π-Extended Rigid Triptycene-Trisaroylenimidazoles as Electron Acceptors

-Supporting Information-

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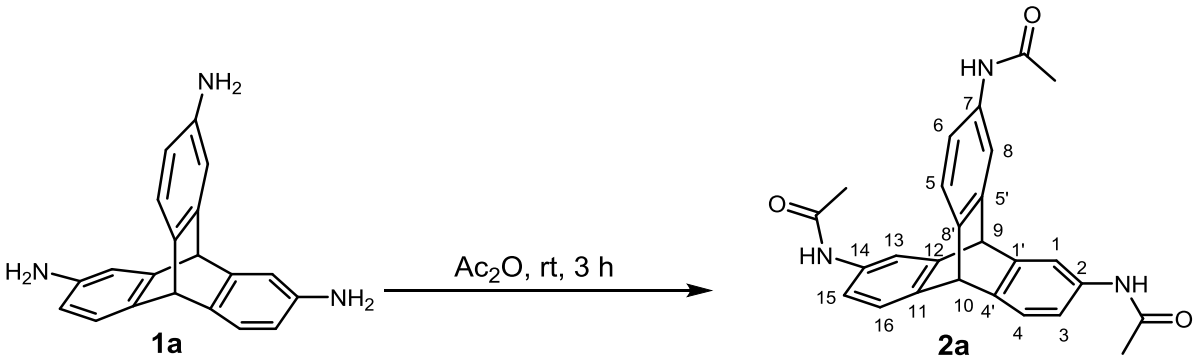
1. General Remarks

All reagents and solvents were obtained from Fisher Scientific, Alfa Aesar, Sigma-Aldrich or VWR and were used without further purification unless otherwise noted. For thin layer chromatography silica gel 60 F254 plates from Merck were used and examined under UV-light irradiation (254 nm and 365 nm). Flash column chromatography was performed on silica gel from Sigma-Aldrich (particle size: 0.04-0.063 mm) using light petroleum ether, dichloromethane, ethyl acetate and/or acetic acid. Size Exclusion Chromatography(SEC) was performed on BioBeads SX1 from BioRad Laboratories, Inc. using chloroform as solvent. Ultra-Performance Liquid Chromatography (UPLC) was performed on a Waters UPLC-SQD2 machine connected to a single quadrupole mass spectrometer with an APCI (Atmospheric Pressure Chemical Ionization) source. A BEH-C8, 2.1/50 mm column with a gradient of 15-5% H_2O/MeCN and a flow of 20.0 mL/min was used. High-Performance Liquid Chromatography (HPLC) was performed on an Agilent Technologies 1200 machine with a Macherey-Nagel VP 250/21 Nucleodur C8 Gravity, 5 μm or a Macherey-Nagel VP 250/21 Nucleosil column. For the normal phase, a Nucleosil 100-7 from Macherey-Nagel (VP 250/21, Cat.No. 715275.210) and a flow of 20.0 mL/min. were used. Melting points (not corrected) were measured with a Büchi Melting Point B-545. IR-Spectra were recorded on a Ge ATR crystal with a Bruker Lumos spectrometer. NMR spectra were taken on a Bruker DRX 400 (400 MHz), Bruker DRX 500 (500 MHz), Bruker Avance 300 (300 MHz) and Bruker Avance 500 (500 MHz) spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to traces of $CHCl_3$ or DMSO in the corresponding deuterated solvent. HRMS experiments were carried out on a Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer solariX (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 7.0 T superconducting magnet and interfaced to an Apollo II Dual ESI/MALDI source with DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile), CCA (α-cyano-4-hydroxycinnamic acid) or dithranol as matrix. DART experiments were performed on a FT-ICR Apex-Qe mass spectrometer. Absorption spectra were recorded on a Jasco UV-VIS V-660 or Jasco UV-VIS V-670. Emission spectra were recorded on a Jasco FP-6500. Electrochemical data were obtained in DCM containing 1 mM experimental compound and 0.1 M Bu_4OCl_4, as indicated. 1 mM ferrocene was used as an internal standard. Cyclic voltammograms were obtained at a scan rate of 0.2 mV/s using Pt as working electrode, a Pt/Ti counter electrode and an Ag reference electrode. Elemental analysis was performed by the Microanalytical Laboratory of the University of Heidelberg using an Elementar Vario EL

machine. Calculations were carried out by Spartan'14, Version 1.1.8 with DFT B3LYP/6-31 G**-level.

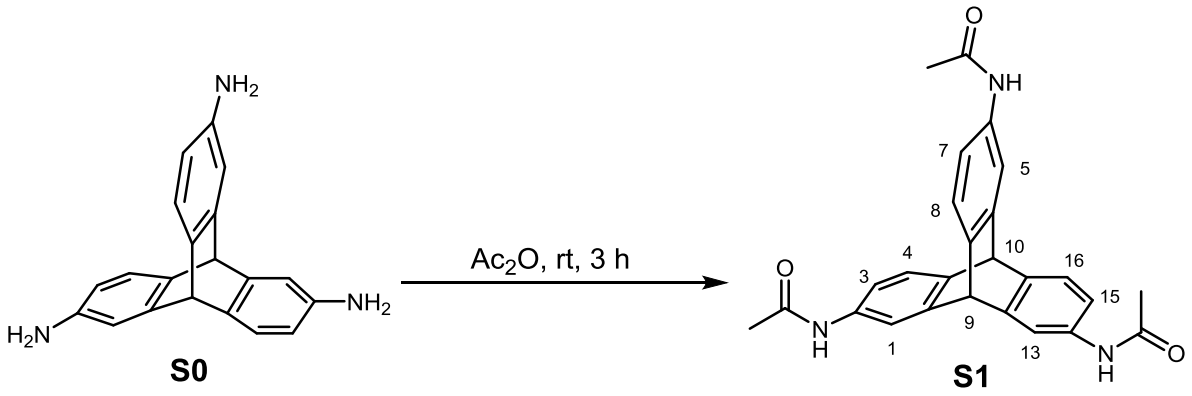
2. Synthesis and Characterization

Synthesis of 2,7,14-triacetamidotriptycene (2a)



Triaminotriptycene **1a** (1.12 g, 3.72 mmol) was dissolved in acetic anhydride (100 mL) and stirred at room temperature for 3 h. The formed precipitate was collected by filtration and dried in vacuum to give 1.6 g of **2a** (quant.) as colorless solid. M.p.: 212 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.79 ppm (s, 3H, -N*H*), 7.72 (s, 3H, Ar-*H*-1,8,13), 7.32-7.26 (m, 3H, Ar-*H*-3,6,15), 7.06-7.08 (m, 3H, Ar-*H*-4,5,16), 5.45 (s, 1H, bridgehead-*H*-9), 5.41 (s, 1H, bridgehead-*H*-10), 1.98 (s, 9H, -C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.1 ppm (*C*-O), 145.6 (Ar-*C*-1',5',12), 140.4 (Ar-*C*-4',8',11), 136.1 (Ar-*C*-2,7,14), 123.2 (Ar-*C*-45,16), 115.4 (Ar-*C*-3,6,15), 115.2 (Ar-*C*-1,8,13), 52.9 (bridgehead-*C*-9), 50.9 (bridgehead-*C*-10), 23.9 (*C*H$_3$). FT-IR (ATR): $\tilde{\nu}$ = 3297 cm^{-1} (m), 3130 (w), 3076 (w), 1660 (s), 1601 (s), 1542 (s), 1476 (s), 1416 (s), 1370 (s), 1336 (s), 1305 (s), 1270 (w), 1185 (w), 1143 (w), 1013 (m), 979 (w), 886 (w), 849 (m), 809 (m), 780 (w), 649 (m). MS (HR-ESI$^+$): *m/z* (%) = 426.18 (12.4) [M+H]$^+$, 443.21 (35.8) [M+NH$_4$]$^+$, 464.14 (9.3) [M+K]$^+$.

Synthesis of 2,6,14-triacetamidotriptycene (S1)

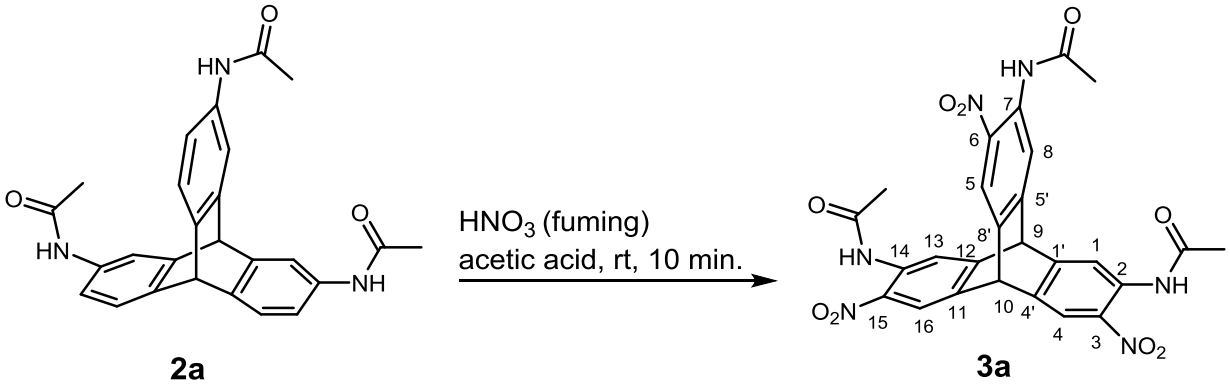


Triaminotriptycene **S0** (3.85 g, 12.8 mmol) was dissolved in acetic anhydride (100 mL) and stirred at room temperature for 3 h. The formed precipitate was collected by filtration and dried in vacuum to give 5.33 g of **S1** (quant.) as colorless solid. M.p.: 208 °C.

^{1}H-NMR (300 MHz, DMSO-d$_6$): δ = 9.79 ppm (s, 3H, -N*H*), 7.72 (s, 3H, Ar-*H*-1,5,13), 7.32-7.26 (m, 3H, Ar-*H*-3,7,15), 7.06-7.08 (m, 3H, Ar-*H*-4,8,16), 5.43 (s, 1H, bridgehead-*H*-9), 5.40 (s, 1H, bridgehead-*H*-10), 1.98 (s, 9H, -C*H*$_3$).

The ^{1}H-NMR-data are in agreement with those reported in literature.[S1]

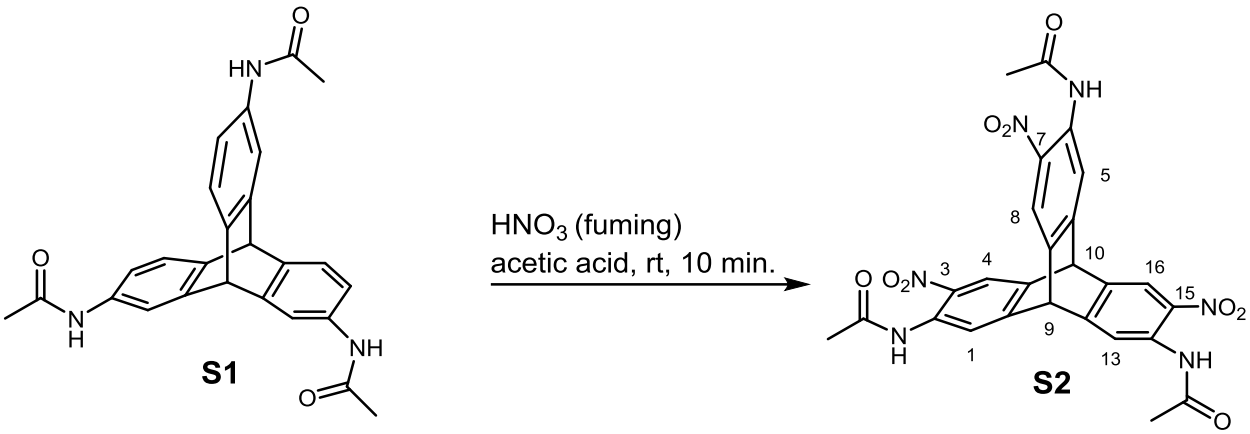
Synthesis of 2,7,14-triacetamido-3,6,15-trinitrotriptycene (3a)



2a **3a**

To a suspension of triacetamidotriptycene **2a** (1.6 g, 3.76 mmol) in acetic acid (44.0 mL) fuming nitric acid (12.8 mL, 294 mmol) was added at 0 °C within one min. The resulting brownish solution was stirred at room temperature for 10 min., before it was poured into H_2O (300 mL). The yellow precipitate was filtered off and washed with H_2O (50 mL), sat. Na_2CO_3-solution (aq) (50 mL) and H_2O (50 mL). Purification by flash chromatography (PE/EE 1:1, R_f = 0.33) gives after drying in vacuum 1.67 g (79%) of 2,7,14-triacetamido-2,6,15-trinitrotriptycene **3a** as yellow solid. M.p. = 255 °C, ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 10.50 ppm (s, 3H, -N*H*), 8.29-8.26 (m, 3H, Ar-*H*-4,5,16), 8.06-8.05 (m, 3H, Ar-*H*-1,8,13), 6.33 (s, 1H, bridgehead-*H*-10), 6.28 (s, 1H, bridgehead-*H*-9), 2.21 (s, 9H, -C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.7 ppm (*C*-O), 148.1 (Ar-*C*-1',5',12), 139.9 (Ar-*C*-3,6,15), 139.0 (Ar-*C*-4',8',11), 130.1 (Ar-*C*-2,7,14), 121.2 (Ar-*C*-4,5,16), 120.6 (Ar-*C*-1,8,13), 51.0 (bridgehead-*C*-10), 49.0 (bridgehead-*C*-9), 23.5 (*C*H$_3$). IR (ATR): $\tilde{\nu}$ = 3361 cm^{-1} (m), 1689 (s), 1618 (s), 1588 (m), 1495 (s), 1475 (s), 1417 (m), 1332 (s), 1315 (s), 1263 (s), 1231 (s), 1143 (s), 1038 (m), 999 (m), 906 (m), 861 (m), 829 (m), 763 (w), 748 (w), 664 (w). MS (HR-MALDI): *m/z* (%) = 561.14 (4) [M+H]$^+$, 583.13 (100) [M+Na]$^+$, 599.10 (57) [M+K]$^+$. Anal. calcd. for $C_{26}H_{20}N_6O_9 \cdot H_2O$: C 53.98%, H 3.83%, N 14.53%, found: C 54.13%, H 4.07%, N 14.13%.

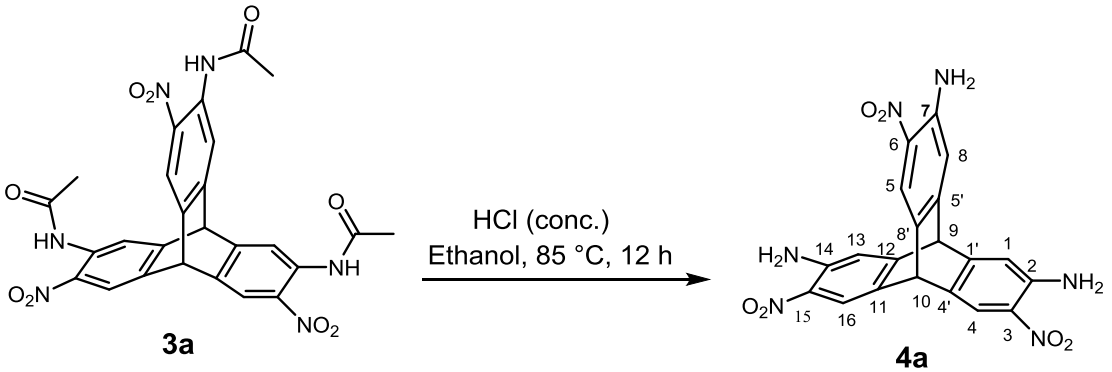
Synthesis of 2,6,14-triacetamido-3,7,15-trinitrotriptycene (S2)



To a suspension of triacetamidotriptycene **S1** (3.00 g, 7.05 mmol) in acetic acid (240 mL) fuming nitric acid (25.0 mL, 575 mmol) was added at 0°C within one min. The resulting brownish solution was stirred at room temperature for 10 min., before it was poured into H_2O (500 mL). The yellow precipitate was filtered off and washed with H_2O (100 mL), sat. Na_2CO_3-solution (aq) (100 mL) and H_2O (100 mL). Purification by flash chromatography (PE/EE 1:1, R_f = 0.31) gives after drying in vacuum 3.40 g (86%) of 2,6,14-triacetamido-2,7,15-trinitrotriptycene **S2** as yellow solid. M.p. = 240 °C, ^{1}H NMR (300 MHz, DMSO-d_6): δ = 10.28 ppm (s, 3H, -N*H*), 8.13 (s, 1H, Ar-*H*-8), 8.11 (s, 2H, Ar-*H*-4,16), 7.90 8.13 (s, 1H, Ar-*H*-5), 7.89 (m, 2H, Ar-*H*-1,13), 6.32 (s, 1H, bridgehead-*H*-10), 6.29 (s, 1H, bridgehead-*H*-9), 2.21 (s, 9H, -C*H*$_3$).

The ^{1}H-NMR-data are in agreement with those reported in literature.[S2]

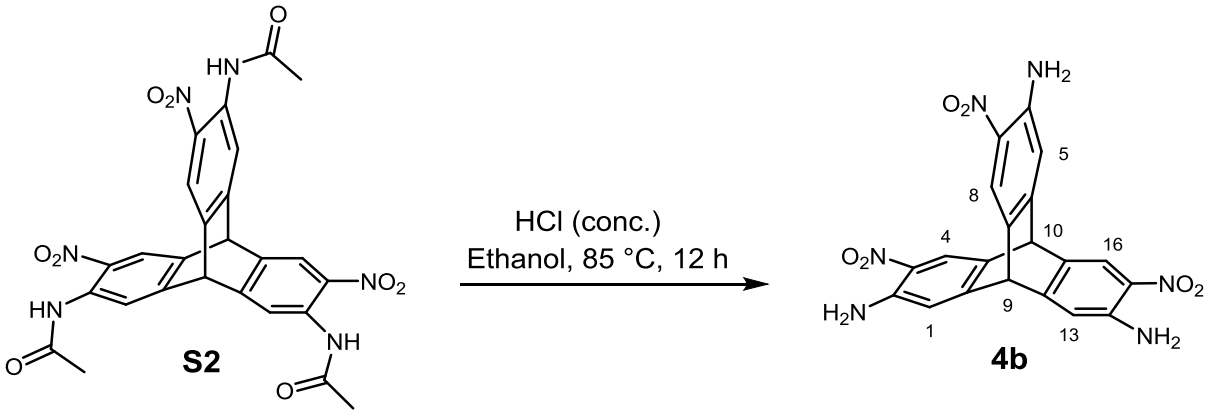
Synthesis of 2,7,14-triamino-3,6,15-trinitrotriptycene 4a



Triacetamidotrinitrotriptycene **3a** (1.00 g, 1.78 mmol) was dissolved in a mixture of conc. HCl (16 mL) and ethanol (10 mL) and stirred at 85°C overnight under argon. The brownish solution was poured into H_2O (300 mL) and the resulting brownish solid was filtered off and

washed with H_2O (50 mL), sat. aq Na_2CO_3 (50 mL) and again with H_2O (50 mL) and dried under vacuum. Purification by flash chromatography on SiO_2 (PE/EE 2:1, R_f = 0.20) gives after drying under vacuum 481 mg (62%) of 2,7,14-triacetamino-3,6,15-trinitrotriptycene (**4a**) as orange solid. M.p. = 376 °C, ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.90 ppm (s, 3H, Ar-*H*-4,5,16), 7.55 (s, 6H, -N*H*$_2$), 7.10 (s, 3H, Ar-*H*-1,8,13), 5.59 (s, 1H, bridgehead-*H*-10), 5.48 (s, 1H, bridgehead-*H*-9). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.7 ppm (Ar-*C*-3,6,15), 145.5 (Ar-*C*-4',8',11), 130.9 (Ar-*C*-2,7,14), 127.3 (Ar-*C*-1',5',12), 118.9 (Ar-*C*-4,5,16), 114.8 (Ar-*C*-1,8,13), 50.8 (bridgehead-*C*-10), 46.75 (bridgehead-*C*-9). FT-IR (ATR): $\tilde{\nu}$ = 3480 cm^{-1} (m), 3365 (m), 1635 (m), 1592 (m), 1494 (s), 1457 (m), 1424 (m), 1391 (m), 1316 (s), 1241 (s), 1196 (m), 1145 (m), 1063 (m), 891 (m), 801 (m), 764 (m), 732 (m), 678 (m), 656 (m), 616 (m). MS (HR-ESI$^+$): *m/z* (%) = 435.1051 (7.1) $[M+H]^+$, 457.0871 (42.5) $[M+Na]^+$, 891.1847 (37.9) $[2M+Na]^+$. Anal. calcd. for $C_{20}H_{14}N_6O_6 \cdot \frac{1}{4} C_4H_8O_2$: C 55.27%, H 3.53%, N 18.41%, found: C 55.59%, H 3.68%, N 18.65%.

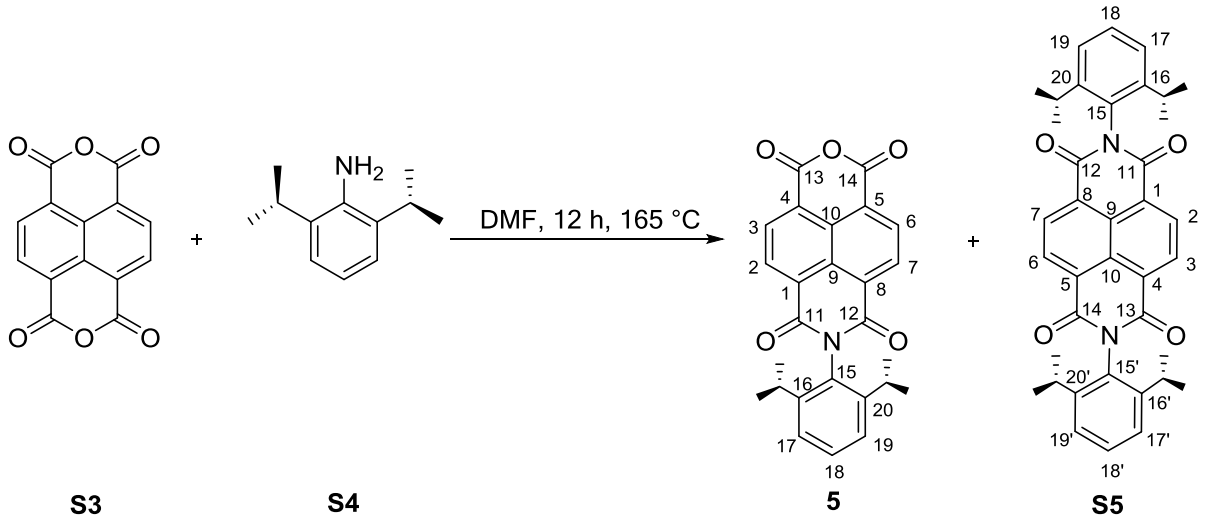
Synthesis of 2,6, 14-triamino-3,7,15-trinitrotriptycene (4b)



Triacetamidotrinitrotriptycene **S2** (2.23 g, 3.97 mmol) was dissolved in a mixture of HCl (conc.) (31 mL) and ethanol (5 mL) and stirred at 85°C overnight under argon. The brownish solution was poured into H_2O (500 mL) and the resulting brownish solid was filtered off and washed with H_2O (100 mL), sat. aq Na_2CO_3 (100 mL) and again with H_2O (100 mL) and dried under vacuum. Purification by flash chromatography on SiO_2 (PE/EE 2:1, R_f = 0.17) gives after drying under vacuum 1.55 g (3.56 mmol) (90%) of 2,6,14-triacetamino-3,7,15-trinitrotriptycene (**4b**) as orange solid. M.p. = 359 °C, ^{1}H NMR (300 MHz, DMSO-d_6): δ = 8.03 ppm (s, 1H, Ar-*H*-8), 7.95 (s, 2H, Ar-*H*-4,16), 7.58 (s, 6H, -N*H*$_2$), 7.05 (s, 3H, Ar-*H*-1,13), 7.03 (s, 1H, Ar-*H*-5), 5.50 (s, 1H, bridgehead-*H*-10), 5.49 (s, 1H, bridgehead-*H*-9).

^{1}H-NMR-data are in agreement with those reported in literature.[S2]

Synthesis of *N*-(2,6-diisopropylphenyl)-1,4,5,8,-naphthalenecarboxylic-1,8-anhydride-4,5-imide (5)[S3]

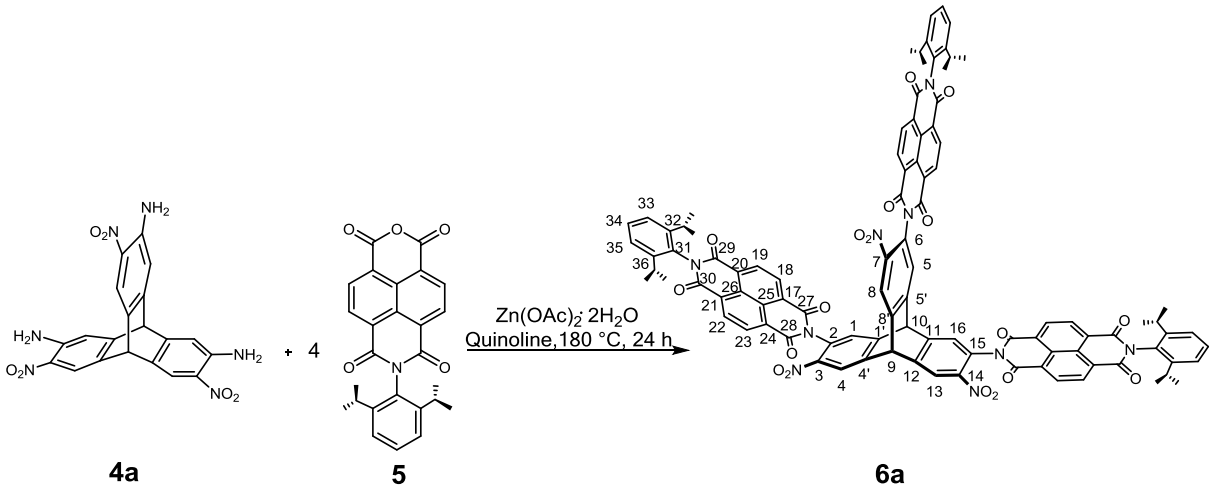


S3 **S4** **5** **S5**

A suspension of naphthalene-1,4,5,8-tetracarboxylic dianhydride **S3** (3.00 g, 11.2 mmol) in DMF (18.0 mL) was stirred for 3 h at 165 °C. Then a solution of 2,6-diisopropylaniline **S4** (661 mg, 703 ml, 3.73 mmol) in DMF (12.0 mL) was added dropwise within 5 min. and the reaction mixture was refluxed overnight. After cooling to room temperature, the solvent was removed by evaporation, DCM (30 mL) was added to the residue and the mixture was filtered. After removing solvents by evaporation, the residue was dissolved in chloroform (60 mL) and washed twice with water (50 mL). The organic phase was separated and dried with $MgSO_4$. The crude product was purified by column chromatography on silica gel with DCM as eluent. TLC (DCM): $R_f = 0.53$ (**S5**), 0.35 (**5**). Separation by flash column chromatography gave after drying in vacuum: 1. fraction with $R_f = 0.53$: 214 mg (13%) of *N,N'*-(di-2,6-diisopropylphenyl)-naphthalene-1,4,5,8,-tetracarboxylic acid bisimide (**S5**) as a colorless solid. M.p. >400 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.89 ppm (s, 4H, Ar-*H*-2,3,6,7), 7.53 (t, J = 7.49 Hz, 2H, Ar-*H*-18,18'), 7.36 (d, J = 7.49 Hz, 4H, Ar-*H*-17,17',19,19'), 2.70 (dt, J = 13.6 Hz; 6.8 Hz, 4H, Ar-C*H*-CH_3), 1.17 (d, J = 6.77 Hz, 24H, -CH-*CH*$_3$). ^{13}C NMR (151 MHz, $CDCl_3$): δ = 163.0 ppm (*C*-O-11,12,13,14), 145.5 (Ar-*C*-16,16',20,20'), 131.6 (Ar-*C*-2,3,6,7), 130.0 (Ar-*C*-15,15'), 130.0 (Ar-*C*-18,18'), 127.7 (Ar-*C*-1,4,5,8), 126.9 (Ar-*C*-9,10), 124.3 (Ar-*C*-17,17',19,19'), 29.3 ($C_{isoproyl}$), 24.0 (-*C*H_3). FT-IR (ATR): $\tilde{\nu}$ = 2966 cm^{-1} (m), 2930 (w), 2871 (w), 1713 (s), 1674 (w), 1580 (s), 1444 (w), 1385 (m), 1363 (s), 1339 (s), 1245 (s), 1210 (s), 1197 (s), 1139 (m), 1122 (m), 1056 (m), 981 (m), 938 (m), 879 (w), 852 (m), 804 (m), 768 (m), 738 (m), 718 (m), 693 (s). UV/VIS (DCM): $\lambda_{max,1}$ (lg ε) = 362 nm (4.2), $\lambda_{max,2}$ (lg ε) = 382 nm (4.4). MS (HR-EI$^+$): *m/z* (%) = 586.28 (100) [M]$^+$, 543.20 (34) [M-C_3H_7]$^+$. Anal. calcd. for $C_{43}H_{38}N_2O_2 \cdot \frac{1}{4} CH_2Cl_2$: C 75.57%, H

6.38% N 4.61%, found: C 75.86%, H 6.32% N 4.52%. 2. fraction with R_f = 0.35: 450 mg (28%) of *N*-(2,6-diisopropylphenyl)-1,4,5,8,-naphthalentetracarboxylic acid-1,8-anhydride-4,5-imide (**5**) as yellow solid with a melting point of 342 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.88 ppm (m, 4H, Ar-*H*-2,3,6,7), 7.52 (m, 1H, Ar-*H*-18), 7.36 (d, *J* = 7.78 Hz, 2H, Ar-*H*-17,19), 2.67 (dt, *J* = 13.7 Hz; 6.9 Hz, 2H, -C*H*-CH_3), 1.15 (d, *J* = 6.84 Hz, 12H, -C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.5 ppm (*C*-O-11,12), 159.0 (Ar-*C*-13,14), 145.7 (Ar-*C*-16,20), 133.4 (Ar-*C*-2,7), 131.9 (Ar-*C*-3,6), 130.3 (Ar-*C*-18), 129.9 (Ar-*C*-15), 129.3 (Ar-*C*-1,8), 128.0 (Ar-*C*-4,5), 127.7 (Ar-*C*-9), 124.5 (Ar-*C*-17,19), 123.3 (Ar-*C*-10), 29.5 (*C*H-CH_3), 24.1 (-*C*H_3). IR (ATR): $\tilde{\nu}$ = 2964 cm^{-1} (m), 2929 (m), 2871 (w), 1790 (s), 1744 (s), 1720 (s), 1680 (s), 1625 (s), 1581 (s), 1515 (m), 1463 (w), 1444 (m), 1389 (w), 1365 (s), 1336 (s), 1284 (s), 1242 (w), 1193 (w), 1154 (w), 1137 (m), 1104 (w), 1055 (w), 1021 (s), 939 (w), 876 (m), 840 (m), 800 (w), 760 (s), 707 (s). UV/VIS (DCM): $\lambda_{Abs,1}$ (lg ε) = 354 nm (4.3), $\lambda_{Abs,2}$ (lg ε) = 371 nm (4.3). MS (HR-EI$^+$): *m/z* (%) = 427.14 (100) [M]$^+$, 384.10 (51) [M-CH_3]$^+$, 412.10 (11) [M-C_3H_7]$^+$ ·. Anal. calcd. for $C_{25}H_{18}NO_5 \cdot \frac{1}{3} CH_2Cl_2$: C 69.40%, H 4.79%, N 3.07%, found: C 69.38%, H 4.85%, N 3.07%.

Synthesis of 2,2',2''-(5,11,18-trinitrotriptycene) 4,12,17-triyl tris {7-[2,6-diisopropylphenyl] -naphthalene-1,3,6,8-tetracarboxylicbisimide 6a

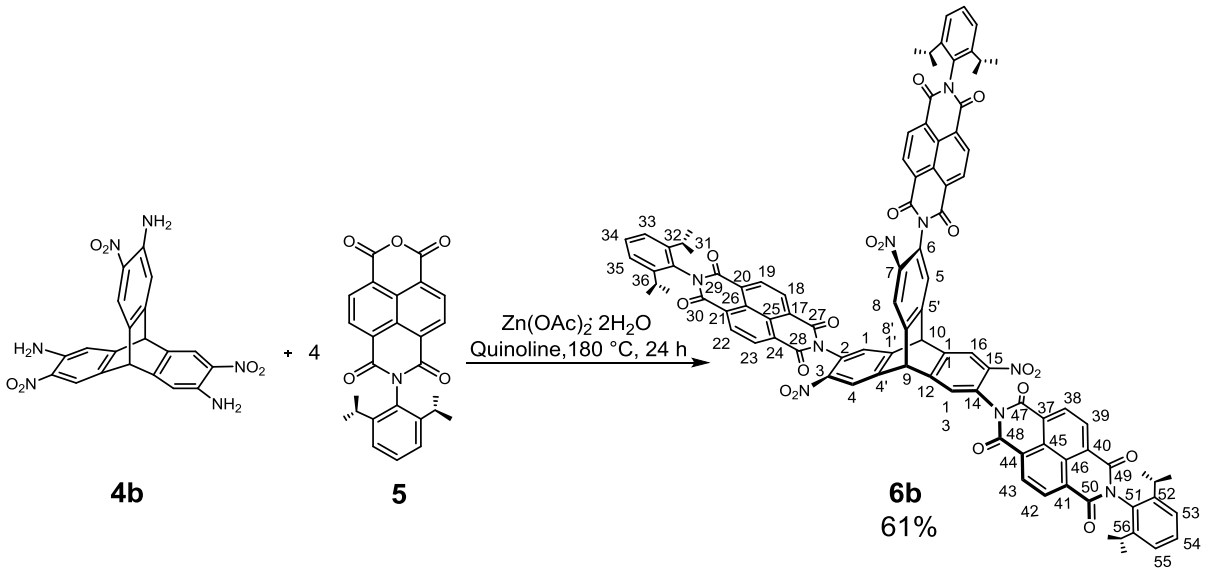


4a **5** **6a**
51%

Triaminotrinitrotriptycene **4a** (100 mg, 230 µmol), NMI **5** (393 mg, 920 µmol, 4 eq) and $Zn(OAc)_2 \cdot 2H_2O$ (37.0 mg, 0.82 µmol) were suspended in quinoline (1.7 mL) and heated up at 180°C for 24 h under argon. The resulting brownish solution was washed with aq HCl (18%) (80 mL) and the aqueous phase was extracted with DCM (2 x 20 mL). The combined organic phase was dried over $MgSO_4$, concentrated under reduced pressure and separated by column chromatography on SiO_2 with DCM as eluent (R_f = 0.1). After washing with aceonitrile and

separation by SEC with $CHCl_3$ as eluent compound **6a** was obtained as orange solid (yield: 52%, 200 mg, 120 μmol). M.p.: 397 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.86 ppm (dd, *J* = 22.5 Hz; 7.6 Hz, 6H, Ar-*H*-18,23,19,22), 8.61 (s, 3H, Ar-*H*-4,8,13), 7.64 (s, 3H, Ar-*H*-1,5,16), 7.53 (t, *J* = 7.8 Hz, 3H, Ar-*H*-34), 7.38-7.34 (m, 6H, Ar-*H*-33,35), 6.21 (s, 1H, bridgehead-*H*-9), 5.91 (s, 1H, bridgehead-*H*-10), 2.74-2.66 (m, 6H,-C*H*-CH_3), 1.18-1.14 (m, 36H, -*CH_3*) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 162.8 ppm (*C*-O-27,28), 162.6 (*C*-O-29,30), 147.8 (Ar-C-3,7,14), 145.8 (Ar-*C*-4',8',12), 145.5 (Ar-*C*-1',5',11), 144.9 (Ar-*C*-2,6,15), 144.2 (Ar-*C*-32), 132.0 (Ar-*C*-18,23), 131.8 (Ar-*C*-19,22), 130.2 (Ar-*C*-34), 130.0 (Ar-*C*-31), 128.1 (Ar-*C*-4,8,13), 127.8 (Ar-C-17,24), 127.7 (Ar-*C*-20,21), 127.6 (Ar-*C*-25), 126.4 (Ar-*C*-26), 124.5-124.4 (Ar-*C*-33,35), 122.7 (Ar-*C*-1,5,16), 52.8 (bridgehead-*C*-9), 52.5 (bridgehead-*C*-10), 29.5-29.4 ($C_{isoprop.}$), 24.1 (-CH_3). IR (ATR): $\tilde{\nu}$ = 2966 cm^{-1} (w), 2930 (m), 2870 (w), 1718 (s), 1674 (s), 1581 (m), 1533 (m), 1466 (m), 1448 (w), 1337 (s), 1245 (s), 1195 (s), 1117 (w), 1057 (w), 981 (m), 879 (m), 859 (w), 833 (m), 800 (s), 767 (w), 723 (s), 699 (w). UV/VIS (DCM): $\lambda_{Abs,1}$ (lg ε) = 361 nm (4.5), $\lambda_{Abs,2}$ (lg ε) = 381 nm (4.5). Fluorescence (DCM): λ_{em1} (λ_{ex}) = 475 nm (391), λ_{em2} (λ_{ex}) = 572 nm (391). CV (DCM, NBu_4OCl_4): $E_{1/2}^{red1}$ = -0.97 V (Fc), $E_{1/2}^{red1}$ = -1.42 V (Fc). MS (HR-MALDI): *m/z* (%) = 1616.5239 (100) [M-NO_2], 1662.5245 (35) [M+H], 1663.5203 (12) [M+2H]. Anal. calcd. for $C_{98}H_{71}N_9O_{18}\cdot\frac{1}{2}CHCl_3$: C 68.69%, H 4.18%, N 7.32%, found: C 68.93%, H 4.66%, N 7.23%.

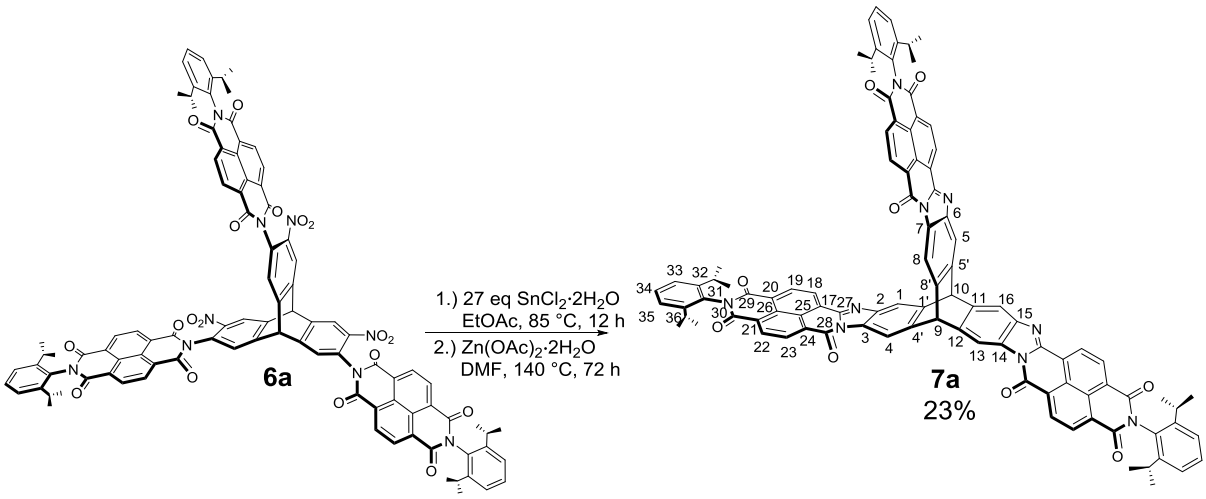
Synthesis of 2,2',2''-(5,12,18-trinitrotriptycene) 4,11,17-triyl tris {7-[2,6-diisopropylphenyl]-naphthalene-1,3,6,8-tetracarbonsäurebisimide 6b



4b + 4 **5** → **6b** 61%

Triaminotrinitrotriptycene **4b** (90.0 mg, 207 μmol), NMI **5** (354 mg, 828 μmol, 4 eq) and $Zn(OAc)_2 \cdot 2H_2O$ (33.0 mg, 0.73 μmol) were suspended in quinoline (1.5 mL) and heated at 180°C for 24 h under argon. The formed brownish solution was washed with HCl (18%, aq) (80 mL) and the organic phase was extracted with DCM (2x 20 mL). The combined organic phase was dried over $MgSO_4$. The crude product was then purified by flash column chromatography on silica gel with DCM as eluent to afford compound **6b** (R_f = 0.10) as orange solid (207 mg, 125 μmol, 61%) in almost pure form and was used without further purifications for the transformation in the next reaction. An analytical pure sample could be obtained by purification by HPLC (RP, gradient: 0-7 min. 15% H_2O, 85% MeCN, 7.01-10 min. 10% H_2O, 90% MeCN, 10.01-14 min. 5% H_2O, 95% MeCN, retention time: 13.073 min.). m.p. 401 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.89-8.83 ppm (m, 12H, $H_{naphthalene}$), 8.55 (s, 2H, Ar-*H*-4,8), 8.49 (s, 1H, Ar-*H*-16), 7.77 (s, 1H, Ar-*H*-13), 7.70 (s, 2H, Ar-*H*-1,5), 7.53 (m, 3H, Ar-*H*-34,54), 7.38-7.36 (m, 6H, Ar-*H*-33,35,53,55), 6.11 (s, 1H, bridgehead-*H*-9), 6.01 (s, 1H, bridgehead-*H*-10), 2.71 (m, 6H,-*CH*), 1.18-1.16 (d, *J* = 6.8 Hz, 36H, -CH_3). ^{13}C NMR (151 MHz, $CDCl_3$): δ = 162.9-162.7 ppm (*C*-O), 148.3 (Ar-*C*-1',4',5',8',11,12), 145.8 (Ar-*C*-31,36,52,56), 145.5 (Ar-C-32, 36), 144.4-144.2 (Ar-*C*-3,7,15), 132.1-131.8 (Ar-$C_{naphthalene}$), 130.2 (Ar-*C*-34), 130.0 (Ar-*C*-54), 128.4-128.3 (Ar-*C*-4,8), 128.2 (Ar-*C*-16), 127.8-127.7 (Ar-*C*q), 127.6-127.4 (Ar-*C*q), 124.5 (Ar-*C*-33,35), 124.4 (Ar-*C*-53,55), 122.8 (Ar-*C*-1,5,13), 52.6 (bridgehead-*C*-9), 52.6 (bridgehead-*C*-10), 29.5-29.4 ($C_{isoprop.}$) 24.1 (C_{methyl}). IR (ATR): $\tilde{\nu}$ = 2965 cm^{-1} (m), 2929 (w), 2870 (w), 1717 (s), 1674 (s), 1580 (m), 1532 (m), 1447 (w), 1337 (s), 1245 (s), 1196 (s), 1118 (w), 1057 (w), 981 (w), 937 (m), 880 (s), 858 (m), 838 (w), 800 (m), 768 (w), 724 (s), 699 (s), 667 (w). UV/VIS (DCM): $\lambda_{Abs\ 1}$ (lg ε) = 361 nm (4.5), $\lambda_{Abs,\ 2}$ (lg ε) = 381 nm (4.6). Fluorescence (DCM): λ_{em1} (λ_{ex}) = 475 nm (389), λ_{em2} (λ_{ex}) = 504 nm (389). CV (DCM, NBu_4OCl_4): $E_{1/2}^{red1}$ = -0.93 V, $E_{1/2}^{red2}$ = -1.39 V (Fc). MS (HR-MALDI): *m/z* (%) = 1616.51 (100) $[M\text{-}NO_2]^+$, 1662.50 (24) $[M+H]^+$, 1685.51 (21) $[M+Na]^+$, 1701.48 (34) $[M+K]^+$. Anal. calcd. for $C_{98}H_{71}N_9O_{18} \cdot \frac{1}{2}CH_2Cl_2$: C 69.38%, H 4.26% N 7.39%, found: C 69.44%, H 4.60% N 7.12%.

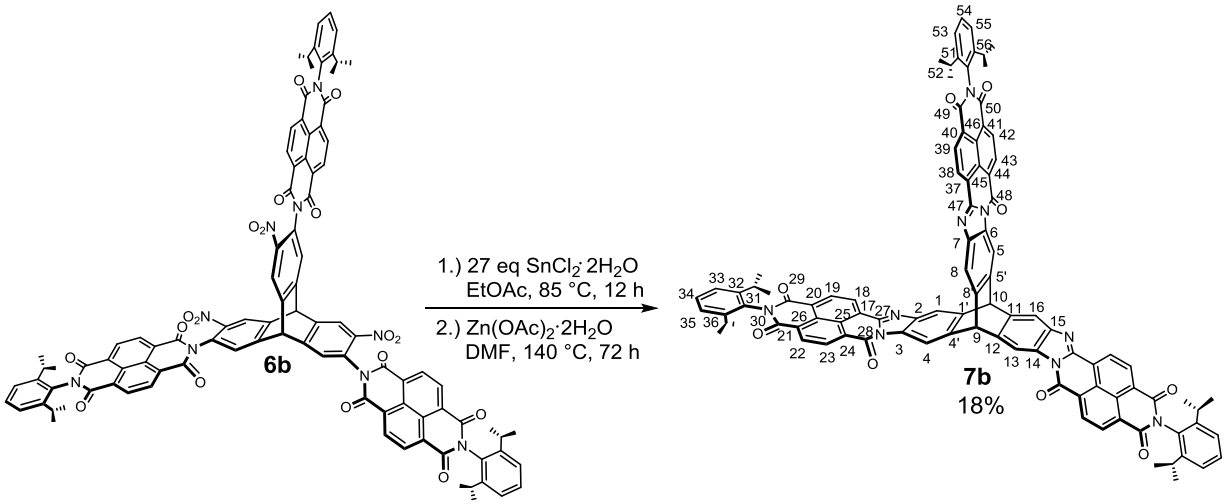
Synthesis of Tris-{*N*-[2,6-Diisopropylphenyl]benzimidazo[2,1-*b*]benzo [lmn] [3,8] phenanthroline-1,3,6(2*H*)-trione} 7a



A mixture of compound **6a** (1 eq, 60 mg, 36.09 µmol) and $SnCl_2 \cdot 2H_2O$ (27 eq, 220 mg, 974 µmol) was dissolved in EtOAc (4 mL) and heated at 85°C for 12 h under argon. After cooling to room temperature, aqueous $NaHCO_3$-solution (10%, 1.00 mL) was added and the mixture was extracted with DCM (3x 40 mL). The combined organic extract was dried over Na_2SO_4 and then the solvent was removed by rotary evaporation. The obtained red solid was used without further purification in the next step. It was mixed with $Zn(OAc)_2 \cdot 2H_2O$ (11.0 mg) and dissolved in DMF (4 mL) and heated at 140°C for three days under argon. After cooling to room temperature, DMF was removed by rotary evaporation and the residue was purified by flash chromatography (silica gel, DCM/ ethyl acetate 10:1, R_f = 0.95). Further purification was performed by HPLC (np, gradient: 0-4 min. 80% DCM, 20% ethyl acetate, retention time: 3.412 min.) to yield 13.0 mg (8.56 µmol, 24%) of compound **7a** as a red solid. M.p. >400 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.01-8.85 ppm (m, 12H, $H_{naphthalene}$), 8.79 (s, 3H, Ar-*H*-1,5,16), 8.10 (s, 3H, Ar-*H*-4,8,13), 7.50 (t, *J* = 7.7 Hz, 3H, Ar-*H*-34), 7.34 (d, *J* = 7.7 Hz, 6H, Ar-*H*-33,35), 6.11 (s, 1H, bridgehead-*H*-9), 6.07 (s, 1H, bridgehead-*H*-10), 2.74-2.65 (m, 6H, C*H*-CH_3), 1.15 (d, *J* = 6.2 Hz, 36H, -CH_3). ^{13}C NMR (151 MHz, $CDCl_3$): δ = 163.2 ppm (*C*-O-28), 163.0 (*C*-O-29,30), 159.7 (Ar-*C*-27), 148.2 (Ar-*C*q), 145.8 (Ar-*C*q), 144.2 (Ar-*C*q), 143.2 (Ar-*C*q), 142.5 (Ar-*C*q), 132.3 (Ar-*C*-18/19/22/23), 131.6 (Ar-*C*-18/19/22/23), 130.3 (Ar-*C*-34, 54), 128.3 (Ar-*C*q-$_{naphthalene}$), 127.9 (Ar-*C*q-$_{naphthalene}$), 127.7 (Ar-*C*q-$_{naphthalene}$), 126.4 (Ar-*C*-18/19/22/23), 126.1 (Ar-*C*q-$_{naphthalene}$), 124.6 (Ar-*C*-32, 36), 124.5 (Ar-*C*-33, 35, 116.4 (Ar-*C*-4,8,13), 112.5 (Ar-*C*-1,5,16), 55.0 (bridgehead-*C*), 54.8 (bridgehead-*C*), 29.4 (*C*H-CH_3), 24.2 (-*C*H_3). IR (ATR): $\tilde{\nu}$ = 2964 cm^{-1} (s), 2931 (w), 2871 (w), 1712 (s), 1674 (s), 1600 (s), 1579 (m), 1509 (m), 1466 (w), 1432 (m), 1403 (w), 1378 (s),

1337 (s), 1308 (s), 1243 (w), 1192 (s), 1126 (w), 1057 (w), 1025 (m), 988 (m), 938 (w), 866 (m), 827 (w), 801 (s), 765 (m), 720 (w). UV/VIS (DCM): λ_{max} (lg ε) = 331 nm (4.7), 370 (4.1), 413 (4.1), 494 (4.2). Fluorescence (DCM): λ_{em1} (λ_{ex}) = 343 nm (331), 418 (413)**.** CV (DCM, NBu_4OCl_4): $E_{1/2}^{red1}$ = -1.07 V, $E_{1/2}^{red2}$ = -1.51 (Fc). MS (HR-MALDI): *m/z* (%) = 1519.56 (100) $[M+2H]^+$, 1518.56 (86) $[M+H]^+$, 1517.55 (20) $[M]^+$. Anal. calcd. for $C_{98}H_{71}N_9O_9 \cdot \frac{3}{4}CH_2Cl_2$: C 73.11%, H 4.55% N 7.72%, found: C 73.36%, H 5.02% N 7.87%.

Synthesis of (21*R*)-2-[2,6-di(propan-2-yl)phenyl]-14-[2-ethyl-6-(propan-2-yl)phenyl]-8,21-[2-[2,6-di(propan-2-yl)phenyl]benzimidazo[2,1-*b*]benzo[*lmn*][3,8]phenanthroline-1,3,6(2*H*)-trione]-8,21 dihydrobenzo[*lmn*]benzo [1''',10'''][3,8]phenanthrolino [2''',3''':2'',3'']imidazo[4'',5'':6',7]anthra[2',3':4,5]imidazo[2,1-*b*][3,8]phenanthroline-1,3,13,15,18,24(2*H*,14*H*)-hexone 7b



A mixture of compound **6b** (1 eq, 60 mg, 36.09 µmol) and $SnCl_2 \cdot 2H_2O$ (27 eq, 220 mg, 974 µmol) was dissolved in EtOAc (4 mL) and heated at 85°C for 12 h under argon. After cooling to room temperature, an aqueous $NaHCO_3$-solution (10%, 1.00 mL) was added and the mixture was extracted with DCM (3x 40 mL). The combined organic extract was dried over Na_2SO_4 and the solvent was removed by rotary evaporation. The obtained red solid was used without further purification in the next step. It was mixed with $Zn(OAc)_2 \cdot 2H_2O$ (11.0 mg) and dissolved in DMF (4 mL) and heated at 140°C for three days under argon. After cooling to room temperature, DMF was removed by evaporation and the residue was purified by flash chromatography (silica gel, DCM/ EE 10:1, R_f = 0.95). Further purification was performed by HPLC (np, gradient: 0-4 min. 95% DCM, 5% EE, retention time: 2.971 min.). The obtained solid was dissolved in DCM and precipitate with n-pentane and washed

with MeOH (3x10 mL) and diethyl ether (3 mL) to yield 10 mg (18%) of compound **7b** as red solid. M.p. > 400 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.01-8.83 ppm (m, 12H, $H_{naphthalene}$), 8.79 (s, 3H, Ar-*H*-1,8,16), 8.09 (s, 3H, Ar-*H*-4,5,13), 7.50 (t, J = 7.7 Hz, 3H, Ar-*H*-34,54), 7.35 (d, J = 7.7 Hz 6H, Ar-*H*-33,35,53,55), 6.10 (s, 1H, bridgehead-*H*-9), 6.07 (s, 1H, bridgehead-*H*-10), 2.71-2.69 (m, 6H, C*H*-CH_3), 1.15 (d, J = 6.2 Hz, 36H, -CH_3). ^{13}C NMR (151 MHz, $CDCl_3$): δ = 163.3 ppm (*C*-O-28,48), 163.1 (*C*-O-29,30,49,50), 159.6 (Ar-*C*-27,47), 148.4 (Ar-*C*q), 145.8 (Ar-*C*q), 144.1 (Ar-*C*q), 143.5 (Ar-Cq), 142.7 (Ar-*C*q), 132.5 (Ar-*C*-18/19/22/23/38/39/42/43), 131.8 (Ar-*C*-18/19/22/23/38/39/42/43), 130.3 (Ar-*C*-34,54), 128.4 (Ar-*C*q-$_{naphthalene}$), 128.0 (*C*q-$_{naphthalene}$), 128.0 (Ar-*C*q-$_{napthalene}$), 127.8 (Ar-*C*q-$_{napthalene}$), 126.8 (Ar-*C*-18/19/22/23/38/39/42/43), 124.6 (*C*-32, 36, 51, 56), 126.1 (*C*q-$_{naphthalene}$), 124.5 (Ar-*C*-33, 35, 53, 55), 116.7 (Ar-*C*-4,5,13), 112.4 (Ar-*C*-1, 8, 16), 55.1 (bridgehead-*C*), 54.9 (bridgehead-*C*), 29.5 (*C*H-CH_3), 24.3 (-*C*H_3). IR (ATR): $\tilde{\nu}$ = 2964 cm^{-1} (s), 2930 (w), 2870 (w), 1712 (s), 1673 (s), 1601 (s), 1580 (m), 1509 (m), 1466 (w), 1432 (m), 1404 (w), 1378 (s), 1337 (s), 1308 (s), 1243 (w), 1191 (s), 1126 (w), 1057 (w), 1025 (m), 988 (m), 937 (w), 866 (m), 839 (w), 827 (w), 800 (s), 764 (m), 719 (w). UV/VIS (DCM): $\lambda_{max,1}$ (lg ε) = 328 nm (4.7), $\lambda_{max,2}$ (lg ε) = 368 nm (4.1), $\lambda_{max,3}$ (lg ε) = 409 nm (4.1), $\lambda_{max,4}$ (lg ε) = 489 nm (4.2). Fluorescence (DCM): λ_{em1} (λ_{ex}) = 620 nm (499). CV (DCM, NBu_4OCl_4): $E_{1/2}^{red1}$ = -1.04 V, -1.45 V (Fc). MS (HR-MALDI): *m/z* (%) = 1519.55 (100) $[M+2H]^+$, 1518.55 (88) $[M+H]^+$, 1517.54 (11) $[M]^+$. Anal. calcd. for $C_{98}H_{71}N_9O_9$·2 CH_2Cl_2: C 68.34%, H 4.19% N 7.17%, found: C 67.93%, H 4.58% N 7.26%.

3. ^{1}H and ^{13}C NMR spectra of all compounds

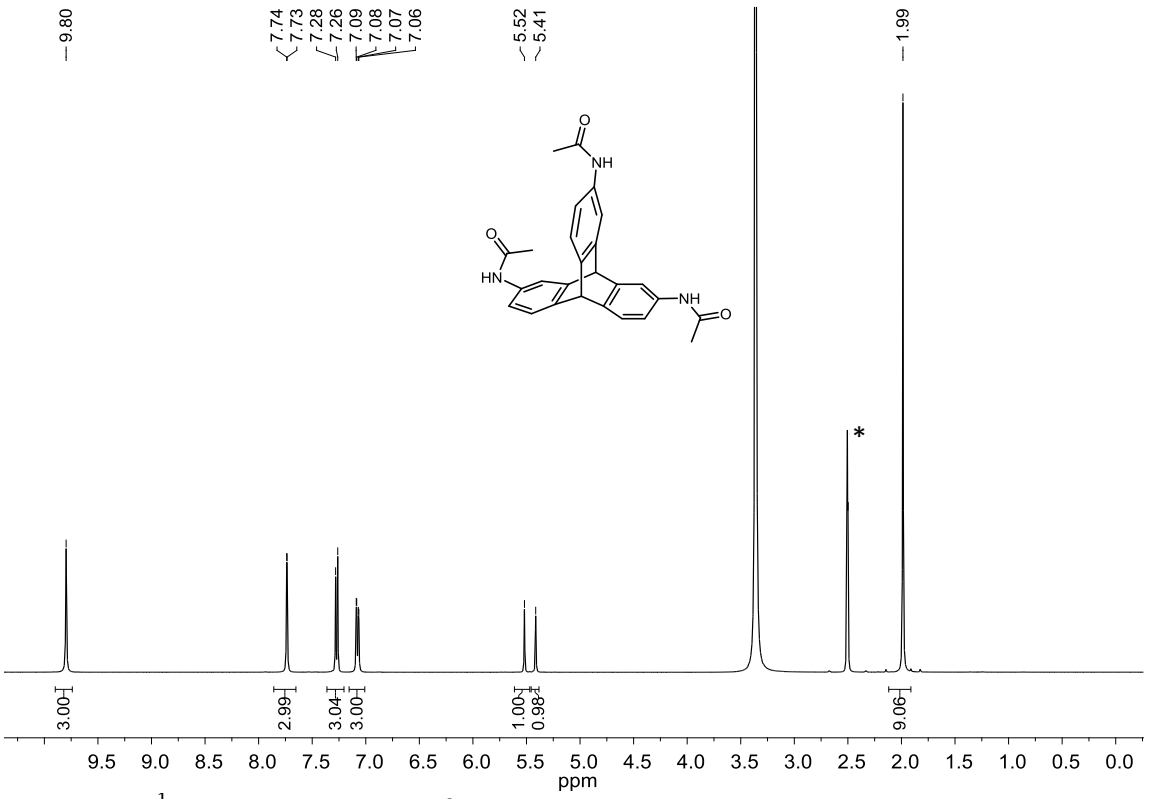


Figure S1: ^{1}H NMR spectrum of 2,7,14-triamidotriptycene (**2a**) in DMSO-d_6 (300 MHz, 25 °C). Residual solvent signals*: H_2O.

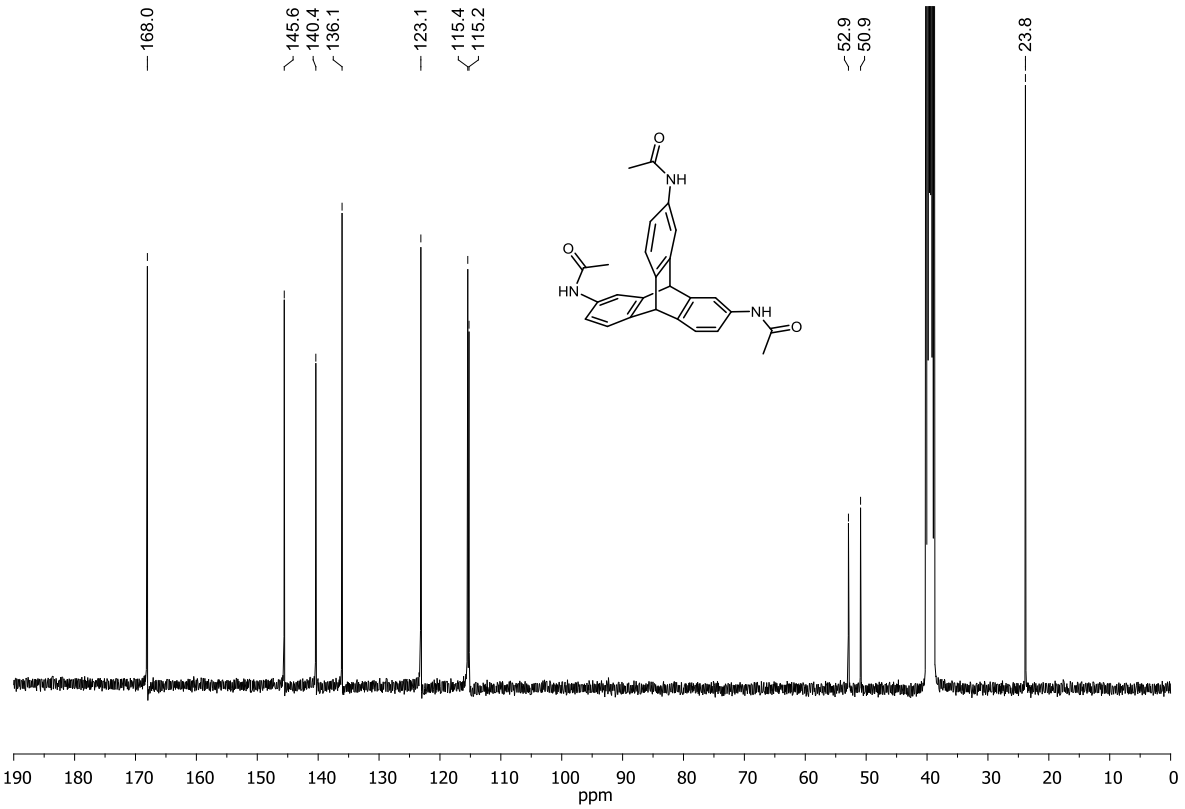


Figure S2: ^{13}C NMR spectrum of 2,7,14-triamidotriptycene (**2a**) in DMSO-d_6 (101 MHz, 25 °C).

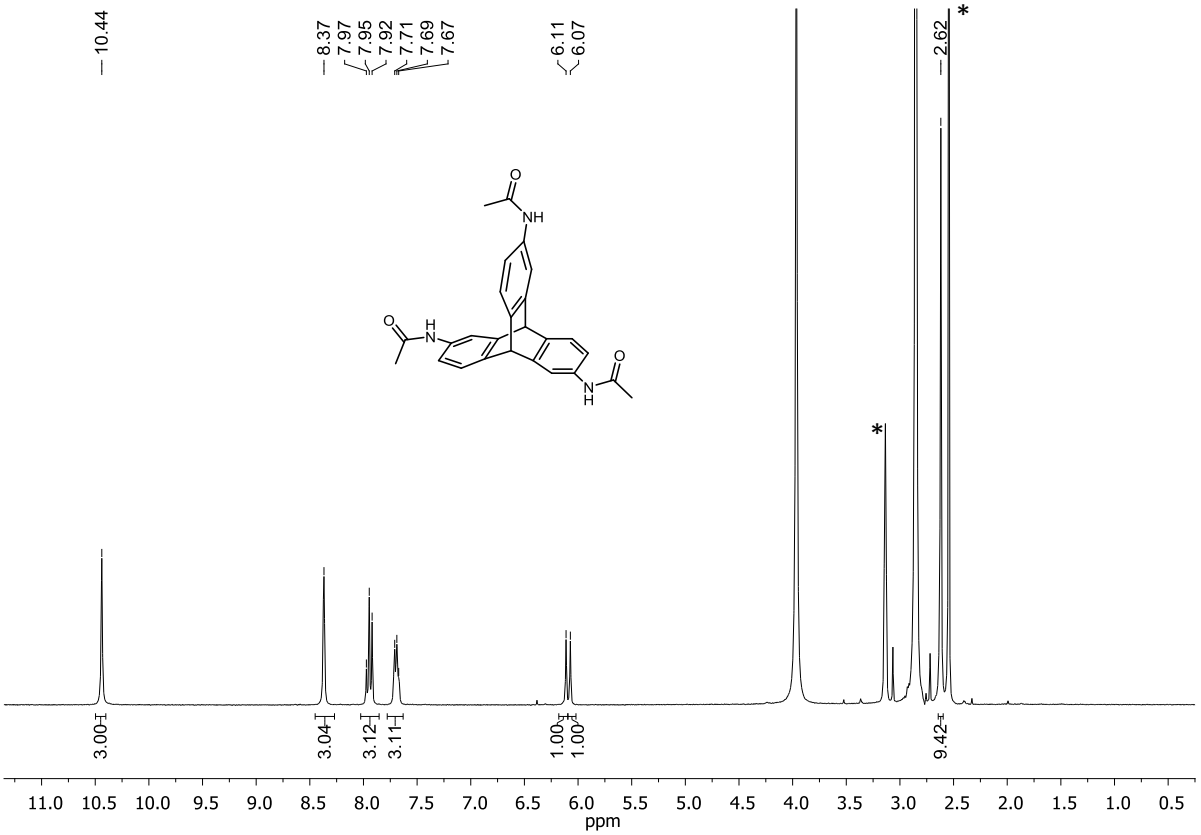


Figure S3: ^{1}H NMR spectrum of 2,6,14-triamidotriptycene (**S1**) in DMSO-d_6 (300 MHz, 25 °C). Residual solvent signals*: acetic acid.

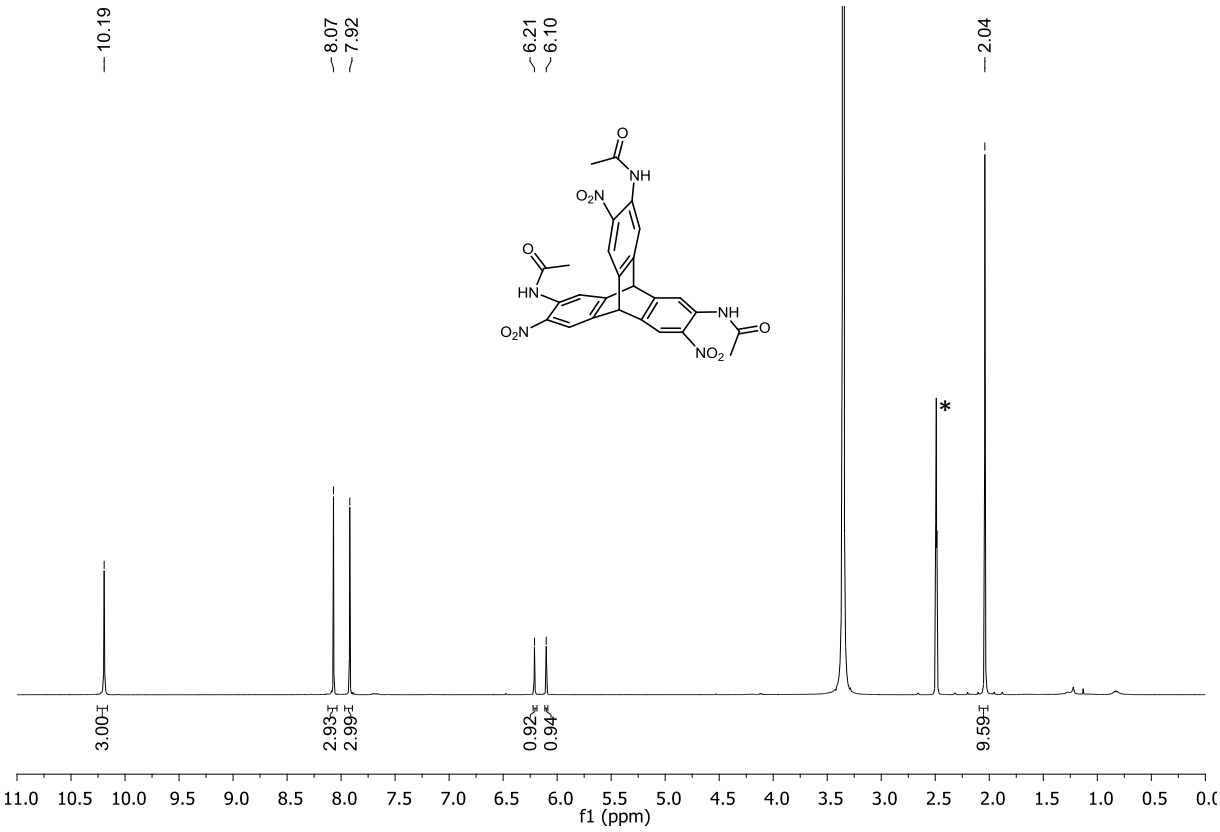


Figure S4: ^{1}H NMR spectrum of 2,7,14-trinitro-3,6,15-triaminotriptycene (**3a**) in DMSO-d_6 (300 MHz, 25 °C). Residual solvent signals*: H_2O.

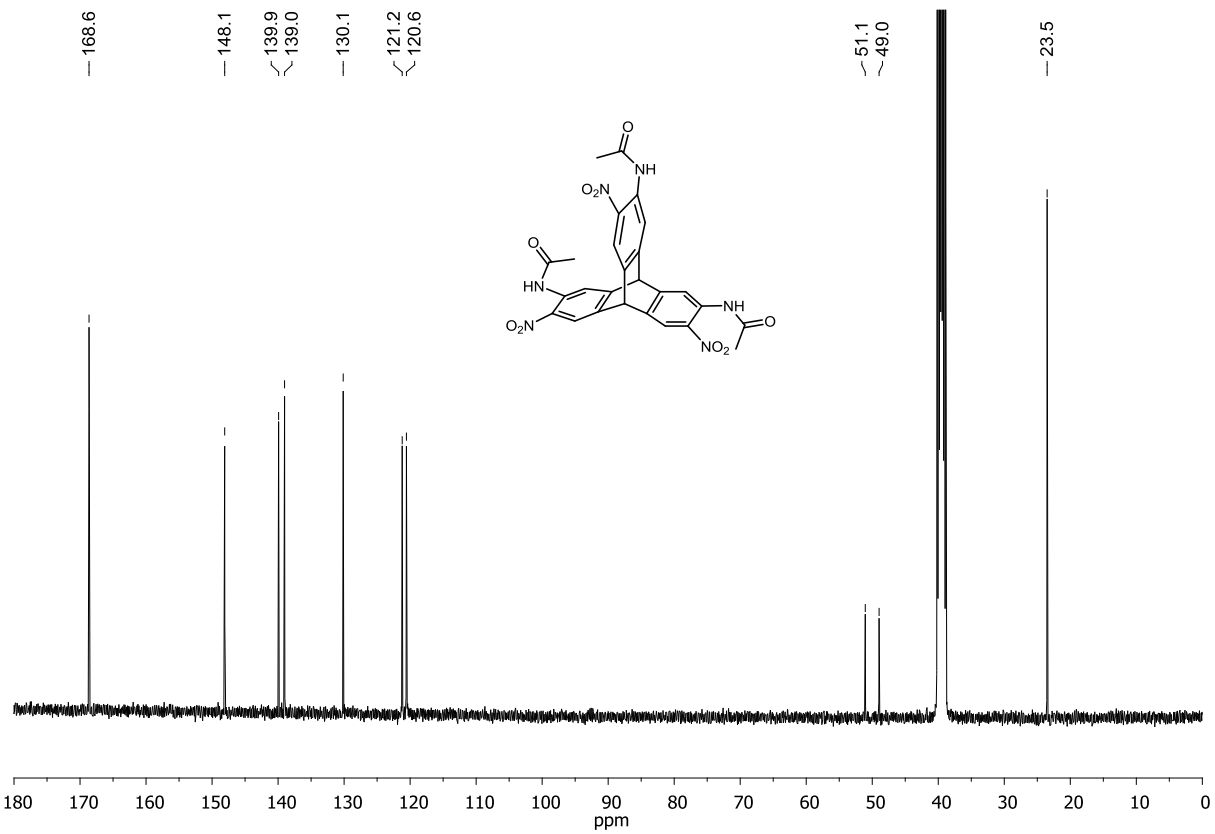


Figure S5: ^{13}C NMR spectrum of 2,7,14-triacetamido-3,6,15-trinitrotriptycene (**3a**) in DMSO-d_6 (101 MHz, 25 °C).

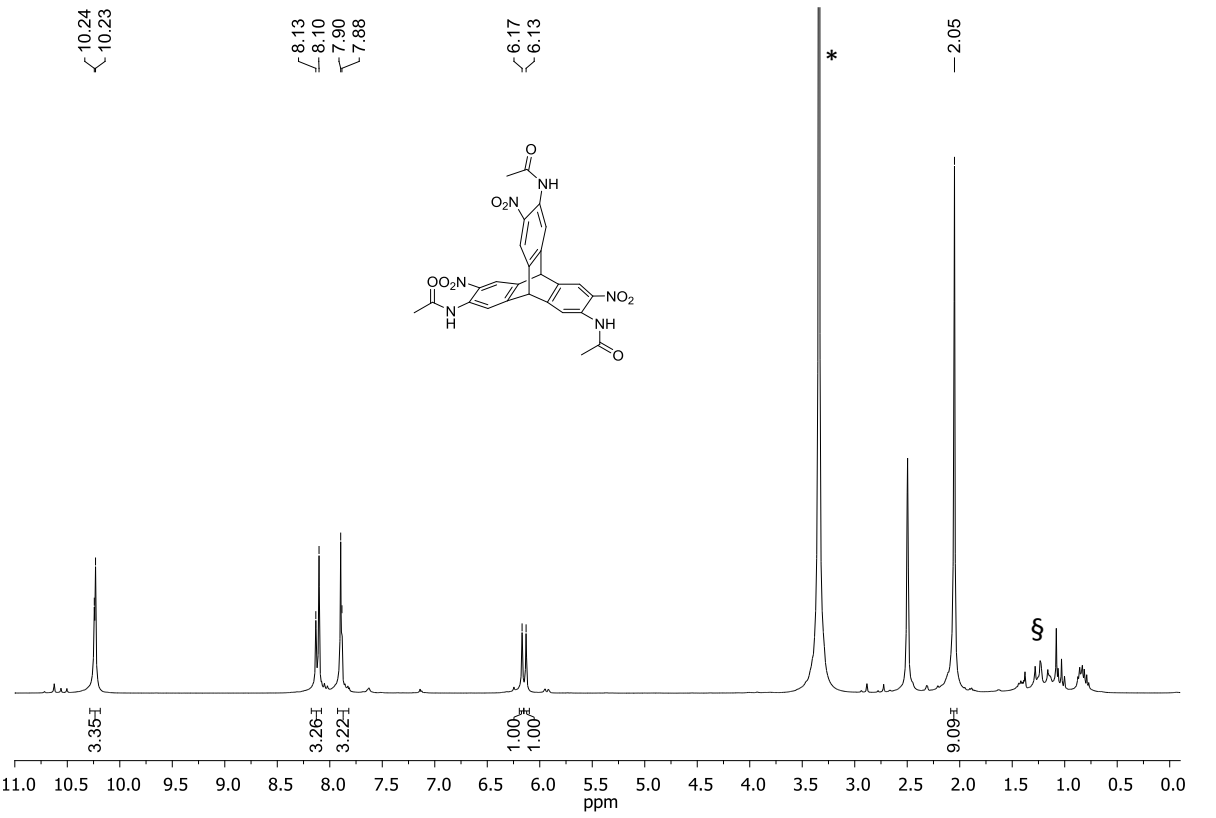


Figure S6: ^{1}H NMR spectrum of 2,6,14-trinitro-3,7,15-triaminotriptycene (**S2**) in DMSO-d_6 (300 MHz, 25 °C). Residual solvent signals*: H_2O, §: petroleum ether.

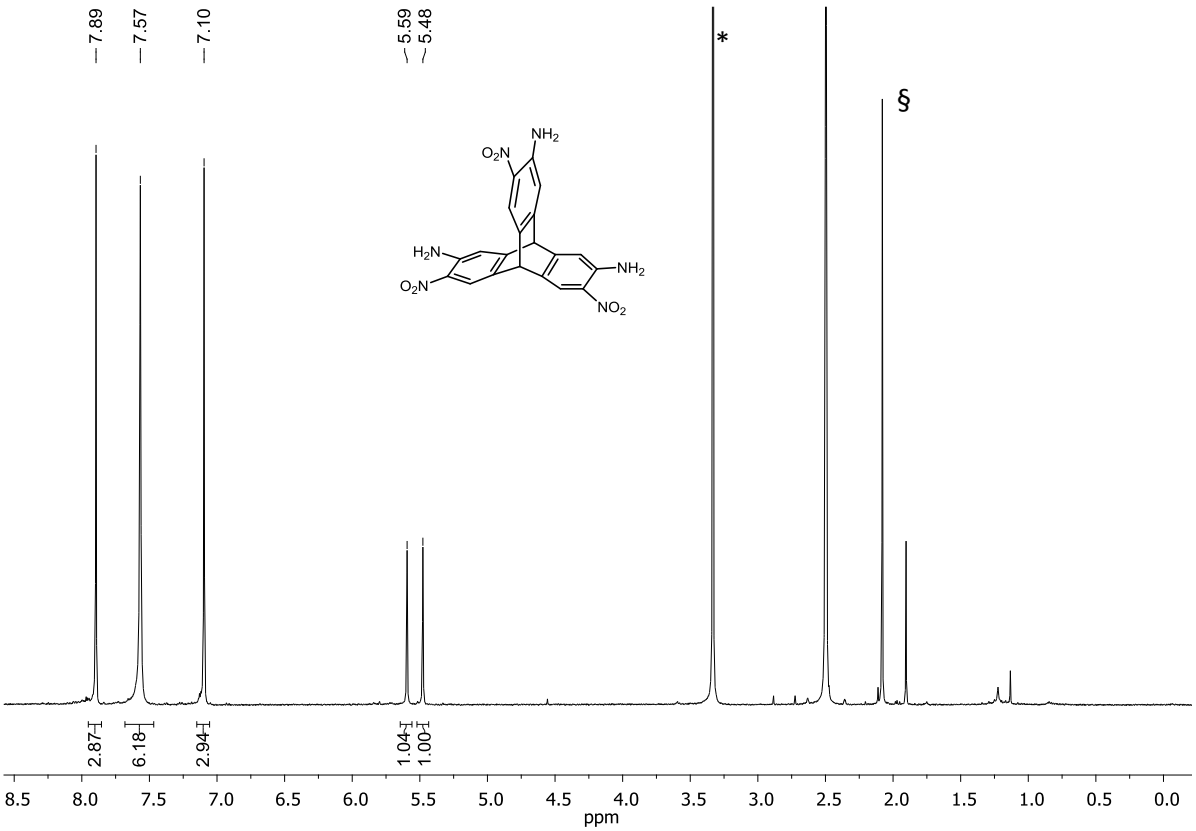


Figure S7: ^{1}H NMR spectrum of 2,7,14-triamino-3,6,15-trinitrotriptycene (**4a**) in DMSO-d_6 (500 MHz, 25 °C). Residual solvent signals*: H_2O, §: acetone.

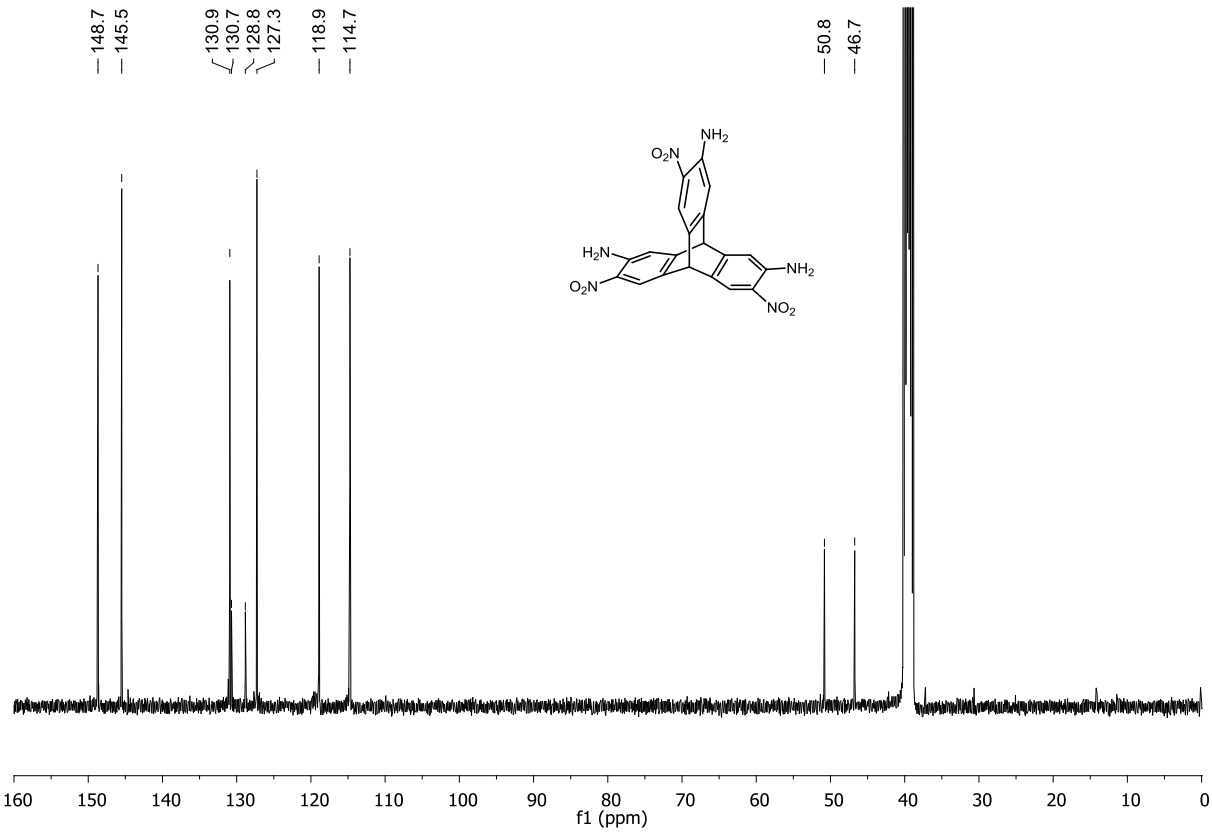


Figure S8: ^{13}C NMR spectrum of 2,7,14-triamino-3,6,15-trinitrotriptycene (**4a**) in DMSO-d_6 (101 MHz, 25 °C).

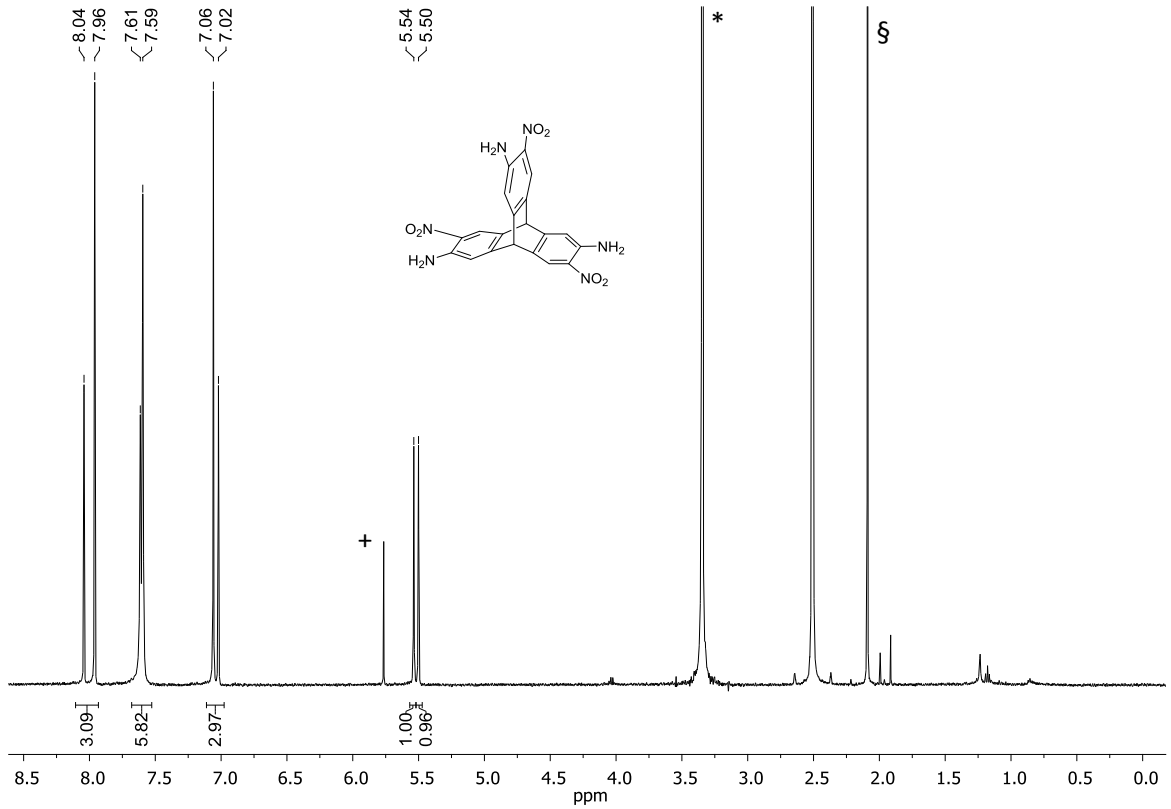


Figure S9: ^{1}H NMR spectrum of 2,6,14-triamino-3,7,15-trinitrotriptycene (**4b**) in DMSO-d_6 (500 MHz, 25 °C). Residual solvent signals*: H_2O, §: acetone, +: DCM.

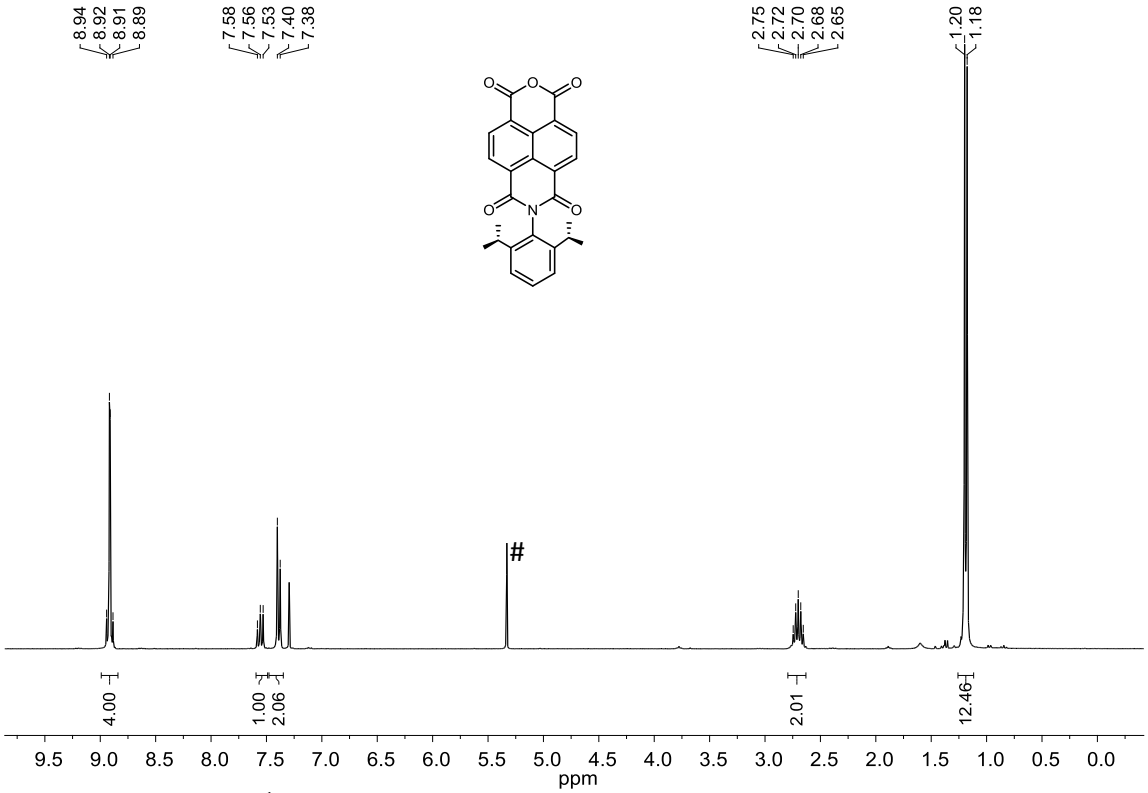


Figure S10: ^{1}H NMR spectrum of *N*-(2,6-diisopropylphenyl)-1,4,5,8,-naphthalenetetracarboxylic acid-1,8-anhydride-4,5-imide (**5**) in $CDCl_3$ (400 MHz, 25 °C). Residual solvent signals #: DCM.

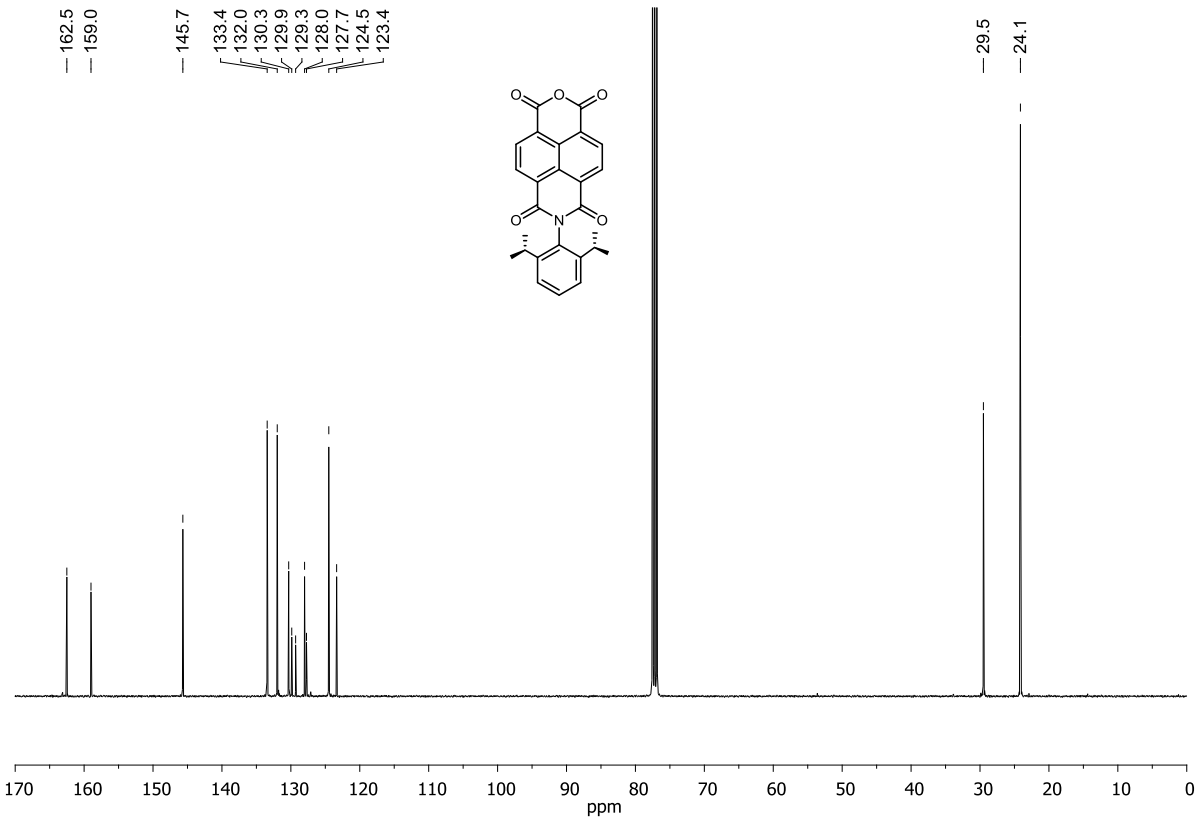


Figure S11: ^{13}C NMR spectrum of *N*-(2,6-diisopropylphenyl)-1,4,5,8,-naphthalene-tetracarboxylic acid-1,8-anhydride-4,5-imide (**5**) in $CDCl_3$ (101 MHz, 25 °C).

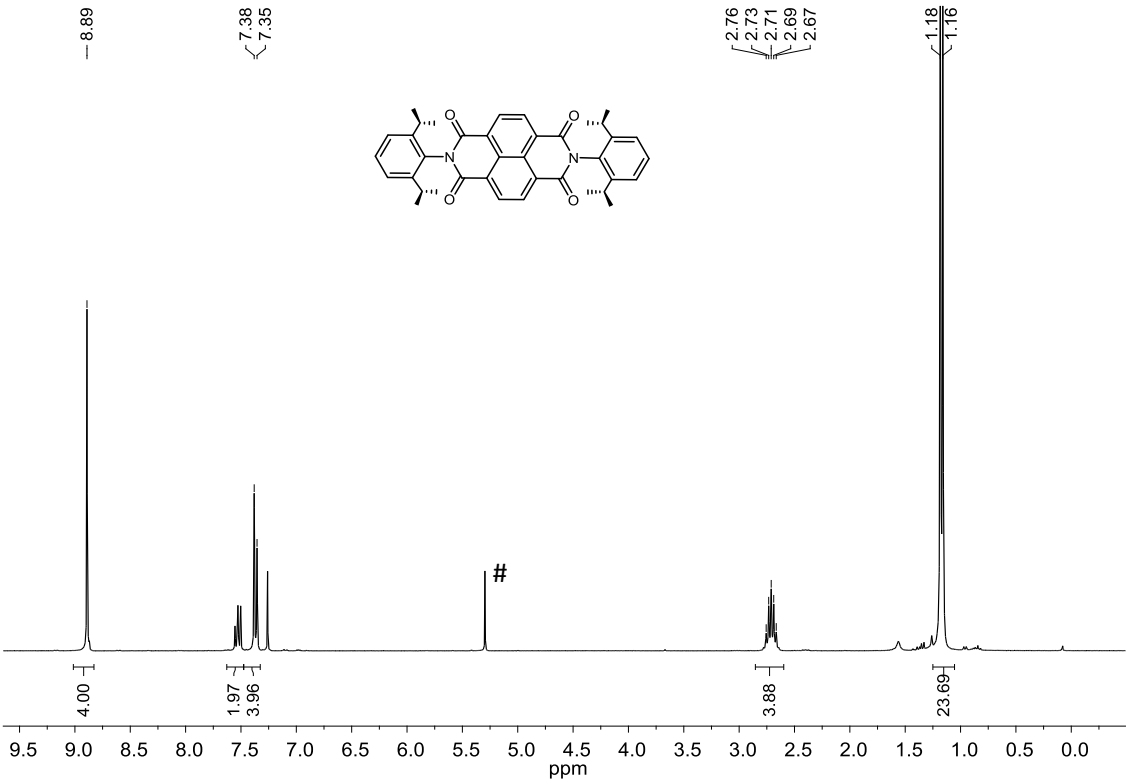


Figure S12: ^{1}H NMR spectrum of *N,N'*-(di-2,6-diisopropylphenyl)-naphthalene-1,4,5,8,-tetracarboxylic acid bisimide (**S5**) in $CDCl_3$ (600 MHz, 25 °C). Residual solvent signals #: DCM.

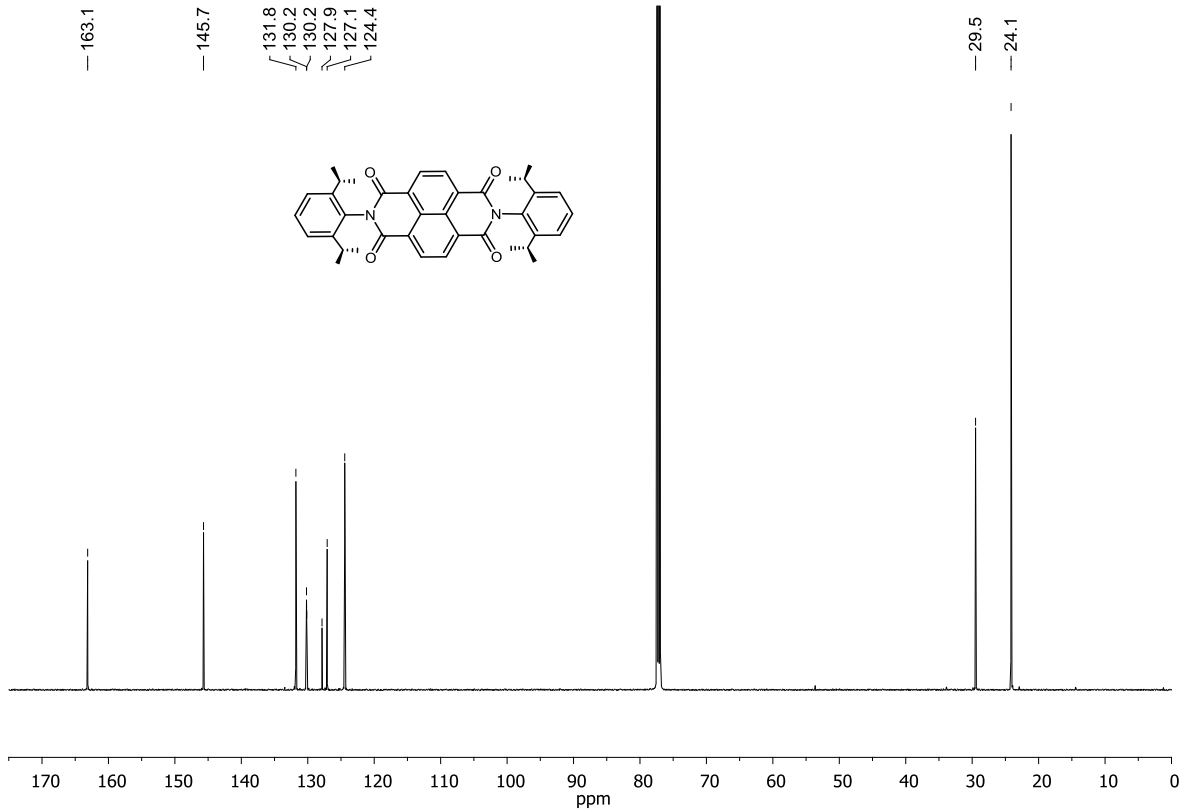


Figure S13: ^{13}C NMR spectrum of *N,N'*-(di-2,6-diisopropylphenyl)-naphthalene-1,4,5,8,-tetracarboxylic acid bisimide (**S5**) in $CDCl_3$ (151 MHz, 25 °C).

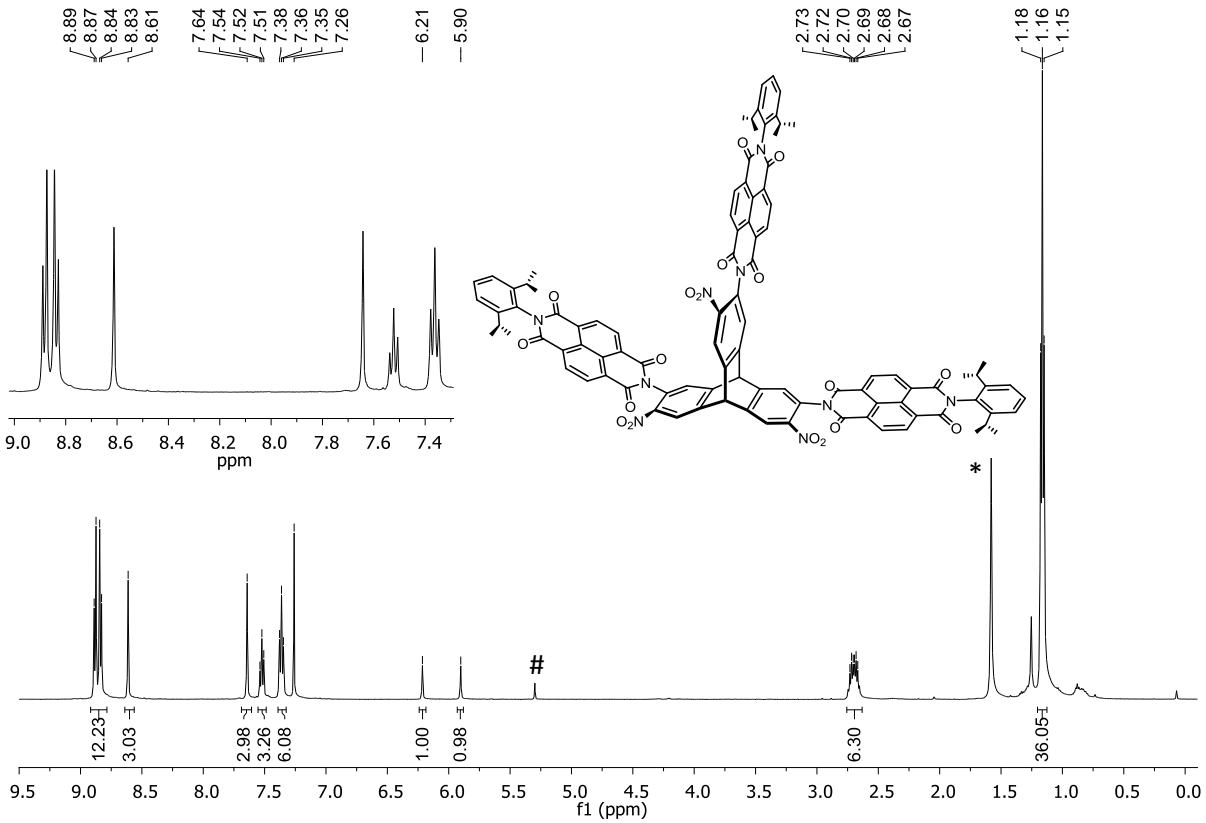


Figure S14: ^{1}H NMR spectrum of C_{3v}-precursor **6a** in $CDCl_3$ (500 MHz, 25 °C). Residual solvent signals*: H_2O, #: DCM.

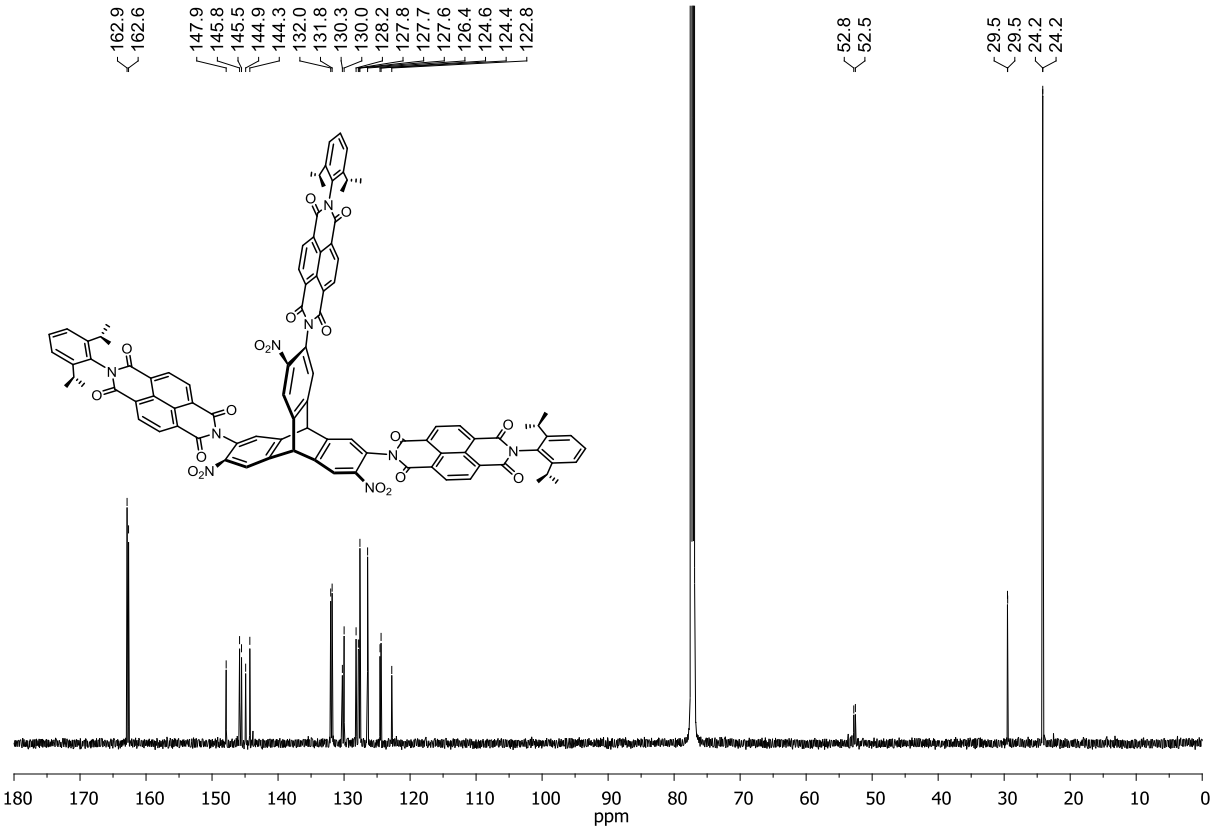


Figure S15: ^{13}C NMR spectrum of C_{3v}-precursor **6a** in $CDCl_3$ (151 MHz, 25 °C).

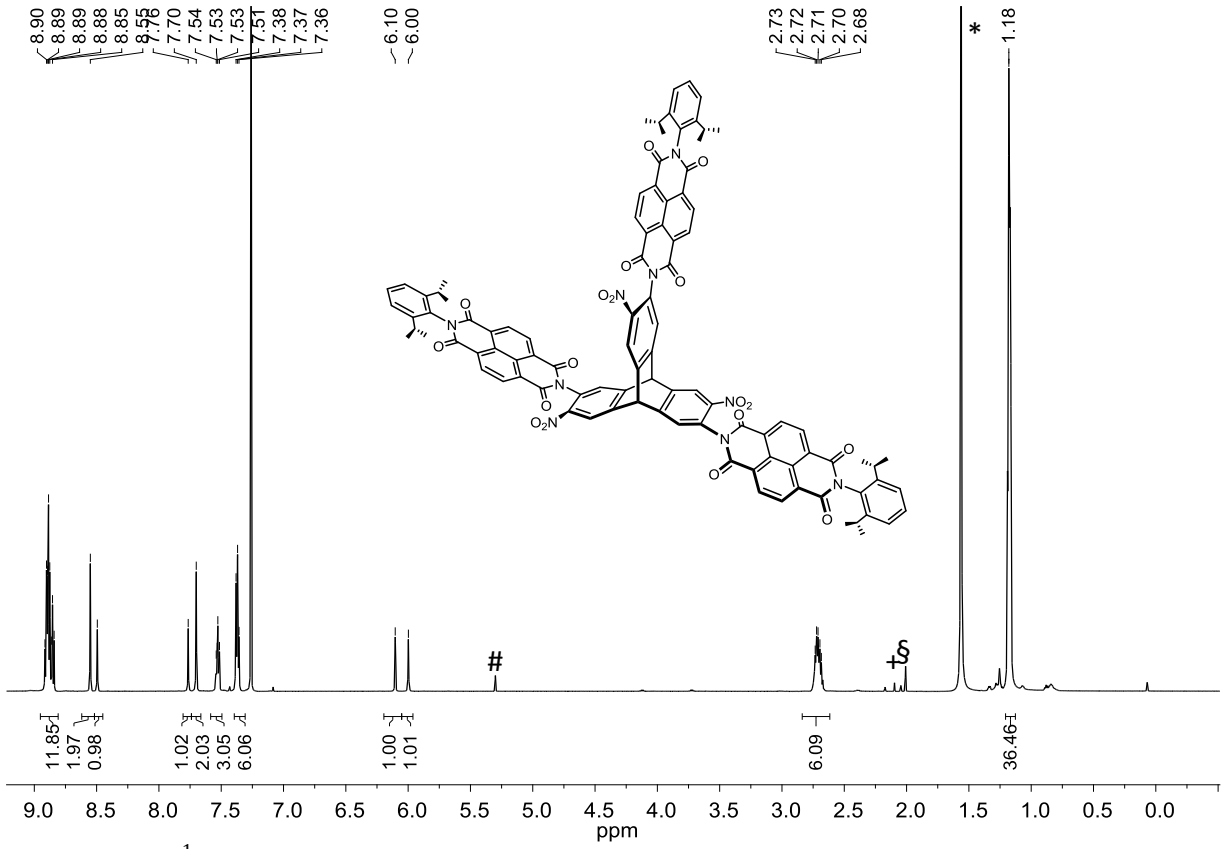


Figure S16: ^{1}H NMR spectrum of C_s-precursor **6b** after purification by HPLC in $CDCl_3$ (600 MHz, 25°C). Residual solvent signals #: DCM, +: MeCN, §: acetone, *: H_2O;.

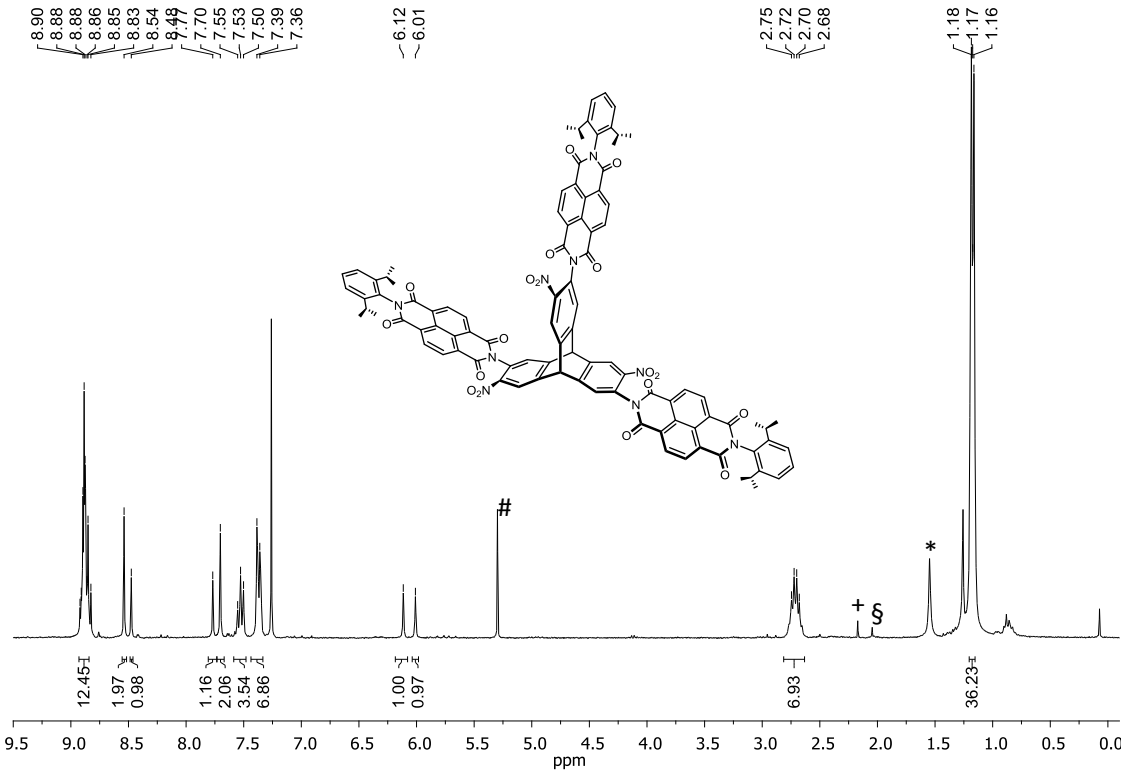


Figure S17: ^{1}H NMR spectrum of C_s-precursor **6b** in $CDCl_3$ (300 MHz, 25°C). Residual solvent signals*: H_2O, +: acetone, §:MeCN, #: DCM.

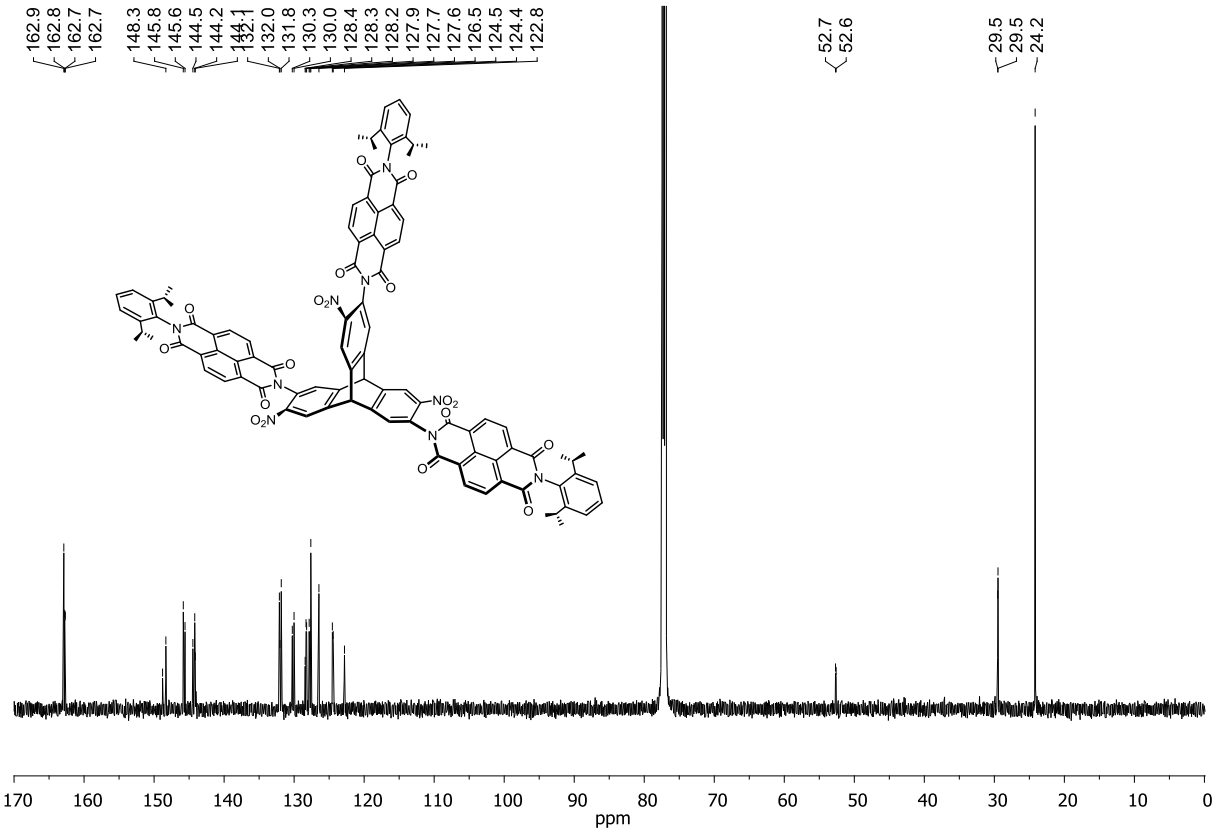


Figure S18: ^{13}C NMR spectrum of C_s-precursor **6b** in $CDCl_3$ (151 MHz, 25°C).

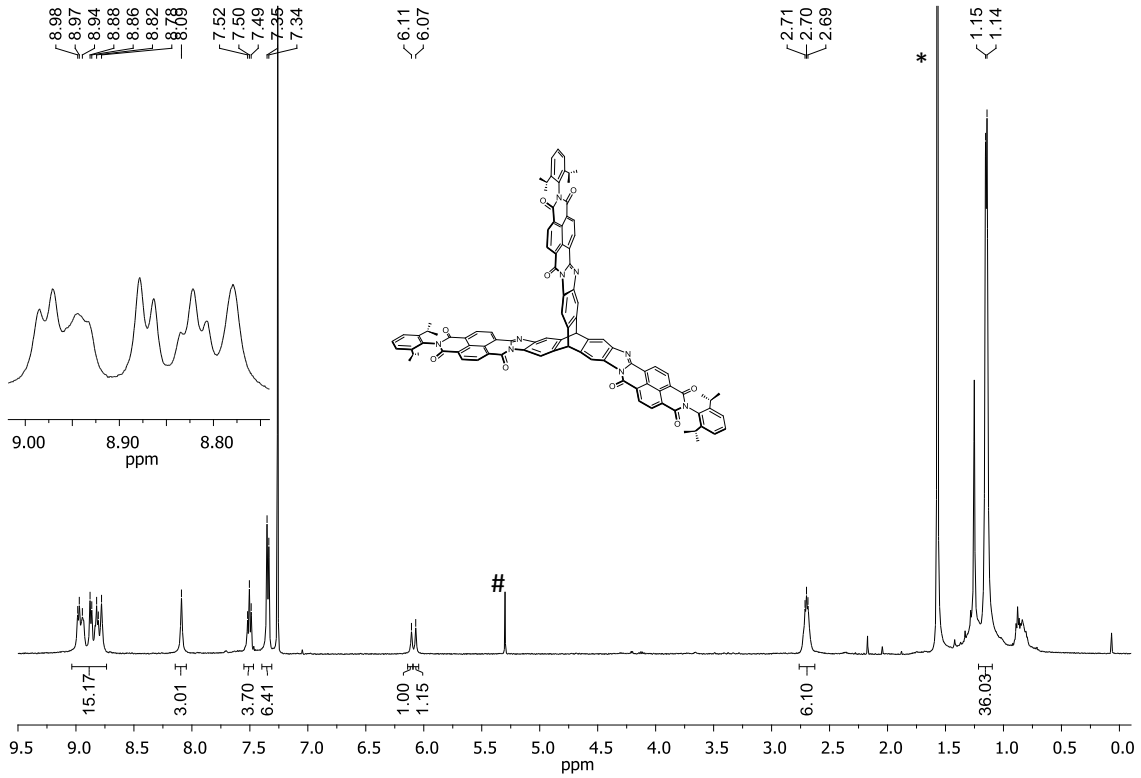


Figure S19: ^{1}H NMR spectrum of C_{3v}-trisaroylenimdazole **7a** in $CDCl_3$ (500 MHz, 25 °C), Residual solvent signals*: H_2O, #: DCM.

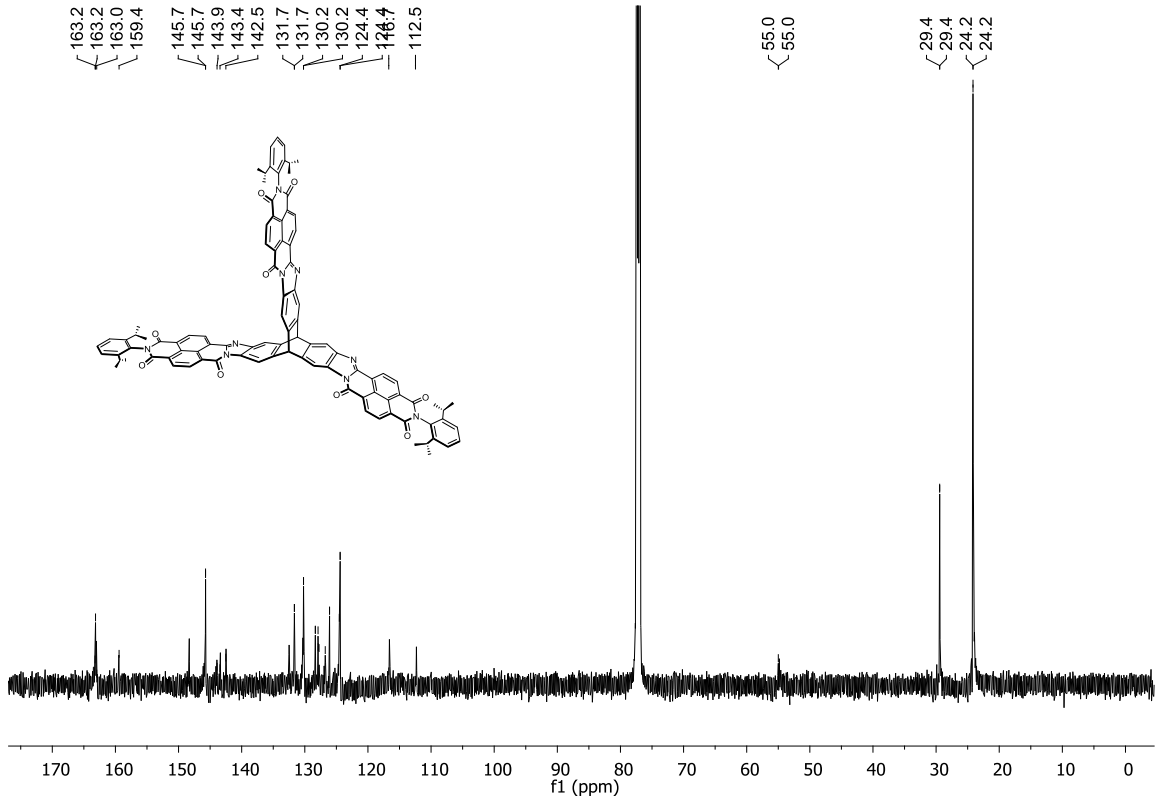


Figure S20: ^{13}C NMR spectrum of C_{3v}-trisaroylenimidazole **7a** in $CDCl_3$ (151 MHz, 25 °C).

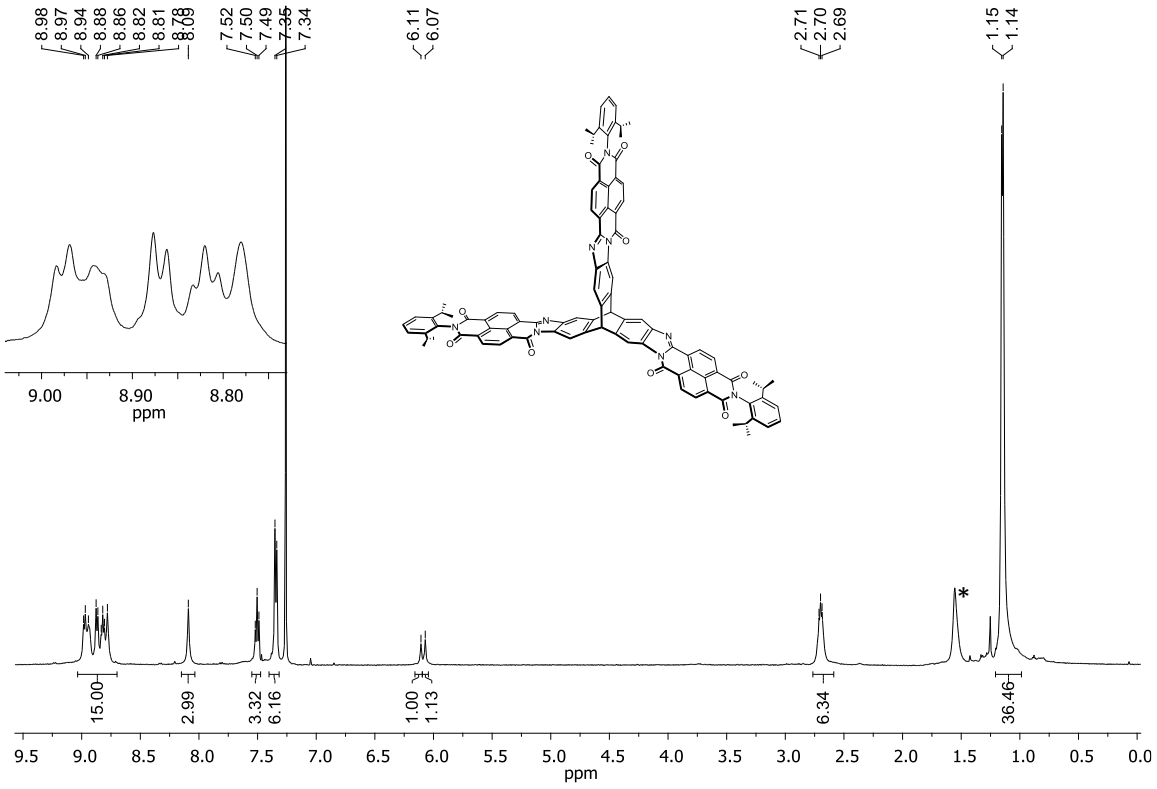


Figure S21: ^{1}H NMR spectrum of C_s-trisaroylenimidazole **7b** in $CDCl_3$ (500 MHz, 25 °C). Residual solvent signals*: H_2O.

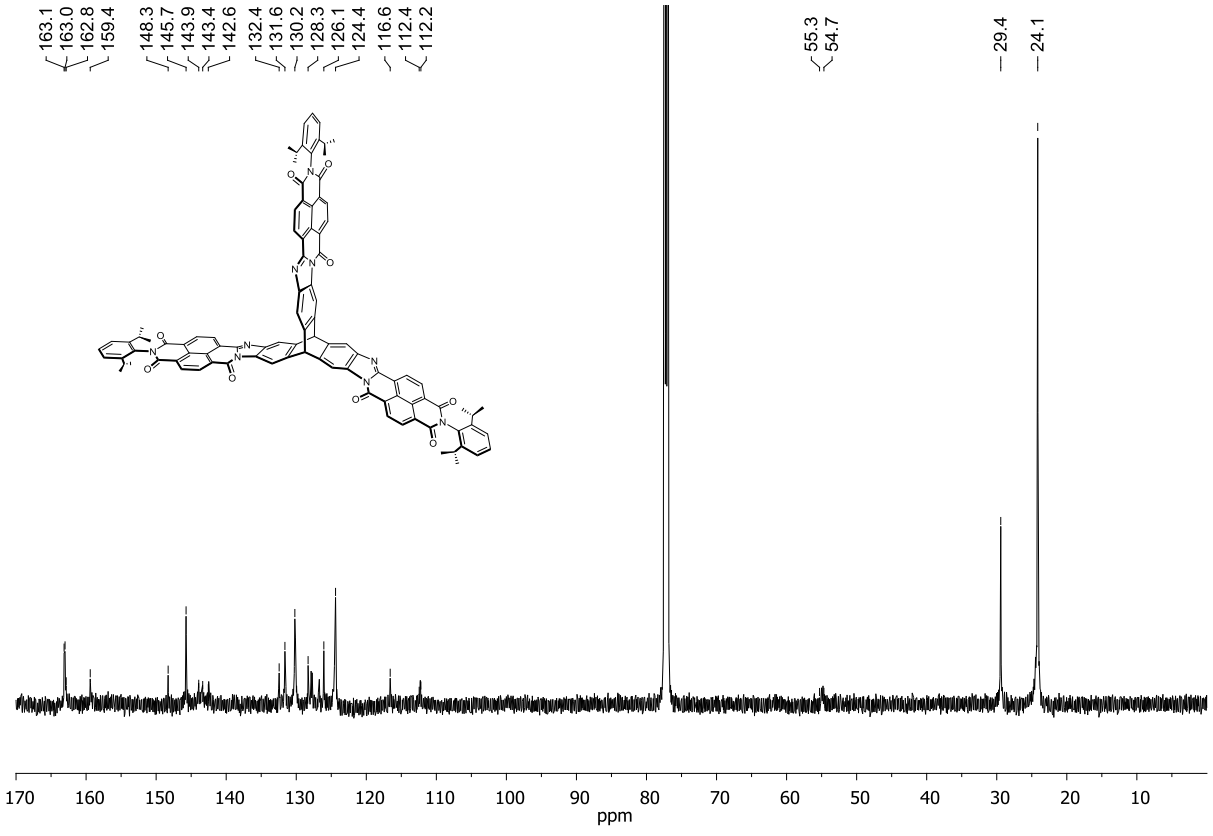


Figure S22: ^{13}C NMR spectrum of C_s-trisaroylenimidazole **7b** in $CDCl_3$ (151 MHz, 25 °C).

4. HPLC-chromatograms

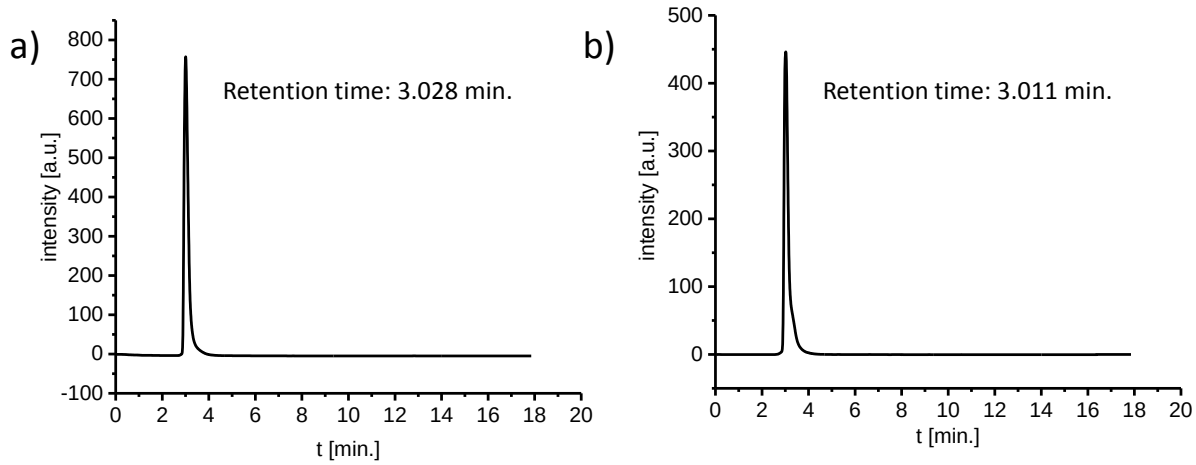


Figure S23: HPLC spectra of the trisaroylenimidazoles, normal phase, DCM/ EE 70:30. a) compound **7a**, b) compound **7b**.

5. IR-spectra of the new compounds

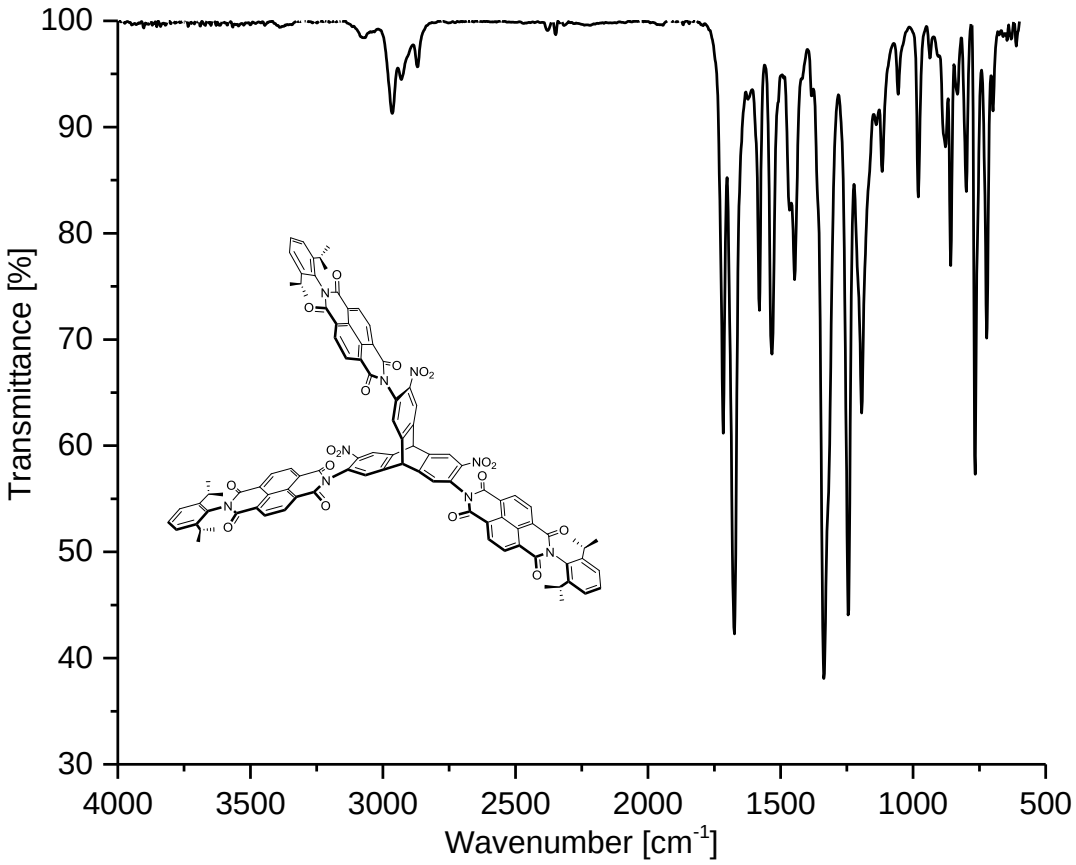


Figure S24: IR-spectrum (ATR) of C_{3v}-isomeric compound **6a**.

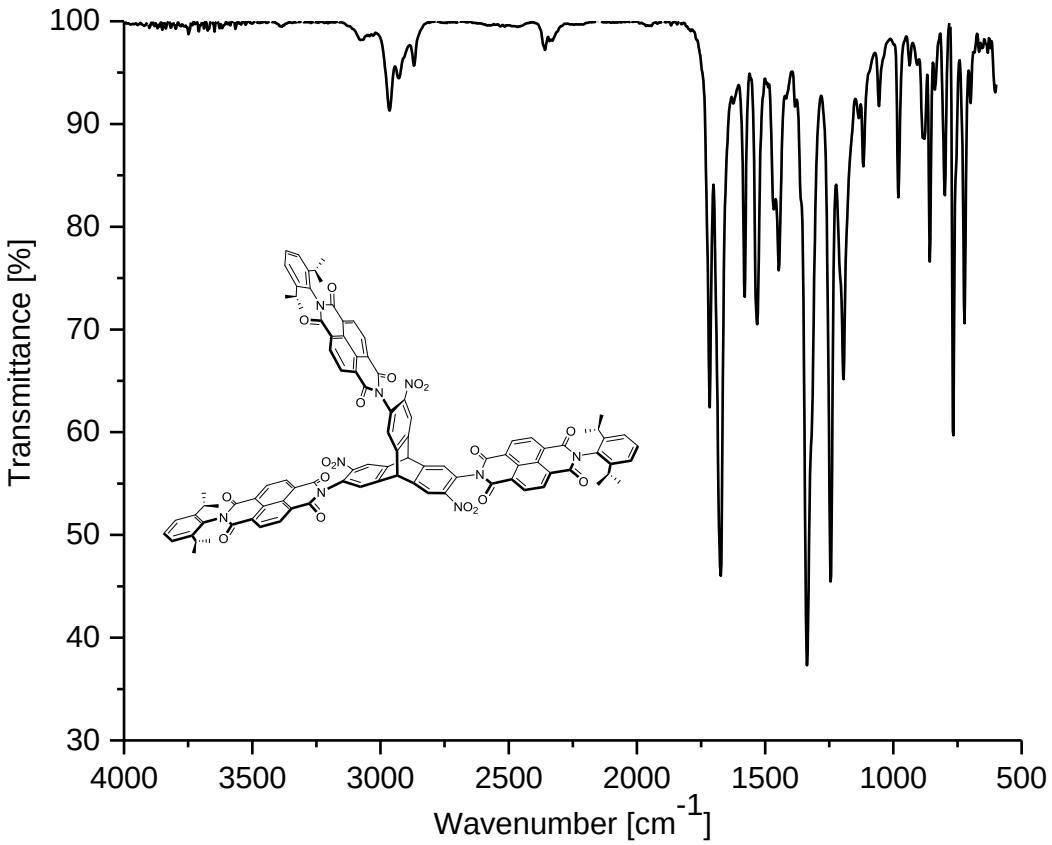


Figure S25: IR-spectrum (ATR) of C_s-isomeric compound **6b**.

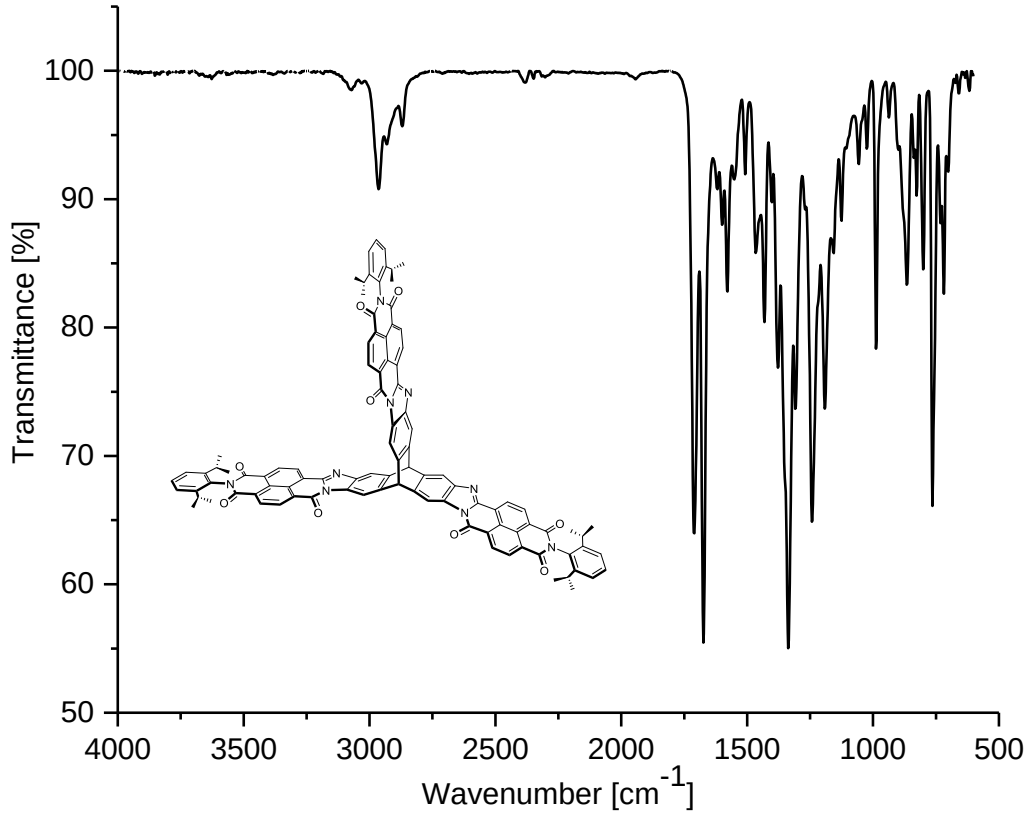


Figure S26: IR-spectrum (ATR) of C_{3v}-isomeric trisaroylenimidazole **7a**.

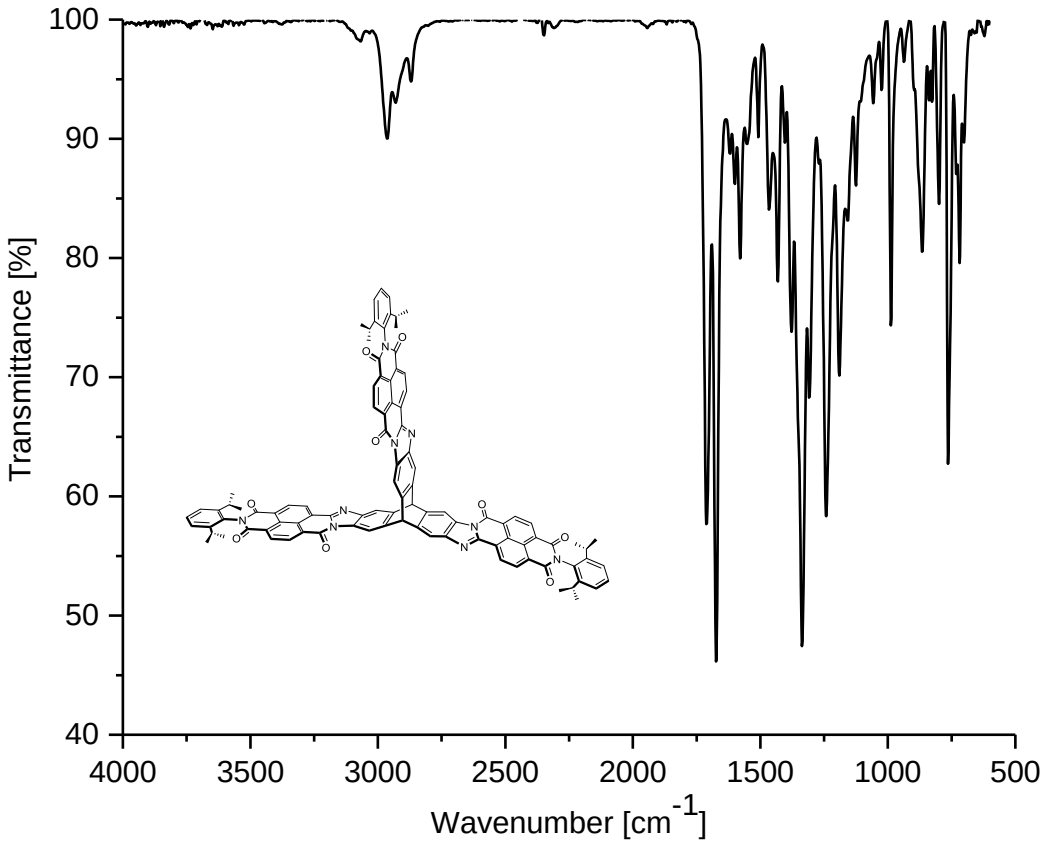


Figure S27: IR-spectrum (ATR) of C_s-isomeric trisaroylenimidazole **7b**.

6. Mass spectra of the new compounds

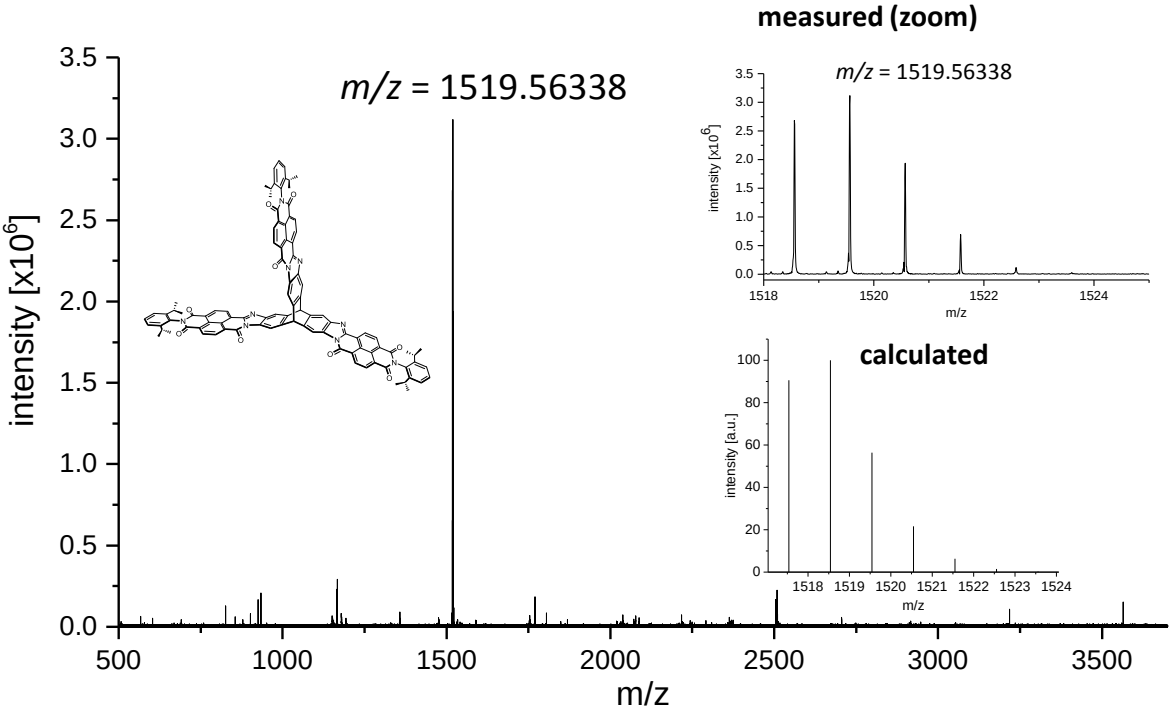


Figure S28: Mass spectrum (HR-MALDI) of C_{3v}-trisaroylenimidazole **7a**.

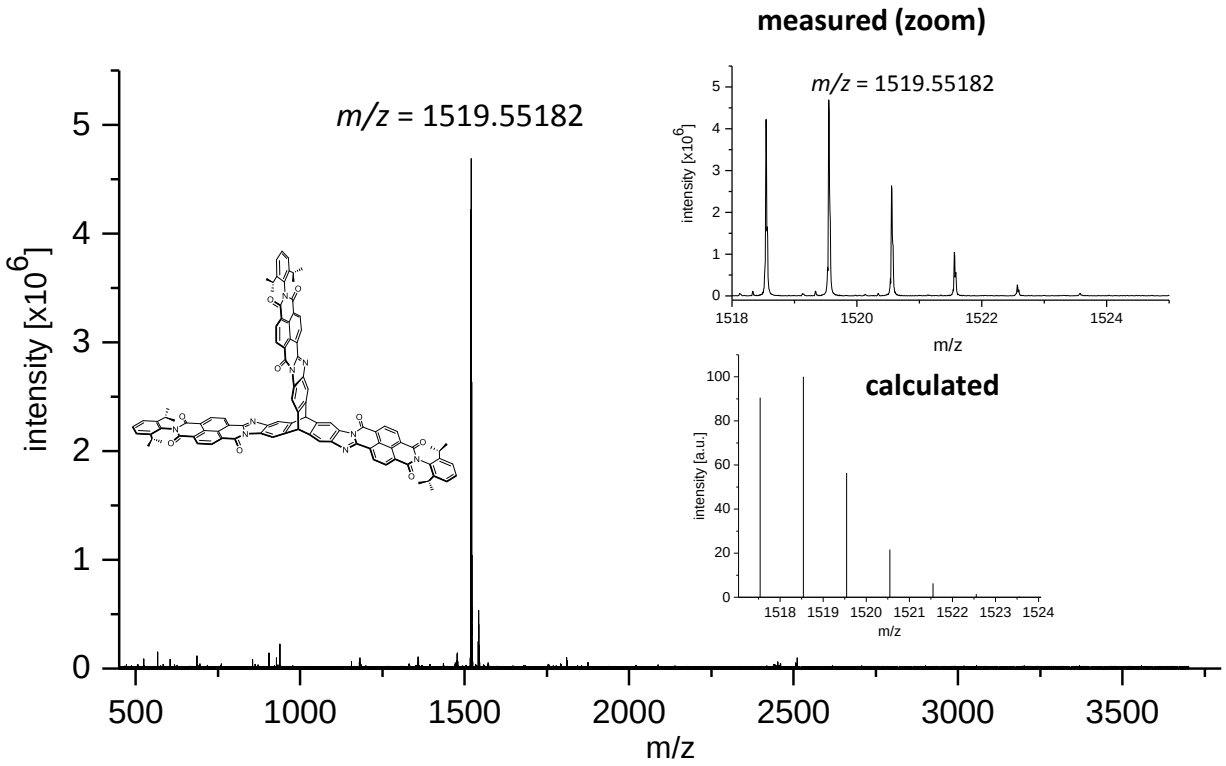


Figure S29: Mass spectrum (HR-MALDI) of C_s-trisaroylenimidazole **7b**.

7. Cyclic voltammograms

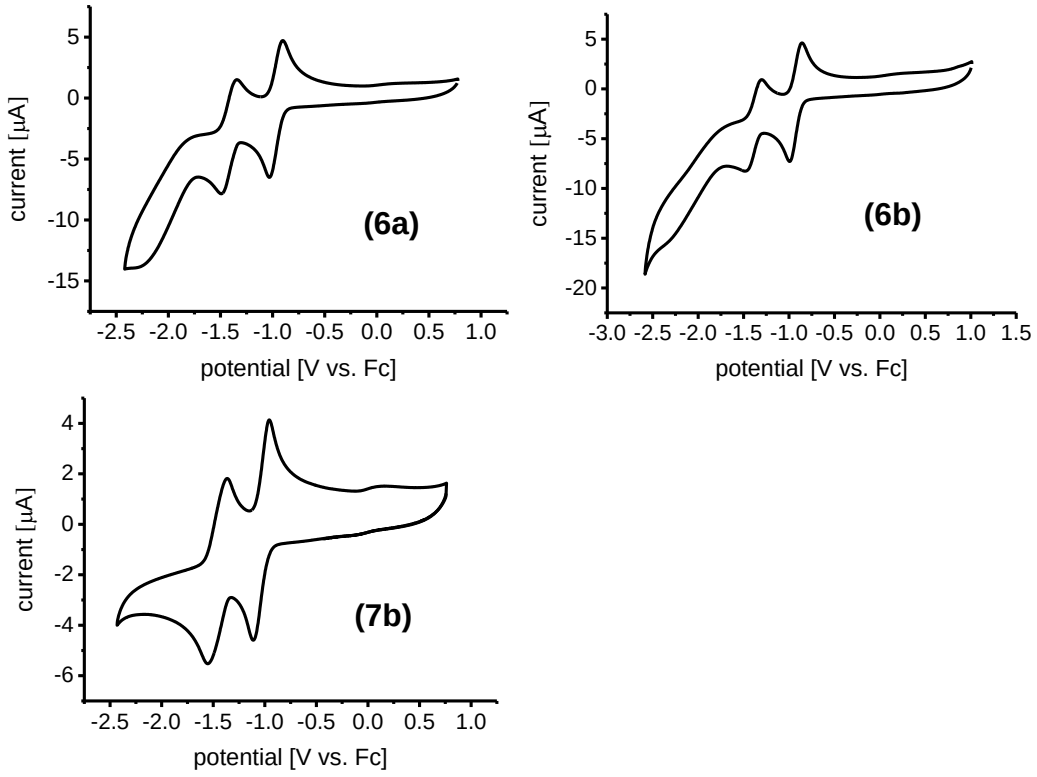


Figure S30: Cyclic voltammograms in DCM/ 0.1 M $[nBu_4N]^+[OCl_4]^-$ at 0.2 mV s^{-1}, the horizontal scale refers to an Ag/Ag^+ electrode, Pt working electrode, Pt/Ti counter electrode.

8. TGA-measurements

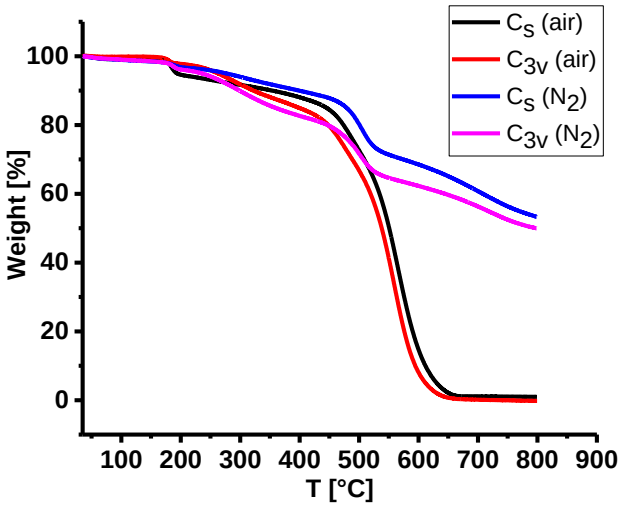


Figure S31: TGA-measurements of compound **7a** and **7b** under air and nitrogen-atomosphere.

9. Mobility measurements

In order to measure the electron mobility of the **7a** and **7b** molecules, space-charge limited current (SCLC) measurements were done. Hence, devices with a unipolar architecture (Figure S31(c)) were fabricated. For the bottom electron transporting layer (ETL), ZnO with 2% Cs doping was used and spin coated at 2000 rpm for 1 minute. For the top ETL a 10 nm thick Ca layer was evaporated on top of the charge carrier layer, which consisted of **7**.

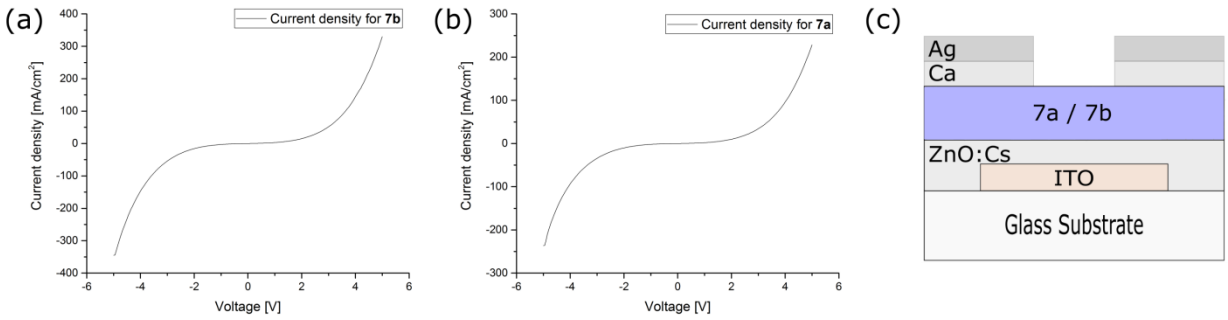


Figure S32: DJV measurements for (a) **7b** and (b) **7a** molecules with a unipolar device architecture (c). In this architecture, two ETL layers are used in order to be able to measure the electron mobility.

The corresponding space charge limited current is known as the Mott-Gurney law and is given by[S4]

(1) $$J = \frac{9\varepsilon_r\varepsilon_0 V^2}{8\,L^3} \cdot \mu$$

where $\varepsilon_r, \varepsilon_0$ and L are the relative permittivity, the vacuum permittivity and the thickness of the active layer, V is the applied voltage and μ is the electron mobility.

Table S1: Calculated electron mobilities from SCLC measurements.

Compound	Electron mobility μ
7a	$3.6 \cdot 10^{-6} cm^2/V \cdot s$
7b	$4.1 \cdot 10^{-6} cm^2/V \cdot s$

The relative permittivity ε_r is estimated to be 3, the active layer thickness L is 40 nm and the ratio $\frac{J}{V^2}$ can be estimated from Figure S31. The calculated electron mobilities (Table S1) are very low, as expected.

10. PLQE measurements

PL and PLQE measurements were carried out following the method of de Mello et al.[S5] A 447 nm diode laser (Dragon Lasers) was used as the excitation source, with a power density of approximately 3 mW/cm². The sample was placed at the centre of an integrating sphere (6" quantum efficiency sphere, LabSphere), and the intensity of both the laser and the PL were measured with a fibre coupled scientific spectrometer equipped with thermoelectric cooling (QE65000, Ocean Optics). The spectral response of the sphere, fibre and spectrometer was calibrated with a NIST traceable calibration light source (HL-2000-CAL-EXT, Ocean Optics).

The measured PL curves (Figure S32) and the calculated PLQE values (Table S2) both show that the PL of the donor materials is clearly quenched by the acceptor molecules **7a** and **7b**.

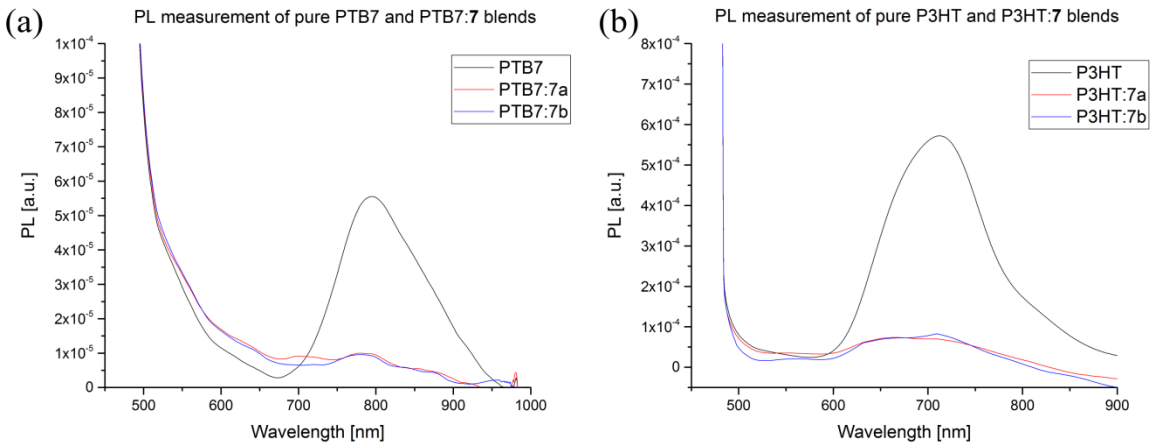


Figure S33: On-axis PL measurements of (a) PTB7 and PTB7:**7** blends and (b) P3HT and P3HT:**7** blends.

Table S2: Results of photoluminescence measurements for different blend compounds. In both cases the PL of the donor molecule, P3HT or PTB7, is quenched by the acceptor molecule **7.**

Blend compound	PLQE [%]
P3HT	5.69
P3HT:**7a**	0.55
P3HT:**7b**	1.25
PTB7	1.10
PTB7:**7a**	0.13
PTB7:**7b**	0.25

11. Energetics in film

In order to compare the HOMO and LUMO levels of the donor and acceptor polymers, UPS and UV-Vis measurements were performed (Figure S33).
For UPS, thin films of **7a**, **7b** and P3HT were spin coated on Au coated Si substrates. The samples were then transferred into an ultrahigh vacuum (UHV) chamber (ESCALAB 250Xi) for UPS measurements. The measurements were performed using a double-differentially pumped He discharge lamp (hν = 21.22 eV) with a pass energy of 2 eV.
The HOMO and LUMO levels of the two isomers were found to be identical within the experimental error of the measurement setups.

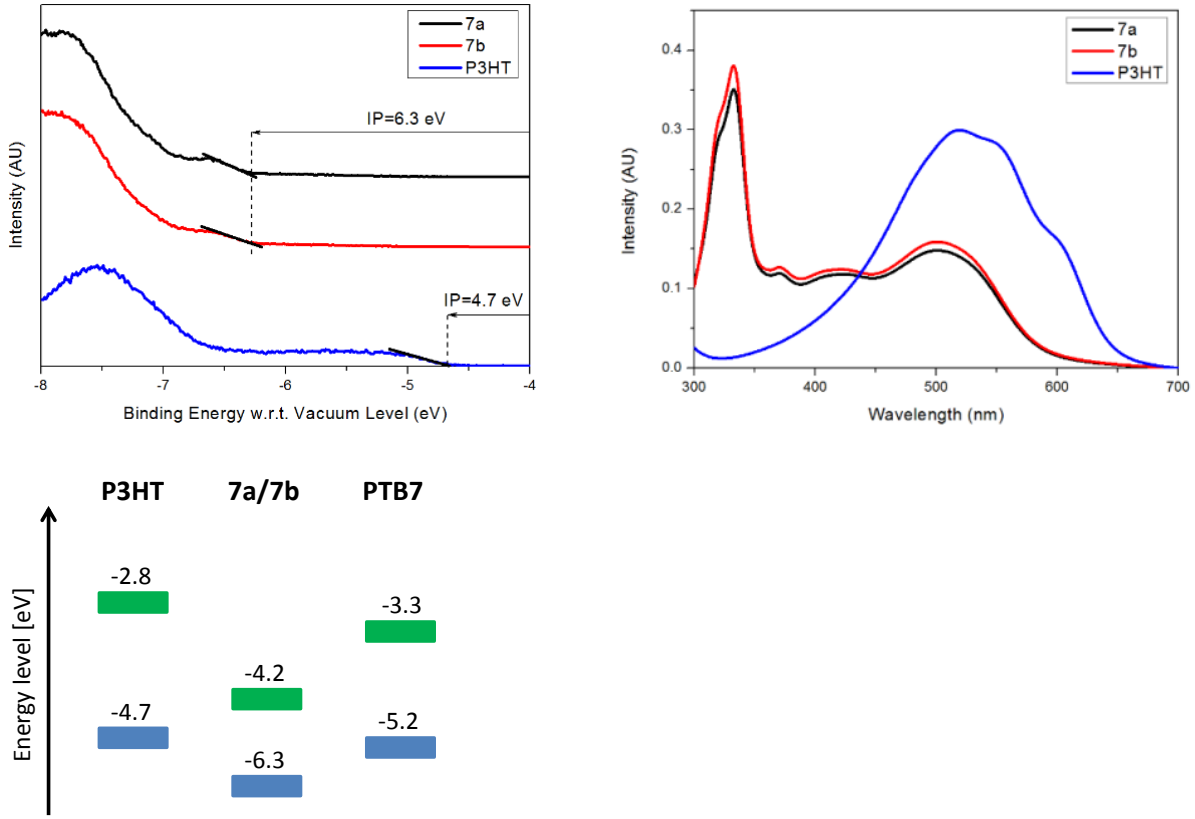


Figure S34: UPS/UV-Vis measurements and the proposed energetics of P3HT and acceptor materials. The energetics for PTB7 were taken from literature.[S6]

12. Fabrication of solar cells

a. Cleaning the substrates

The pre-patterned ITO substrates for the OPV devices were cleaned by sonicating first in acetone and secondly in isopropanol for 5 min each. The substrates were then O_2 plasma treated for 10 minutes.

b. Architecture

Both standard and inverted architectures were tested in order to optimize performance. Inverted architecture devices (Figure S35) performed the best and were used for further investigations.

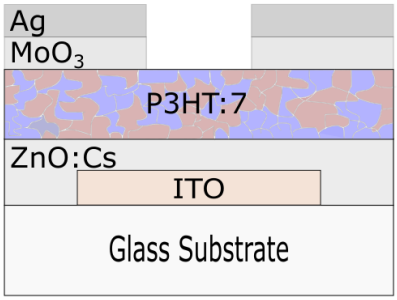


Figure S35: Inverted architecture: The ZnO, which was doped with 2% Cs, is used as the ETL and the MoO_3 as the HTL. The electrodes are ITO and Ag. The active layer is a blend of **7** and P3HT.

As an electron transport layer (ETL), ZnO with 2% Cs doping was used and spin coated at 2000 rpm for 1 minute. The materials were transported into a nitrogen filled glovebox and solved in chloroform. Unlike P3HT:PCBM solar cells, to obtain optimized performance of the P3HT:7 active layer, its thickness had to be significantly reduced which is an indication of a low conductivity of **7**. Low concentrations (~5 mg/ml) and spin speeds of ~500 rpm were used for spin-coating to obtain thin films of ~40 nm thickness as measured by a profilometer (Bruker DektakXT). On top of the blend a 10 nm thick hole transporting layer (HTL), consisting of MoO_3, and a 80 nm thick Ag anode electrode were thermally evaporated at a base pressure of $2 \cdot 10^{-6}$ mbar.

c. Post-annealing methods

In the construction of OPV devices, two main concepts for post-annealing were used.
On the one hand, the non-encapsulated devices were annealed inside the glovebox under nitrogen atmosphere after evaporating.
On the other hand, devices were annealed outside of the glovebox. In this case one can either anneal non-encapsulated or encapsulated devices. Encapsulation was done under nitrogen atmosphere with a 0.7 mm thick cover glass and epoxy glue (UHU Plus Endfest), though reactions with the glue can occur. In the non-encapsulated case, the devices interact with the normal atmosphere and therefore degrade with time.
Devices underwent a ramp annealing process, where they were annealed up to varying maximum temperatures (beginning with 70 °C, and from 125 °C on with 10 °C increments).

The duration for each annealing step was 10 min and the devices were cooled down in between each step.
Best performances were reached for encapsulated devices annealed outside of the glovebox with a maximum temperature of ~165 °C (Figure S35).

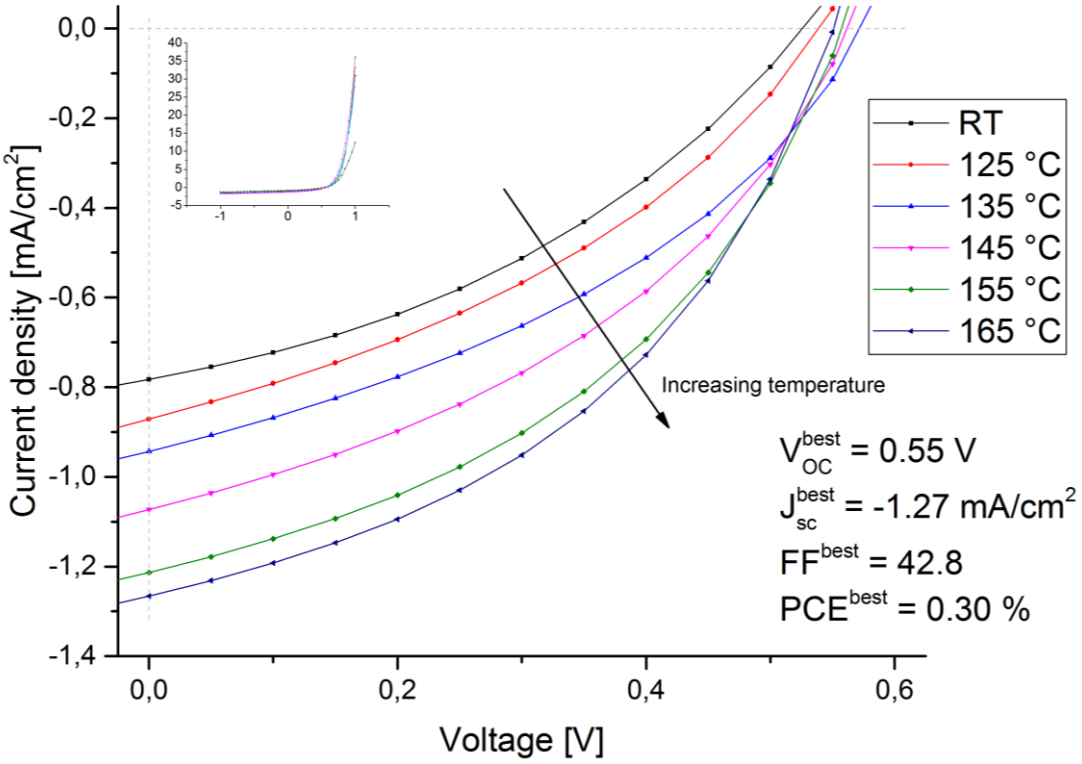


Figure S36: JV curves for a P3HT:**7a** ratio of 1:1 for different post-annealing temperatures after encapsulation.

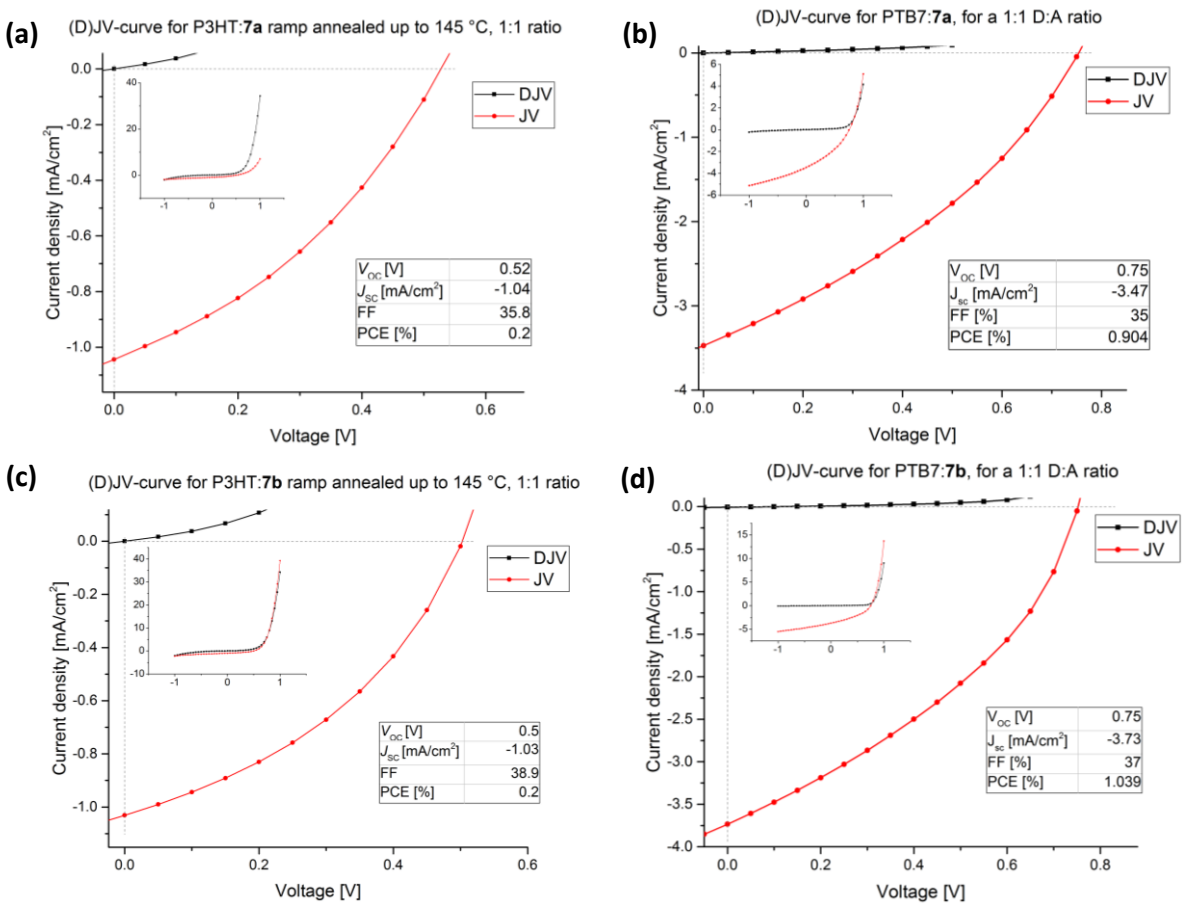


Figure S37: DJV and JV curves for comparison between isomers **7a** and **7b** for 1:1 blend ratio under nitrogen atmosphere. (a) P3HT: **7a** (annealing temperature: 145°C), (b) first try PTB7:**7a (**annealing temperature: rt) (c) P3HT: **7b** (annealing temperature: 145°C) and (d) first try PTB7:**7b (**annealing temperature: rt). Photovoltaic parameters are summarized in the inset.

13. AFM Measurements

For the AFM measurements the active layer was deposited on Si substrates. Micrographs of the active layer surfaces with AFM were compared for **7a** and **7b**. A similar kind of domains for both materials for the same D:A ratios can be observed. For **7a**, AFM pictures are shown in Figure S39.

The observed big domains are formed for all tested ratios. Such big domains imply a large scale phase separation for the BHJ layer. The formation of such aggregates can be explained by the low solubility of **7** compared to that of P3HT.

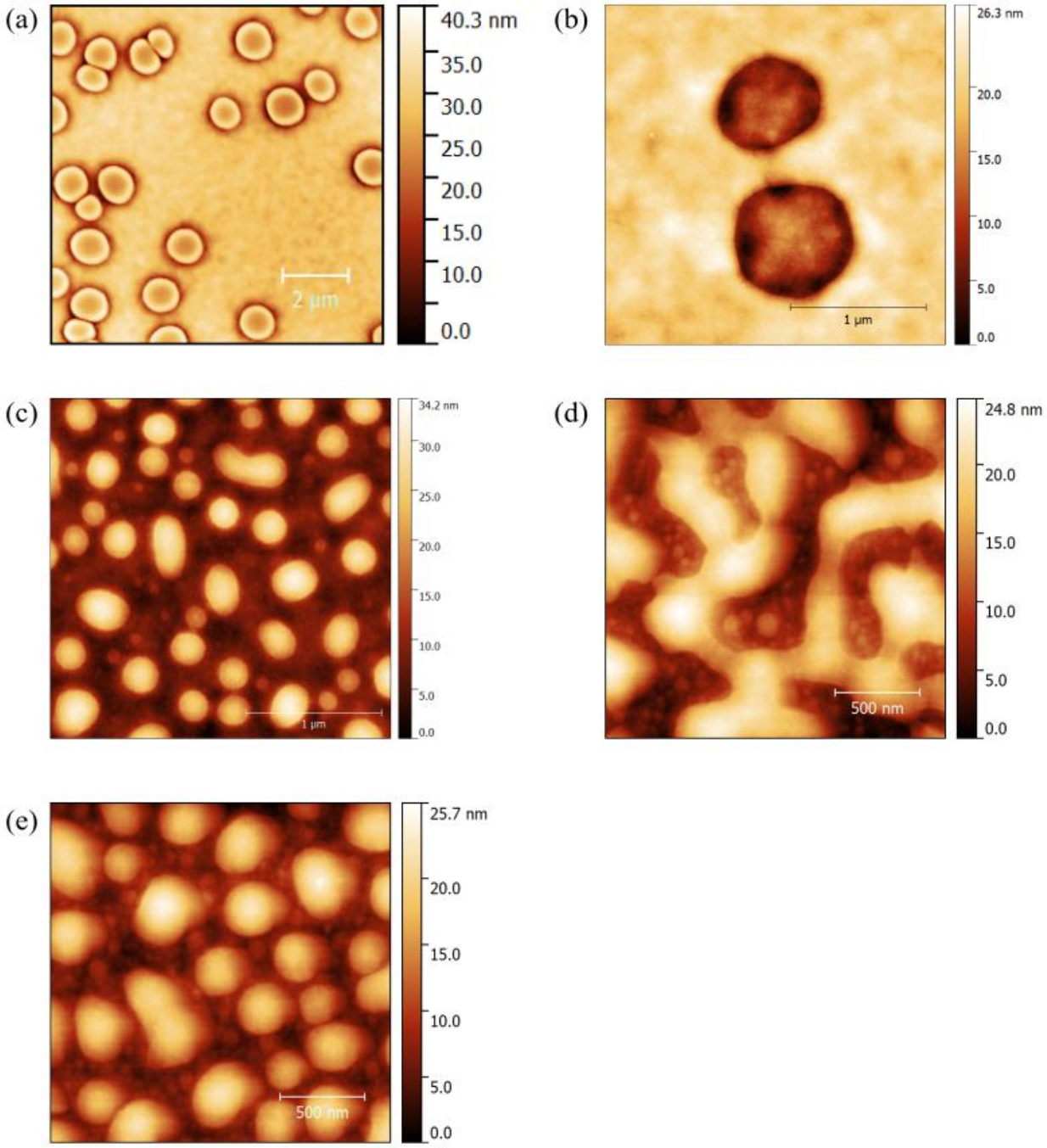


Figure S38: AFM pictures for (D:A) ratios (a) 1:3, (b) 1:2, (c) 1:1, (d) 2:1 and (e) 3:1, with P3HT as the donor and **7a** as the acceptor material (for **7b** the same behavior was observed). Already a small change in the blend ratio causes completely different domains: in (a) round structures of ~1 µm diameter, in (b) big holes, about 800 nm in diameter and in (c) small droplet-like objects of the size of 50 - 500 nm occur. In (d) a growing number of droplets aggregate by forming connected channels and in (e), as the concentration of P3HT further increases, densely packed hills (200-700 nm in diameter) are formed.

Literature:

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(S2) Chong, J. H.; MacLachlan, M. J. *Inorg. Chem*. **2006**, *45*, 1442-1444.

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(S4) N.F. Mott and R. W. Gurney, Electronic processes in ionic crystals, (Oxford University Press, **1940**)

(S5) J.C. de Mello, H.F. Wittmanm, R.H. Friend: An improved experimental determination of external photoluminescence quantum efficiency, *Adv. Mater., 9* (**1997**), pp. 230–232

(S6) H. Zeng, X. Zhu, Y. Liang, X. Guo: Interfacial Layer Engineering for Performance Enhancement in Polymer Solar Cells, *Polymers* **2015**, *7*(2), 333-372