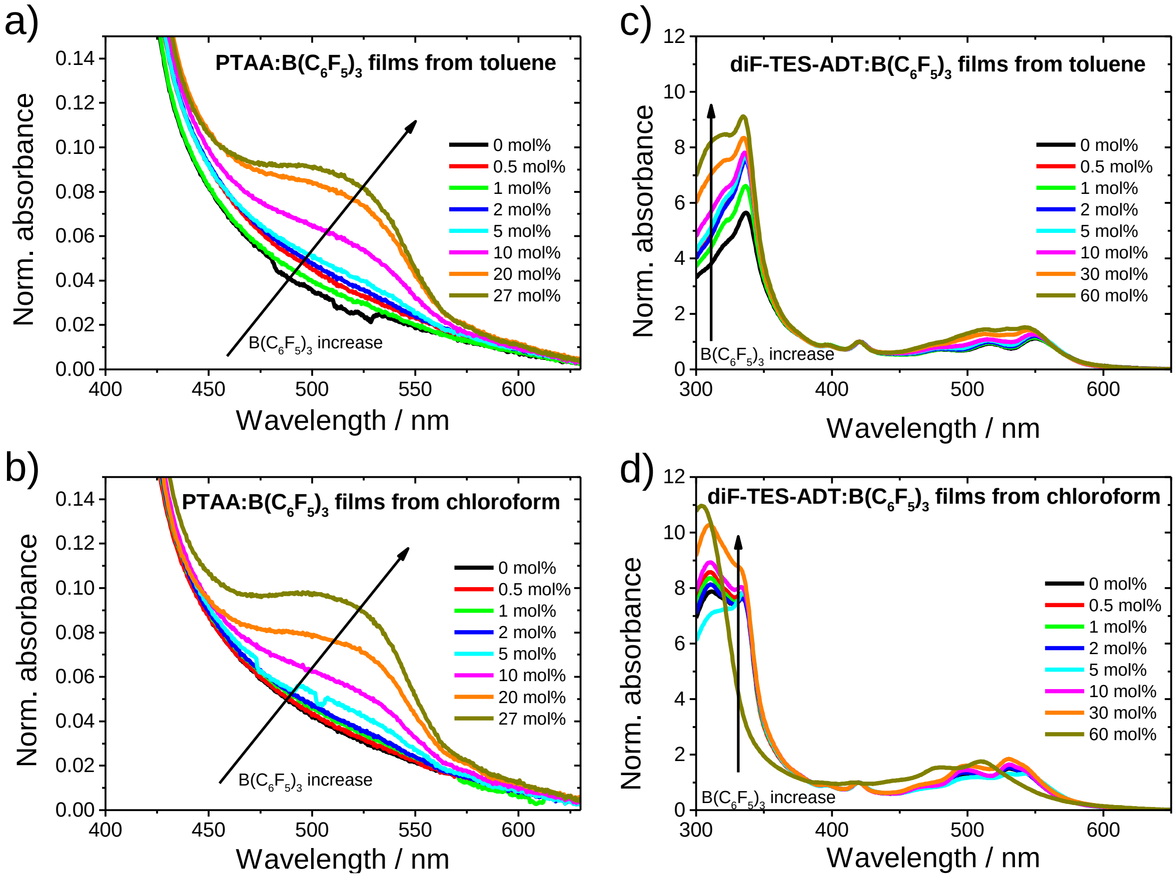

**Figure S10.** $B(C_6F_5)_3$ composition-dependent normalized UV-Vis absorption spectra of spin-coated PTAA:$B(C_6F_5)_3$ films developed from a) toluene solutions and b) chloroform solutions, and of diF-TES-ADT:$B(C_6F_5)_3$ films developed from c) toluene solutions and d) chloroform solutions.

## References

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