

Supporting Information

Thiol-yne crosslinked triarylamine hole transport layers for solution-processable organic light-emitting diodes

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S1. Layer thicknesses

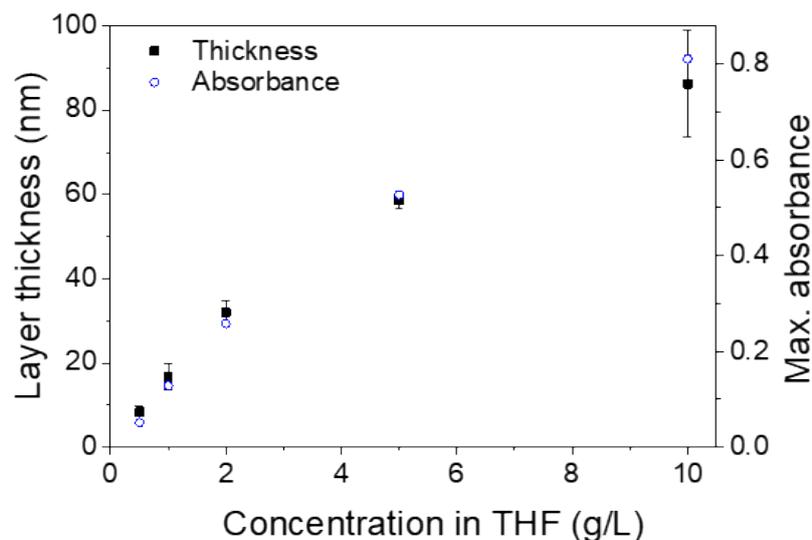


Figure S1: The thicknesses of the polymer **6** layers and the corresponding maximum absorbance at $\lambda = 342$ nm as a function of the monomer concentration in THF. The error bars show the standard deviation of the layer thickness measurements. The layer thickness is also in agreement with the absorbance of the layer.

S2. Materials and methods

Monitoring of reactions was performed using silica gel coated aluminium plates (Merck, silica gel 60, F254) which were analyzed under UV-light at 254 nm and/or dipped into a solution of Seebach reagent (2.5% phosphor molybdic acid, 1.0% Cerium(IV) sulfate tetrahydrate and 6.0% sulfuric acid in H₂O, dipping solution) and heated with a heat gun. Solvent mixtures are understood as v/v. Solvents, reagents and chemicals were purchased from Sigma-Aldrich, Alfa Aesar, TCI and VWR and used without further purification.

¹H NMR spectra were recorded on Bruker Avance AV 300 (300 MHz) and Avance AV 400 (400 MHz) spectrometers. Chemical shifts are given in parts per million (δ /ppm), downfield from tetramethylsilane (TMS), referenced to chloroform (7.26 ppm) as internal standard. The description of signals includes: s = singlet, m = multiplet. The spectra were analyzed according to first order. ¹³C NMR spectra were recorded on Bruker Avance AV 300 (75 MHz) and Avance 400 (100 MHz) spectrometers. Chemical shifts are expressed in parts per million (δ /ppm) downfield from tetramethylsilane (TMS), referenced to chloroform (77.16 ppm) as internal standard. HRMS: all HRMS data were recorded with the Finnigan MAT 95 (EI-method). IR (infrared spectroscopy): ATR spectra of powder compounds **3**, **5** and **6** were recorded by diamond crystal on Bruker ALPHA-IR.

DSC experiments were performed with a DSC821e (Mettler Toledo) calorimeter using 40 μ l aluminum crucibles under nitrogen atmosphere. A heating cycle of 25-180 °C with heating rate of 5 K min⁻¹ was used with 2.5-4 mg sample for each measurement.

The obtained data were deposited in the repository Chemotion (reaction details and compound characterization, <https://www.chemotion-repository.net/home/publications>). The related DOIs which link to the Chemotion repository submissions are added at the end of the characterization section for the individual compounds.

S3. Synthesis

Synthesis of tris(4-((trimethylsilyl)ethynyl)phenyl)amine 2

Tris(4-iodophenyl)amine **1** (2.12 g, 3.40 mmol, 1.00 equiv), bis(triphenylphosphine)palladium(II) dichloride (56.20 mg, 0.08 mmol, 0.0235 equiv) and copper(I)iodide (15.20 mg, 0.08 mmol, 0.0235 equiv) were mixed in a 100 mL flask and sealed. The flask was evacuated and backfilled with Ar three times. Then toluene (40.0 mL), 1,8-diazabicyclo[5.4.0]-7-undecene (5.09 g, 5.00 mL, 33 mmol, 9.83 equiv) and trimethylsilylacetylene (1.03 g, 1.45 mL, 11 mmol, 3.09 equiv) were added *via* syringe. The resulting mixture was stirred at room temperature (22 °C) for 5 hours. The reaction was quenched by addition of 2M HCl (5 mL) and the mixture was extracted with EtOAc (3 x 25 mL). Combined organic phases were washed with H₂O (3 x 25 mL) and brine (2 x 25 mL), dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent cyclohexane/DCM 10:1) to yield tris(4-((trimethylsilyl)ethynyl)phenyl)amine **2** (1.62 g, 3.0 mmol, 89% yield) as a yellow solid. ¹H NMR (300 MHz, CDCl₃, ppm) δ = 7.36 – 7.33 (m, 6H), 6.97 – 6.94 (m, 6H), 0.24 (s, 27H); ¹³C NMR (75 MHz, CDCl₃, ppm) δ = 146.9 (3C), 133.3 (6C), 124.0 (6C), 117.9 (3C), 105.0 (3C), 94.1 (3C), 0.1 (9C); IR (ATR, $\tilde{\nu}$) = 2956 (vw), 2156 (w), 1595 (w), 1493 (m), 1319 (w), 1269 (m), 1247 (m), 1228 (w), 1177 (w), 1012 (vw), 862 (m), 833 (m), 757 (m), 725 (w), 697 (w), 649 (m), 635 (m), 596 (w), 546 (w), 411 (w), 387 (vw) cm⁻¹; HRMS (C₃₃H₃₉N₁²⁸Si₃): Calcd 533.2390, Found 533.2391. Additional reaction details and data obtained from the characterization of the target compound can be accessed at: <https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-WWJQSYANN-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ>

Synthesis of tris(4-ethynylphenyl)amine 3

Tris(4-((trimethylsilyl)ethynyl)phenyl)amine **2** (267 mg, 0.05 mmol, 1.00 equiv) was placed in a crimp cap vial. The vial was sealed, evacuated and backfilled with Ar three times. Then dichloromethane (5.0 mL) was added *via* syringe and the mixture was cooled down to 0 °C. Tetrabutylammonium fluoride (1.5 mL of a 1M solution in THF, 1.5 mmol, 3.00 equiv) was added *via* syringe. The reaction mixture was stirred for 2 h at 0 °C and successively absorbed onto silica gel. The crude product was purified by column chromatography on silica gel (eluent cyclohexane/DCM 4:1) to yield tris(4-ethynylphenyl)amine **3** (138 mg, 435 μmol, 87% yield) as an off-white solid. ¹H NMR (400 MHz, CDCl₃, ppm) δ = 7.40 – 7.37 (m, 6H), 7.03 – 6.99 (m, 6H), 3.06 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm) δ = 147.2 (3C), 133.5 (6C), 124.1 (6C), 117.0 (3C), 83.5 (3C), 77.1 (3C); IR (ATR, $\tilde{\nu}$) = 3265 (w), 3067 (vw), 3036 (vw), 2920 (vw), 2850 (vw), 2101 (w), 1594 (m), 1495 (m), 1317 (m), 1269 (m), 1175 (m), 1110 (w), 919 (w), 833 (m), 761 (w), 723 (w), 672 (m), 634 (m), 557 (m), 539 (m), 516 (w), 428 (w), 387 (w) cm⁻¹; HRMS (C₂₄H₁₅N₁): Calcd 317.1204, Found 317.1202. Additional reaction details and data obtained from the characterization of the target compound can be accessed at: <https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-QGICIDGCKP-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ>

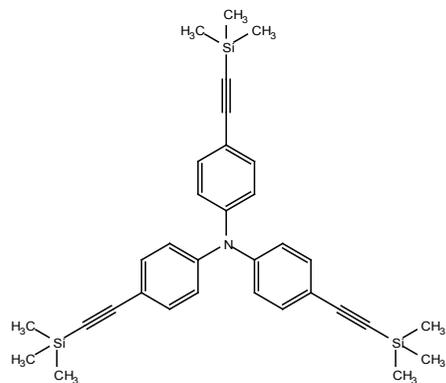
Synthesis of tris(4-thiophenyl)amine 5

Tris(4-bromophenyl)amine **4** (1.45 g, 3.00 mmol, 1.00 equiv) and sodium 2-propanethiolate (2.94 g, 30 mmol, 10.00 equiv) were suspended under Ar atmosphere in N,N-dimethylacetamide (25.0 mL), and the mixture was heated for 16 h at 100 °C. Subsequently, Na (1.38 g, 60 mmol, 20.00 equiv) was added under vigorous stirring and the mixture was heated for additional 24 hours. The mixture was carefully hydrolyzed with H₂O (250 mL), and tert-butyl methyl ether (MTBE) (150.0 mL) was added before acidifying the mixture with conc. hydrochloric acid to pH < 1. The layers were separated and

the aqueous layer was extracted with MTBE (2 x 75 mL). The combined organic layers were washed with H₂O (5 x 100 mL), dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent DCM) to yield tris(4-thiophenyl)amine **5** (786 mg, 2.3 mmol, 77% yield) as a pale yellow solid. ¹H NMR (300 MHz, CDCl₃, ppm) δ = 7.19-7.16 (m, 6H), 6.93 – 6.90 (m, 6H), 3.40 (s, 3H); ¹³C NMR (75 MHz, CDCl₃, ppm) δ = 145.7 (3C), 131.5 (6C), 124.8 (6C), 123.7 (3C); IR (ATR, $\tilde{\nu}$) = 3023 (w), 2551 (w), 1585 (m), 1486 (m), 1316 (m), 1263 (m), 1182 (m), 1100 (m), 1010 (w), 919 (w), 811 (m), 718 (m), 689 (w), 530 (m), 512 (m), 440 (w), 410 (w) cm⁻¹; HRMS (C₁₈H₁₅N₁³²S₃): Calcd 341.0367, Found 341.0369. Additional reaction details and data obtained from the characterization of the target compound can be accessed at: <https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-ZLULXIUFJW-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ>

S4. NMR spectra

tris(4-((trimethylsilyl)ethynyl)phenyl)amine



7.36
7.35
7.33
7.33
7.26
6.97
6.96
6.95
6.94

C (m)
7.34

A (m)
6.96

0.24

B (s)
0.24

5.63
5.66

27.00

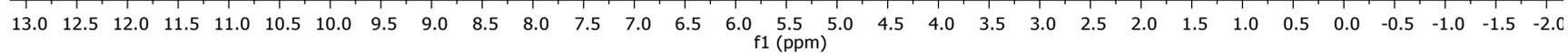
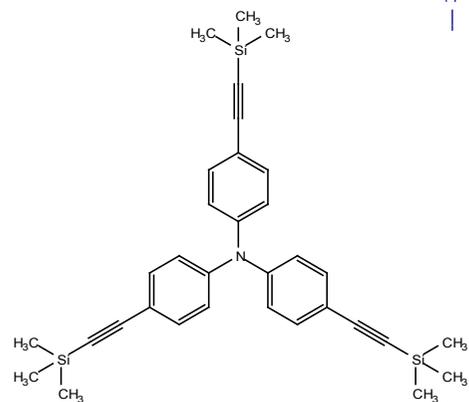


Figure S4a: ^1H NMR spectrum of tris(4-((trimethylsilyl)ethynyl)phenyl)amine **2**.

tris(4-((trimethylsilyl)ethynyl)phenyl)amine



146.93

133.32

123.95

117.94

104.99

94.11

77.16

0.10

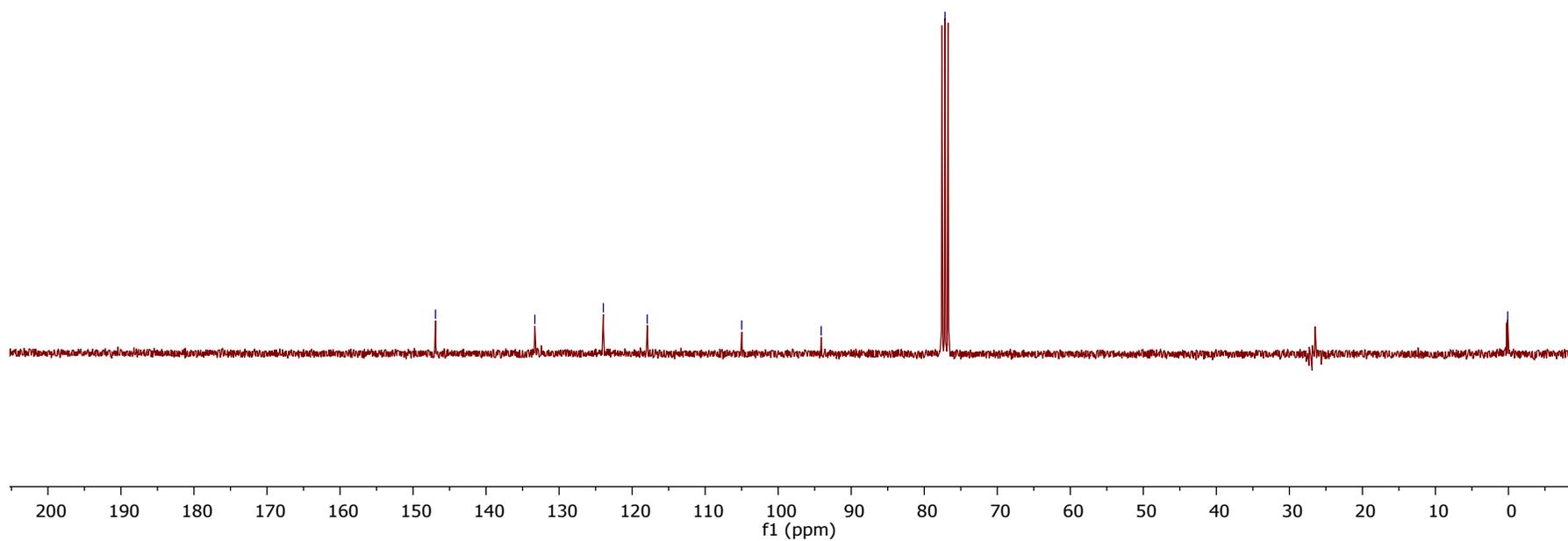
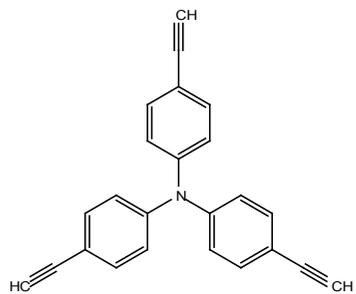


Figure S4b: ^{13}C NMR spectrum of tris(4-((trimethylsilyl)ethynyl)phenyl)amine **2**.

tris(4-ethynylphenyl)amine



7.40
7.39
7.39
7.38
7.37
7.37
7.26
7.03
7.02
7.02
7.00
7.00
6.99

3.06

C (m)
7.38

B (m)
7.01

A (s)
3.06

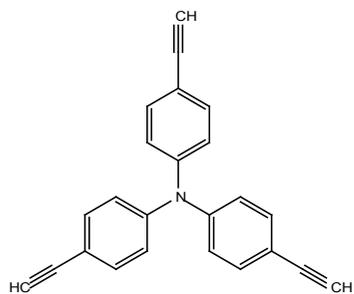
6.05
6.00

2.96

13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)

Figure S4c: ¹H NMR spectrum of tris(4-ethynylphenyl)amine **3**.

tris(4-ethynylphenyl)amine



— 147.16
— 133.51
— 124.07
— 116.99
— 83.54
77.16
77.13

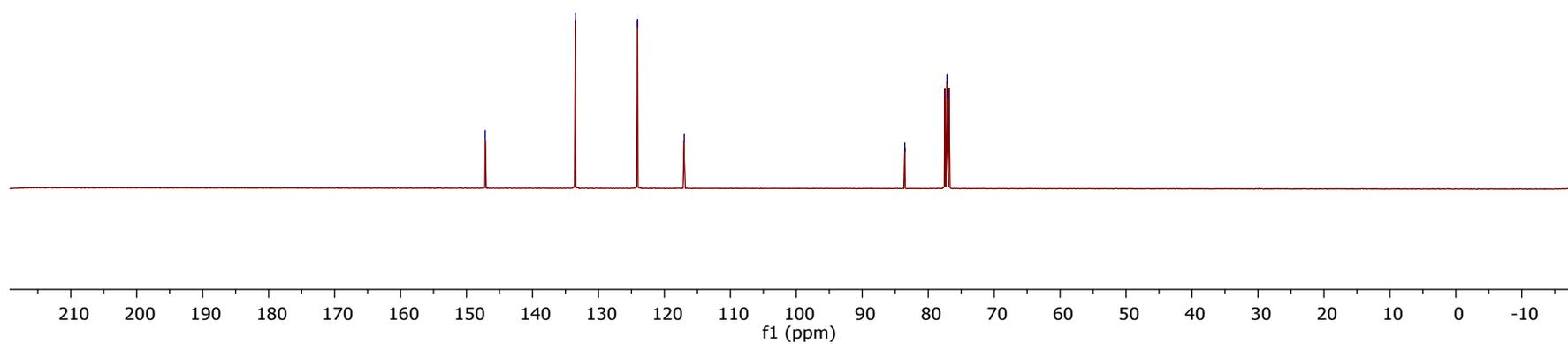


Figure S4d: ¹³C NMR spectrum of tris(4-ethynylphenyl)amine 3.

tris(4-thiophenyl)amine

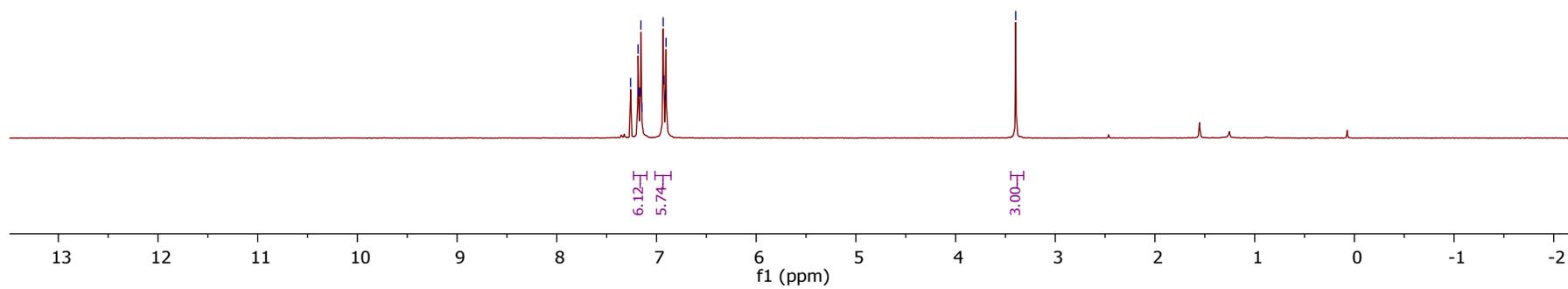
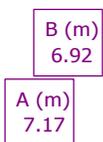
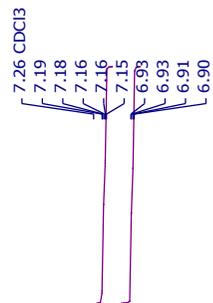
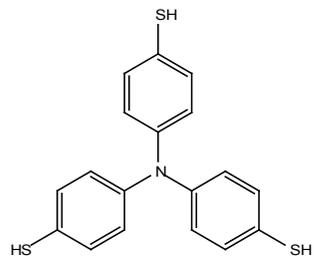
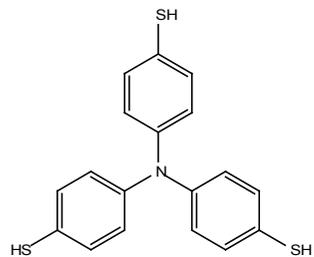


Figure S4e: ¹H NMR spectrum of tris(4-thiophenyl)amine **5**.

tris(4-thiophenyl)amine



— 145.71
— 131.48
— 124.81
— 123.72
— 77.16

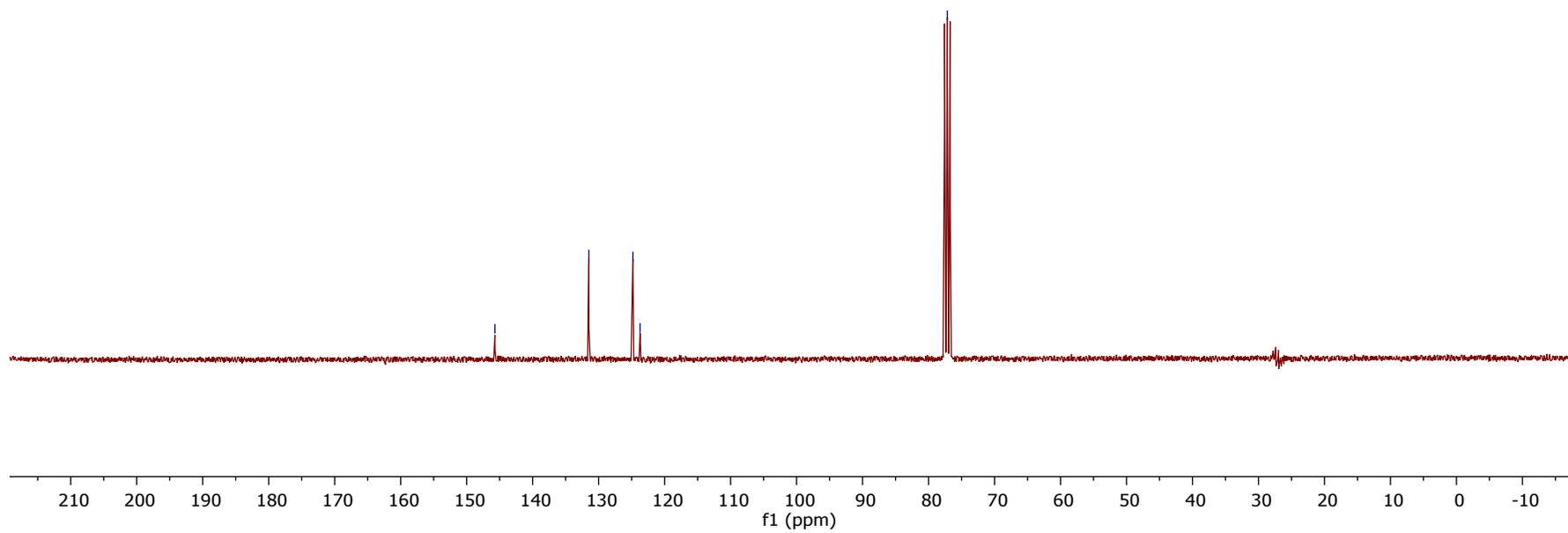


Figure S4f: ¹³C NMR spectrum of tris(4-thiophenyl)amine 5.

S5. ATR-FTIR spectra

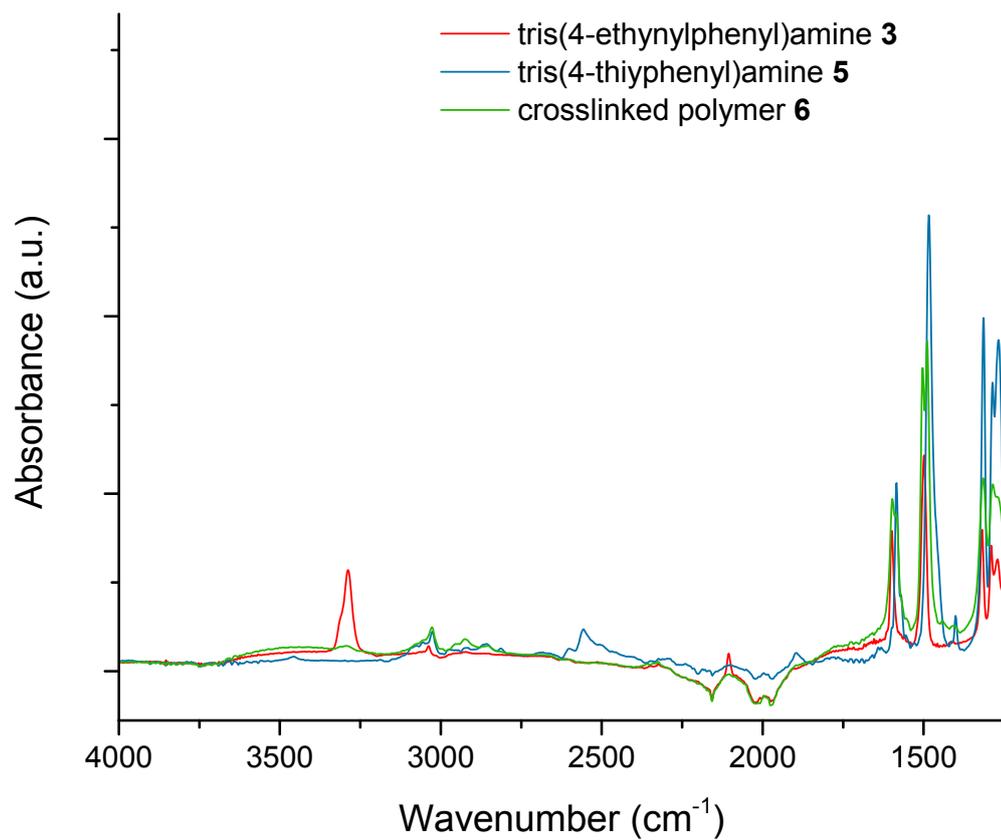


Figure S5: ATR-FTIR spectra of alkyne **3** (red), thiol **5** (blue) and the crosslinked polymer **6** (green).

S6. DSC curves

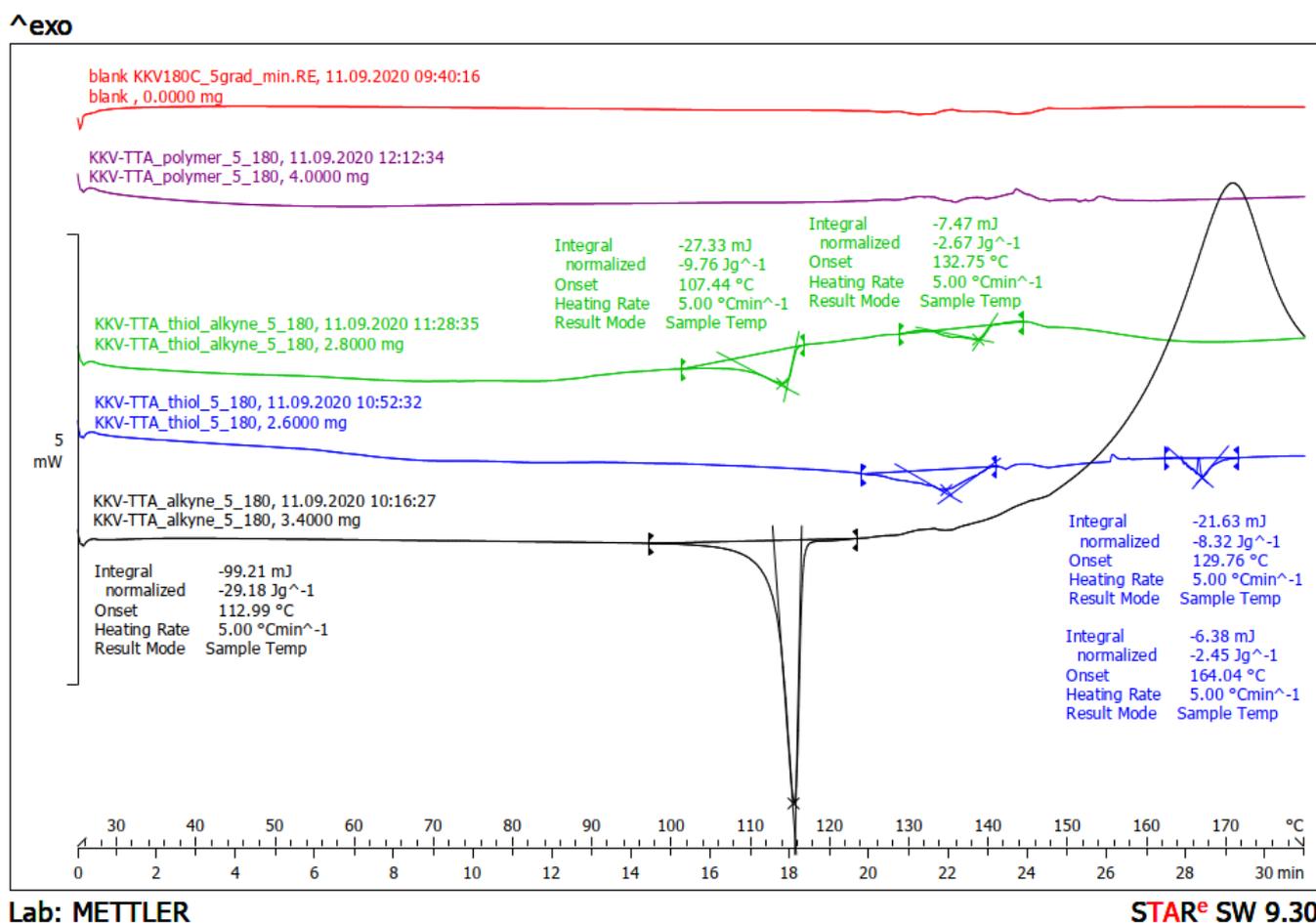


Figure S6: DSC curves of alkyne **3** (black), thiol **5** (blue), 1:1 molar mixture of alkyne **3** and thiol **5** (green) and the crosslinked polymer **6** (violet). The background curve is in red.

S7. Commission Internationale de l'Eclairage (CIE 1931) coordinates

The CIE 1931 coordinates of the OLEDs from Figure 5 were calculated with the software ColorCalculator (OSRAM Semiconductors).

Table S7: Full width at half maximum (FWHM) of the emission spectra and CIE 1931 coordinates of the OLEDs displayed in Figure 5.

Polymer 6 thickness (nm)	Emission FWHM (nm)	CIEx	CIEy
8	77	0.26	0.57
17	79	0.26	0.57
37	81	0.27	0.57
57	85	0.28	0.57
86	88	0.28	0.55
PEDOT:PSS	78	0.25	0.57