Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Planar versus triptycenylene-end capped aroyleneimidazoles as electron acceptors in organic photovoltaic

-Supporting Information-

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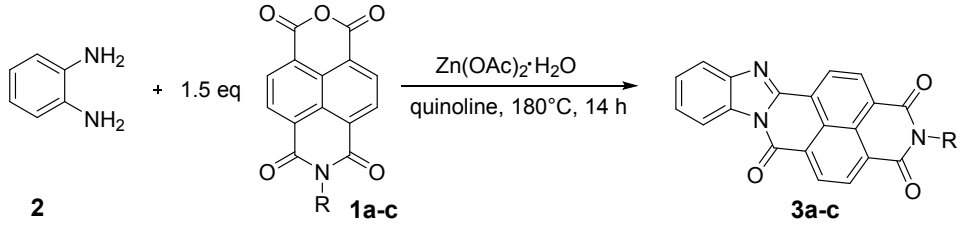
1. General Remarks

All reagents and solvents were obtained from Fisher Scientific, Alfa Aesar, Sigma-Aldrich or VWR and were used without further purification unless otherwise noted. Diisopropylphenyl-NMI **1a**[S1], Heptandecan-9-yl-NMI **1b**[S2], Ethylhexyl-NMI **1c**[S3] and Monoaminomononitrotriptycene **4**[S4], were synthesized following literature known procedures. 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 and/or ethyl acetate. Size Exclusion Chromatography (SEC) was performed on BioBeads SX1 from BioRad Laboratories, Inc. using chloroform as solvent. 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 $CHCl_3$ 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. 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_4NOCl4, as indicated. 1 mM ferrocene was used as an internal standard. Cyclic voltammograms were obtained at a scan rate of 0.1 V/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.

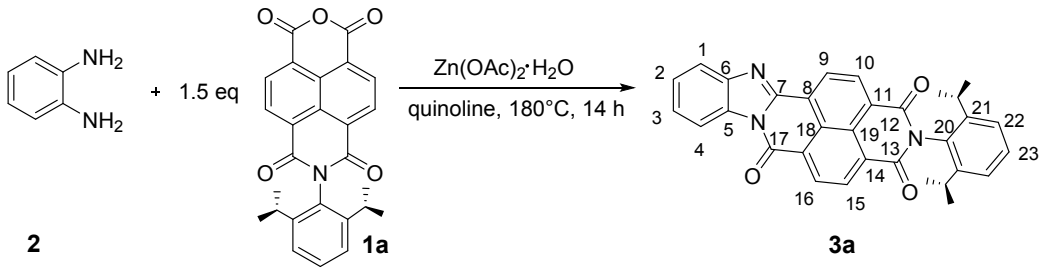
2. Synthesis and Characterization

General procedure A (GPA) for the synthesis of aroylenimidazoles



Phenylendiamine **2**, naphthalene monoimide **1a-c** and $Zn(OAc)_2 \cdot 2H_2O$ were suspended in quinoline (400 µl) and heated at 180°C for 24 h under argon. The resulting brownish solution was cooled to room temperature, HCl (18%, aq) (80 mL) was added and the organic phase was extracted with DCM (2x 40 mL). The combined organic phase was dried over Na_2SO_4 and solvent was removed by rotary evaporation. The crude product was purified by flash column chromatography on silica gel.

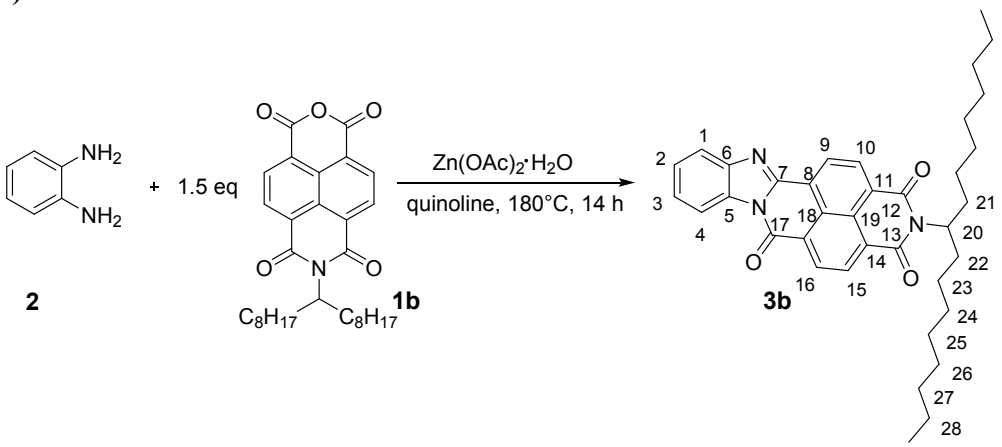
Synthesis of 2-[2,6-di(propan-2-yl)phenyl]benzimidazo[2,1*b*]benzo[*lmn*][3,8]phenanthroline-1,3,6(2*H*)-trione 3a



According to GPA, phenylenediamine **2** (50 mg, 462 µmol, 1 eq), NMI **1a** (297 mg, 694 µmol, 1.5 eq) and $Zn(OAc)_2 \cdot 2H_2O$ (20 mg) in quinoline (400 µL) were reacted. Purification by column chromatography on SiO_2 (DCM, $R_f = 0.26$) gave **3a** as an orange solid (199 mg, 398 µmol, 86%). Mp.: 333 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.99 ppm (d, J = 3.8 Hz, 1H, Ar-*H*-15), 8.95 (d, J = 7.6 Hz, 1H, Ar-*H*-10), 8.87 (d, J = 7.6 Hz, *H*-16), 8.84 (d, J = 4.2 Hz, *H*-9), 8.57-8.50 (m, 1H, *H*-4), 7.94-7.92 (m, 1H, *H*-1), 7.52-7.49 (m, 3H, *H*-2, 3, 23), 7.36 (d, J = 7.8 Hz, 2H, *H*-22), 2.75 (hept, J = 6.9 Hz, 2H, -C*H*), 1.19 (dd, J = 6.8 Hz, 1.8 Hz, 12H, -C*H*$_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.2 ppm (*C*-O-13), 163.1 (*C*-O-12), 159.4 (*C*-O-17), 147.9 (Ar-*C*-7), 145.8 (Ar-*C*-21), 144.2 (Ar-*C*-6), 132.4 (Ar-*C*-5), 131.7 (C_{Naph}), 131.7 (C_{Naph}), 131.5 (C_{Naph}), 130.1 (*C*-23), 127.3 (C_{Naph}), 126.9 (*C*-2/3), 126.8 (*C*-2/3), 124.8 (C_q), 124.4 (*C*-22), 121.2 (*C*-4), 116.2 (C-1), 29.5 (CH), 24.2 (-C*H*$_3$). IR (ATR): $\tilde{\nu}$ = 3071 cm^{-1} (w), 2965 (m), 2929 (w), 2870 (w), 1712 (s), 1673 (vs), 1614 (w), 1599 (w), 1579 (m), 1551 (w), 1509 (w), 1466 (m), 1445 (m), 1403 (m), 1375 (m), 1345 (vs), 1312 (m), 1242 (s), 1193 (m),

1153 (m), 1127 (w), 1008 (w), 987 (m), 939 (w), 913 (vw), 878 (w), 847 (w), 817 (w), 803 (m), 761 (s), 725 (m), 702 (w), 651 (vw). UV/VIS (DCM): λ_{abs} (lg ε) = 302 nm (4.4), 314 nm (4.4), 368 nm (4.2), 440 nm (4.3). Fluorescence (DCM): λ_{em} (λ_{ex}) = 569 nm (450). MS (MALDI-TOF): *m/z* (%) = 499.192 (100) $[M]^-$. Anal. calcd. for $C_{32}H_{25}N_3O_3 \cdot \frac{1}{8} CHCl_3$: C 75.63%, H 4.99%, N 8.24%, found: C 75.69%, H 5.07%, N 7.96%.

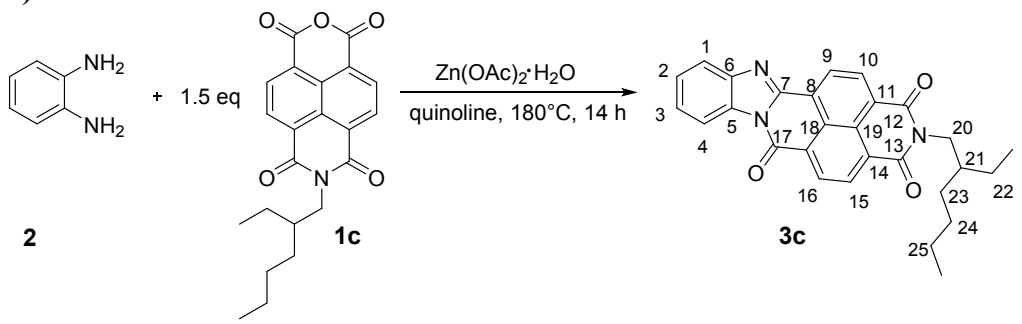
Synthesis of 2-(heptadecan-9-yl)benzimidazo[2,1-*b*]benzo[*lmn*][3,8]phenanthroline-1,3,6(2*H*)-trione 3b



According to GPA, phenylenediamine **2** (50 mg, 462 µmol, 1 eq), NMI **1b** (351 mg, 694 µmol, 1.5 eq) and $Zn(OAc)_2 \cdot 2H_2O$ (20 mg) in quinoline (400 µL) were reacted. Purification by column chromatography on SiO_2 (PE/DCM 1:1, R_f = 0.3) followed by desolving the compound in $CHCl_3$ (1 mL) and precipitation with MeOH gave after filtration **3b** as an orange solid (71 mg, 123 µmol, 40%). M.p. 225 °C (dec.). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.92 ppm (d, *J* = 7.6 Hz, 1H, Ar-*H*-15), 8.88 (d, *J* = 7.5 Hz, 1H, Ar-*H*-10), 8.81-8.70 (m, 2H, *H*-9,16), 8.48 (d, *J* = 7.1 Hz, 1H, *H*-4), 7.88 (d, *J* = 7.0 Hz, 1H, *H*-1), 7.51 (m, 2H, *H*-2, 3), 5.24-5.06 (m, 1H, *H*-20), 2.33-2.00 (m, 2H, *H*-21/22), 1.87-1.86 (m, 2H, H-21/22), 1.45-1.12 (m, 24H, H-23-27), 0.82 (t, 6H, -*CH*$_3$) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 164.1 ppm (*C*-O-13), 163.2 (*C*-O-12), 159.5 (*C*-O-17), 147.9 (Ar-*C*-7), 144.0 (Ar-*C*-6), 132.3 (Ar-*C*-5), 132.1 (C_{Naph}), 131.5 (C_{Naph}), 131.4 (C_{Naph}), 131.1 (C_q), 130.8 (C_q), 127.7 (C_q), 127.3 (C_q), 127.6 (C_q), 127.1 (C_{Naph}), 126.9 *C*-2/3), 126.7 (*C*-2/3), 125.9 (C_q), 125.5 (C_q), 120.0 (*C*-1), 116.1 (*C*-4), 55.4 (*C*-20), 32.5 (*C*-21), 32.0 (*C*-22/23), 29.7 (*C*-24), 29.7 (*C*-25), 29.4 (*C*-26), 27.1 (C-27), 22.8 (C-28), 14.3 (-C*H*$_3$), 10.8 (-C*H*$_3$). IR (ATR): $\tilde{\nu}$ = 2955 (m) cm^{-1}, 2923 (s), 2854 (m), 1702 (vs), 1658 (vs), 1618 (m), 1580 (m), 1547 (m), 1510 (w), 1447 (s), 1408 (m), 1376 (s), 1342 (vs), 1308 (s), 1242 (s), 1197 (m), 1171 (m), 1109 (m), 1040 (w), 1012 (w), 985 (m), 938 (vw), 869 (w), 826 (vw), 762 (s), 744 (m), 734 (m), 723 (w), 708 (w), 658 (vw). UV/VIS (DCM): λ_{abs} (lg

ε) = 299 nm (4.4), 312 nm (4.4), 370 nm (4.1), 435 nm (4.3). Fluorescence (DCM): λ_{em} (λ_{ex}) = 561 nm (450). MS (MALDI-TOF): *m/z* (%) = 577.332 (100) $[M]^-$. Anal. calcd. for $C_{37}H_{43}N_3O_3 \cdot \frac{1}{4} CH_2Cl_2$: C 74.69%, H 7.32%, N 7.02%, found: C 74.76%, H 7.25%, N 6.65%.

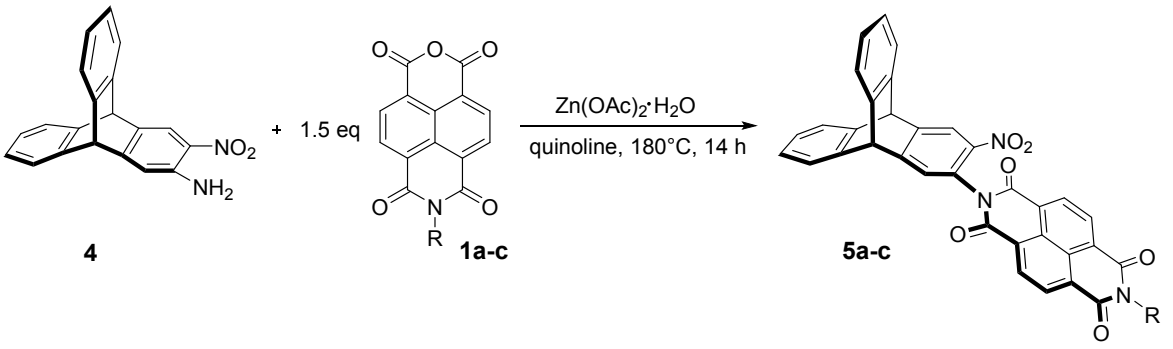
Synthesis of 2-(2-ethylhexyl)benzimidazo[2,1-*b*]benzo[*lmn*][3,8]phenanthroline-1,3,6(2*H*)-trione 3c



According to GPA, phenylenediamine **2** (50 mg, 462 µmol, 1 eq), NMI **1c** (264 mg, 694 µmol, 1.5 eq) and $Zn(OAc)_2 \cdot 2H_2O$ (20 mg) in quinoline (400 µL) were reacted. Purification by column chromatography on SiO_2 (PE/ DCM 1:1, R_f = 0.17) afforded a orange solid which still contains NMI **1c**. This mixture was suspended in DCM (4 mL), filtered off and the solid was washed with cold DCM (10 mL) giving the desired product **3c** as orange solid (78.2 mg, 173 µmol, 37%). M.p. 232 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.94 ppm (d, *J* = 7.7 Hz, 1H, Ar-*H*-15), 8.90 (d, *J* = 7.6 Hz, 1H, Ar-*H*-10), 8.80 (d, J = 7.6 Hz, 1H, *H*-16), 8.77 (d, *J* = 7.7 Hz, *H*-9), 8.53-8.40 (m, 1H, *H*-4), 7.95-7.84 (m, 1H, *H*-1), 7.58-7.46 (m, 2H, *H*-2,3), 4.41-3.82 (m, 2H, *H*-20), 1.91-1.86 (m, 1H, *H*-21), 1.35-1.32 (m, 8H, *H*-22, 23, 24, 25), 0.90-0.80 (m, 6H, -*CH*$_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.5 ppm (*C*-O-13), 163.3 (*C*-O-12), 159.4 (*C*-O-17), 147.9 (Ar-*C*-7), 144.2 (Ar-*C*-6), 132.2 (Ar-*C*-5), 131.9 (C_{Naph}), 131.4 (C_{Naph}), 131.2 (C_{Naph}), 127.9 (C_q), 127.7 (C_q), 127.6 (C_q), 127.2 (C_{Naph}), 126.9 *C*-2/3), 126.7 (*C*-2/3), 126.1 (C_q), 125.8 (C_q), 124.9 (C_q), 120.1 (*C*-1), 116.2 (*C*-4), 44.8 (*C*-20), 38.2 (*C*-21), 31.0 (*C*-23), 28.9 (*C*-24), 24.3 (*C*-22), 23.3 (*C*-25), 14.3 (-C*H*$_3$), 10.8 (-C*H*$_3$). IR (ATR): $\tilde{\nu}$ = 3079 cm^{-1} (w), 2953 (m), 2925 (m), 2869 (w), 1960 (w), 1700 (vs), 1665 (vs), 1613 (m), 1579 (m), 1552 (m), 1507 (m), 1446 (m), 1405 (m), 1379 (s), 1367 (m), 1341 (vs), 1324 (s), 1307 (s), 1284 (m), 1233 (s), 1207 (m), 1174 (m), 1149 (w), 1133 (m), 1086 (m), 1051 (w), 1031 (w), 1010 (w), 991 (w), 947 (w), 878 (m), 856 (vw), 827 (vw), 798 (vw), 761 (vs), 727 (w), 709 (vw), 645 (vw), 623 (w), 611 (w). UV/VIS (DCM): λ_{abs} (lg ε) = 300 nm (4.4), 310 nm (4.4), 370 nm (4.1), 442 nm (4.3). Fluorescence (DCM): λ_{em} (λ_{ex}) = 565 nm (450). MS (MALDI-TOF): *m/z*

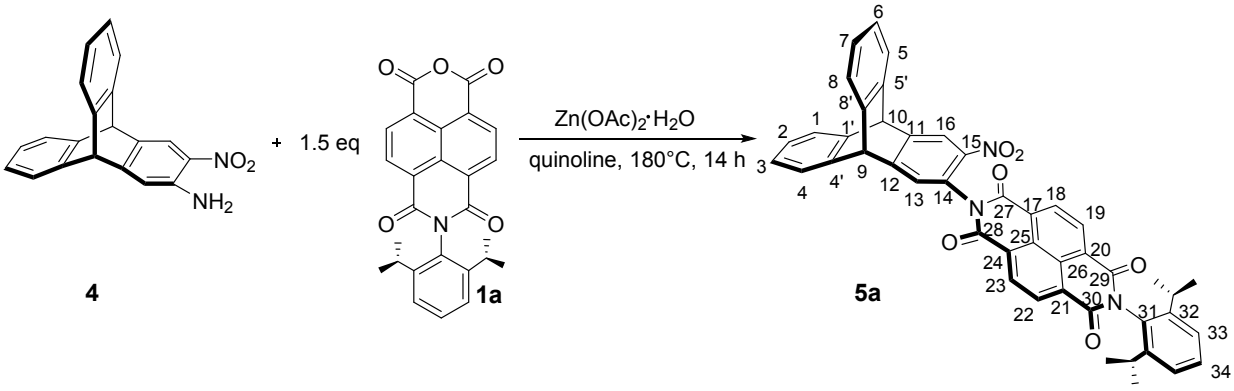
(%) = 451.186 (100) $[M]^-$. Anal. calcd. for $C_{98}H_{71}N_9O_{18} \cdot \frac{1}{8} CH_2Cl_2$: C 73.10%, H 5.51%, N 9.09%, found: C 73.24%, H 5.37%, N 9.37%.

General procedure B (GPB) for the synthesis of triptycenenaphthalenediimides 5a-c



Monoaminomononitrotriptycene **4** (1 eq), NMI **1a-c** (1.5 eq) and $Zn(OAc)_2 \cdot 2H_2O$ were suspended in quinoline (1.0 mL) and heated at 180°C for 24 h under argon. The resulting brownish solution was cooled to room temperature, HCl (18%, aq, 80 mL) was added and the organic phase extracted with DCM (2x 40 mL). The combined organic phase was dried over Na_2SO_4, concentrated under reduced pressure and separated by column chromatography on silica gel. After removing the solvent, size exclusion chromatography (SEC) with $CHCl_3$ as eluent was performed giving the desired products as orange solid after drying under reduced pressure.

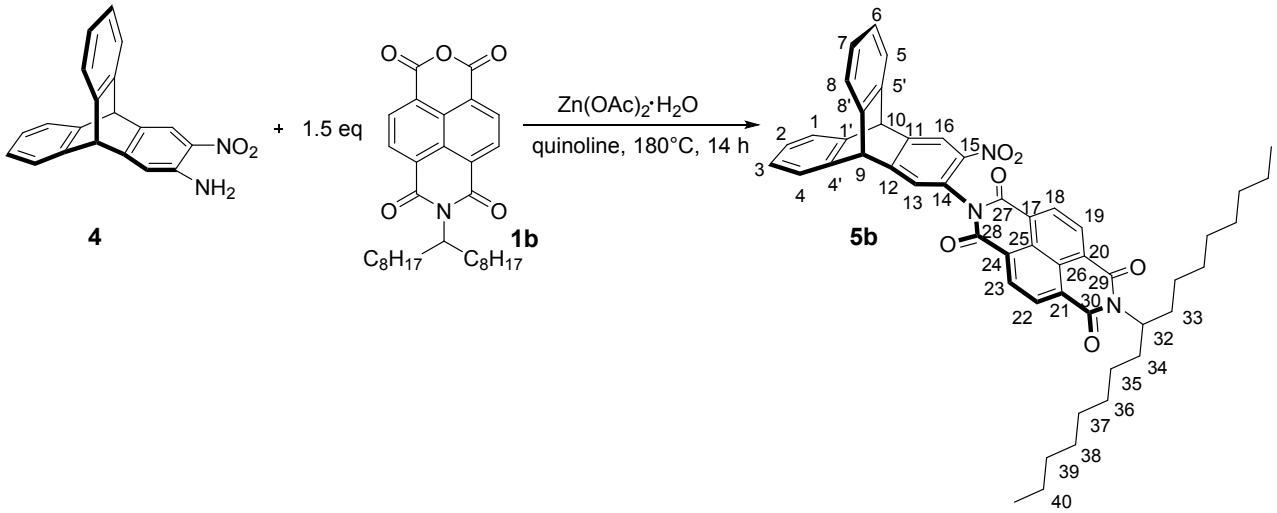
Synthesis of 2-[2,6-di(propan-2-yl)phenyl]-7-(5-nitropentacyclo[6.6.6.$0^{2,7}$.$0^{9,14}$.$0^{15,20}$]icosa-2,4,6,9,11,13,15,17,19-nonaen-4-yl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetrone 5a



According to GPB, monoaminomononitrotriptycene **4** (200 mg, 636 µmol, 1 eq), NMI **1a** (408 mg, 954 µmol, 1.5 eq) and $Zn(OAc)_2 \cdot 2H_2O$ (30 mg) in quinoline (1 mL) were reacted. Purification by column chromatography on SiO_2 (PE/ DCM 1:1, $R_f = 0.62$), followed by SEC

with $CHCl_3$ gave the desired product **5a** as orange solid (309 mg, 427 µmol, 67%). M.p.: 300 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.81 ppm (dd, J = 24.8 Hz, 7.5 Hz, 4H, Ar-*H*-18, 19, 22, 23), 8.36 (s, 1H, Ar-*H*-16), 7.54-7.47 (m, 4H, Ar-*H*-13, 33, 34), 7.42 (d, J = 6.7 Hz, 2H, Ar-*H*-1,5), 7.37 (d, J = 6.7 Hz, 2H, Ar-*H*-4,8), 7.12-7.07 (m, 4H, Ar-*H*-2,3,6,7), 5.67 (s, 1H, bridgehead-*H*-10), 5.57 (s, 1H, bridgehead -*H*-9), 2.74-2.69 (m, 2H,-C*H*-CH_3), 1.18-1.16 (m, 36H, -*CH_3*) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163 ppm (*C*-O-27,28), 162.9 (*C*-O-29,30), 152.7 (Ar-C_q), 152.6 (Ar-C_q), 148.3 (Ar-C_q), 145.9 (Ar-C_q), 145.7 (Ar-C_q), 143.8 (Ar-C_q), 143.3 (Ar-C_q), 131.8 (Ar-*C*-18, 19, 22, 23), 131.7 (Ar-C_q), 130.2 (Ar-*C*-34), 130.1 (Ar-C_q), 127.8 (Ar-*C*-17, 20, 21, 24), 127.7 (Ar-C_q), 126.7 (Ar-*C*-14), 126.7 (Ar-*C*-4,8,13), 126.5, 126.3 (Ar-C-2, 3, 6, 7), 126.2 (Ar-C_q), 124.5 (Ar-*C*-1, 5), 124.4 (Ar-*C*-13), 121.4 (Ar-*C*-16), 54.0 (bridgehead -*C*-10), 53.8 (bridgehead -*C*-9), 29.5 (*C*H-CH_3), 24.2, 24.1 (-*C*H_3). IR (ATR): $\tilde{\nu}$ = 3070 cm^{-1} (w), 2963 (w), 2929 (w), 2870 (w), 1716 (m), 1674 (s), 1581 (m), 1527 (m), 1459 (w), 1384 (s), 1339 (s), 1246 (m), 1196 (w), 1135 (w), 1119 (w), 1057 (m), 982 (w), 938 (w), 881 (w), 857 (w), 841 (m), 799 (m), 768 (s), 745 (m), 723 (m), 699 (m), 629 (m). UV/VIS (DCM): λ_{abs} (lg ε) = 380 nm (4.6), 360 nm (4.5). MS (MALDI-TOF): *m/z* (%) = 723.236 (100) [M]$^-$. Anal. calcd. for $C_{46}H_{33}N_3O_6 \cdot \frac{1}{5} CH_2Cl_2$: C 75.47%, H 4.55%, N 5.69%, found: C 75.47%, H 4.92%, N 5.25%.

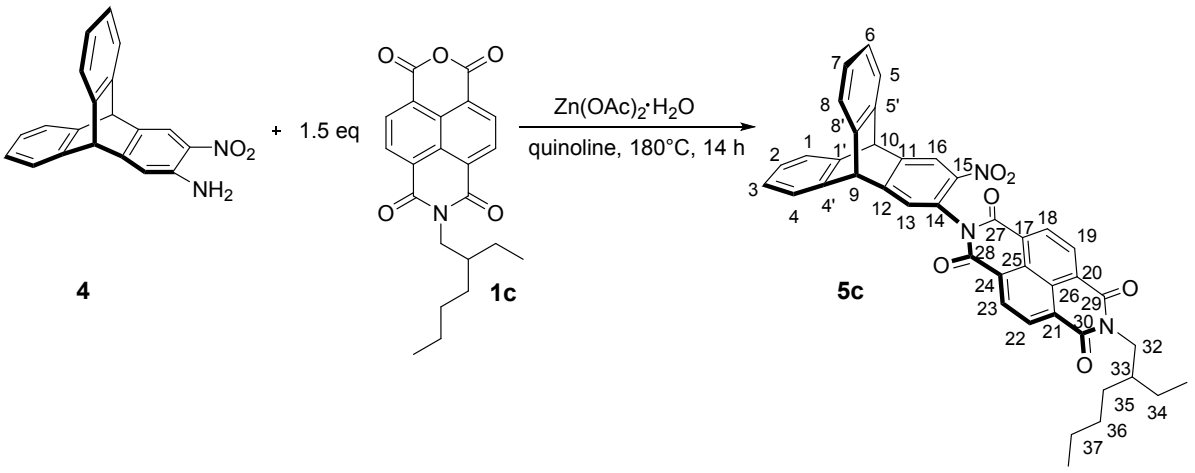
Synthesis of 2-(heptadecan-9-yl)-7-(5-nitropentacyclo[6.6.6.0^{2,7}.0^{9,14}.0^{15,20}]icosa-2,4,6,9,11,13,15,17,19-nonaen-4-yl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetrone 5b



According to GPB, monoaminomononitrotriptycene (200 mg, 636 µmol, 1 eq), NMI **1b** (482 mg, 954 µmol, 1.5 eq) and $Zn(OAc)_2 \cdot 2H_2O$ (30 mg) in quinoline (1 mL) were reacted. Purification by column chromatography on SiO_2 (PE/ DCM 2:1, R_f = 0.13), followed by SEC

with $CHCl_3$ gave the desired product as orange solid (356 mg, 444 µmol, 70%). M.p.: 125 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.77-8.72 ppm (m, 4H, Ar-*H*-18, 19, 22, 23), 8.33 (s, 1H, Ar-*H*-16), 7.49-7.47 (m, 2H, Ar-*H*-1,5), 7.45 (s, 1H, Ar-*H*-13), 7.42-7.40 (m, 2H, Ar-*H*-4, 8), 7.11-7.7.05 (m, 4H, Ar-*H*-2, 3, 6, 7), 5.64 (s, 1H, bridgehead-*H*-9), 5.54 (s, 1H, bridgehead -*H*-10), 5.19-5.13 (tt, J = 9.3 Hz, 5.7 Hz, 1H, C*H*-32), 2.26-2.21 (m, 2H, CH_2-33/34), 1.88-1.86 (m, 2H, CH_2-33/34), 1.31-1.27 (m, 24 H, CH2-Alkyl), 0.84 (dt, J = 13.6, 4.8 Hz, -CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163 ppm (*C*-O-27,28), 162.9 (*C*-O-29,30), 152.6 (Ar-C_q), 148.2 (Ar-C_q), 143.8 (Ar-C_q), 143.3 (Ar-C_q), 142.9 (Ar-C_q), 131.1 (Ar-*C*-18, 19, 22, 23), 127.4 (Ar-*C*-17, 20, 21, 24), 127.3 (Ar-C_q), 126.7 (Ar-*C*-14), 126.5 (Ar-*C*-4,8,13), 126.3, 162.2 (Ar-C-2, 3, 6, 7), 124.5 (Ar-*C*-1, 5), 124.4 (Ar-*C*-13), 121.3 (Ar-*C*-16), 55.6 (*C*-32), 54.0 (bridgehead -*C*-10), 53.8 (bridgehead -*C*-9), 32.5 (*C*-33/34), 32.0 (*C*-33/34), 31.1 (*C*-35), 29.7 (*C*-36), 29.6 (*C*-37), 29.4 (*C*-38), 27.1 (*C*-39), 22.8 (*C*-40), 14.2 (-*C*H$_3$). IR (ATR): $\tilde{\nu}$ = 2924 cm^{-1} (m), 2854 (m), 1787 (m), 1706 (s), 1686 (m), 1666 (vs), 1580 (m), 1526 (s), 1453 (m), 1401 (m), 1340 (s), 1324 (vs), 1246 (vs), 1190 (s), 1102 (m), 1023 (w), 978 (w), 880 (w), 856 (w), 831 (w), 798 (w), 769 (s), 739 (s), 639 (w), 629 (w). UV/VIS (DCM): λ_{abs} (lg ε) = 361 nm (4.4), 381 nm (4.5). MS (MALDI-TOF): *m/z* (%) = 801.380 (100) [M]$^-$. Anal. calcd. for $C_{51}H_{51}N_3O_6$: C 76.38%, H 6.41%, N 5.24%, found: C 76.21%, H 6.66%, N 5.06%.

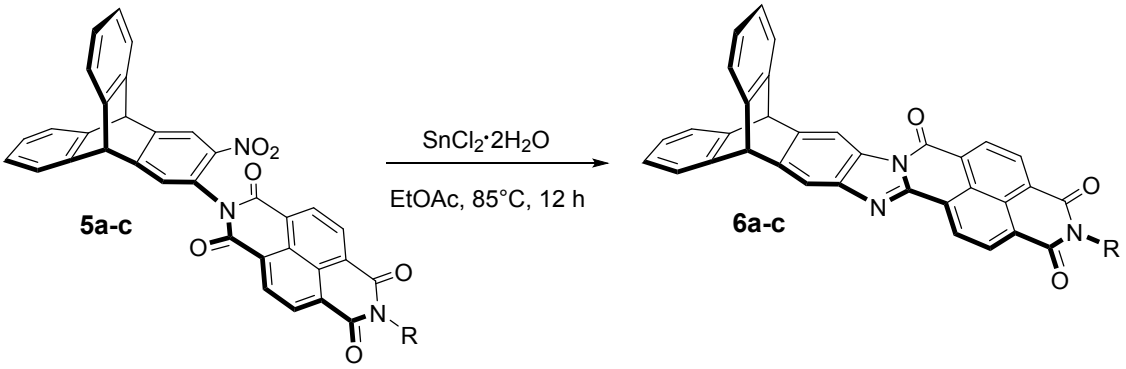
Synthesis of 2-[(2-ethylhexyl]-7-(5-nitropentacyclo[6.6.6.0^{2,7}.0^{9,14}.0^{15,20}]icosa-2,4,6,9,11,13,15,17,19-nonaen-4-yl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetrone



According to GPB, monoaminomononitrotriptycene **4** (200 mg, 636 µmol, 1 eq), NMI **1c** (362 mg, 954 µmol, 1.5 eq) and $Zn(OAc)_2 \cdot 2H_2O$ (30 mg) in quinoline (1 mL) were reacted. Purification through column chromatography on SiO_2 (PE/ DCM 1:1, R_f = 0.29), followed by SEC with $CHCl_3$ gave the desired product **5c** as orange solid (313 mg, 463 µmol, 73%). M.p.: 198 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.76 ppm (d, J = 7.6 Hz, 2H, Ar-*H*-18,23), 8.74 (d, *J*

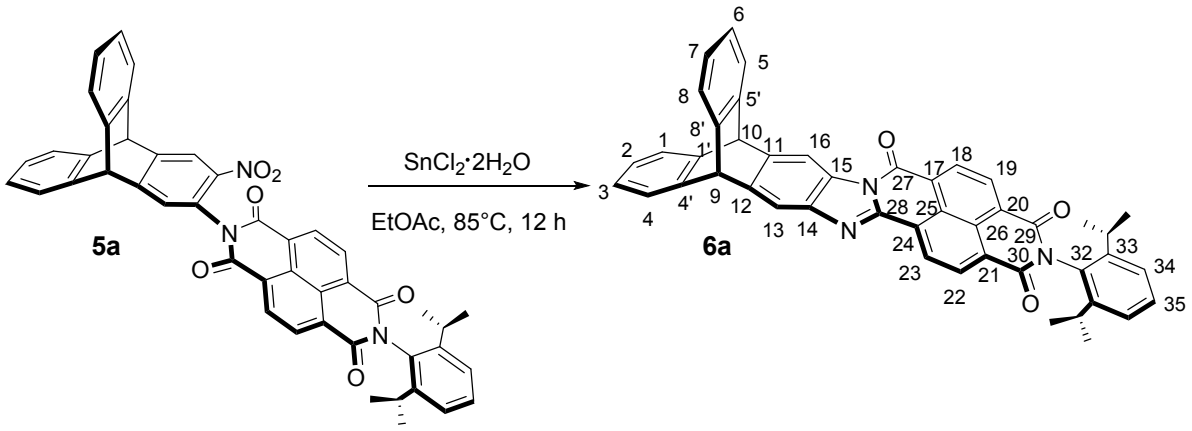
= 7.6 Hz, 2H, Ar-*H*-19,22), 8.33 (s, 1H, Ar-*H*-16), 7.49-7.47 (m, 2H, Ar-*H*-1,5), 7.45 (s, 1H, Ar-*H*-13), 7.42-7.40 (m, 2H, Ar-*H*-4,8), 7.12-7.05 (m, 4H, *H*-2,3,6,7), 5.64 (s, 1H, bridgehead-*H*-10), 5.54 (s, 1H, bridgehead -*H*-9), 4.22-4.12 (m, 2H, *H*-32), 1.97-1.94 (m, 1H, *H*-33), 1.42-1.32 (m, 8H, *H*-34, 35, 36, 37) 0.97-0.89 (m, 6H, -CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.2 ppm (*C*-O-27,28), 162.9 (*C*-O-29,30), 152.6 (Ar-C_q), 148.2 (Ar-C_q), 143.8 (Ar-C_q), 143.3 (Ar-C_q), 142.9 (Ar-C_q), 131.7 (Ar-*C*-18, 23), 131.2 (Ar-*C*-19, 22), 127.5 (Ar-*C*-17, 24), 127.5 (Ar-*C*-20, 21), 127.2 (Ar-C_q), 126.7 (Ar-*C*-14), 126.5 (Ar-*C*-4,8,13), 126.4/126.2 (Ar-C-2, 3, 6, 7), 124.5 (Ar-*C*-1, 5), 124.4 (Ar-*C*-13), 121.3 (Ar-*C*-16), 54.0 (bridgehead -*C*-10), 53.8 (bridgehead -*C*-9), 44.9 (*C*-32), 38.2 (*C*-33), 30.9 (*C*-35), 28.8 (*C*-36), 24.3 (*C*-34), 23.2 (*C*-37), 14.2 (-*C*H_3), 10.8 (-*C*H_3). IR (ATR): $\tilde{\nu}$ = 2960cm^{-1} (w), 2932 (w), 2870 (w), 1709 (s), 1668 (vs), 1583 (m), 1528 (m), 1459 (s), 1342 (s), 1248 (s), 1191 (s), 1157 (m), 1119 (w), 1094 (w), 984 (w), 940 (w), 881 (w), 855 (w), 831 (w), 799 (w), 768 (s), 747 (m), 629 (m). UV/VIS (DCM): λ_{abs} (lg ε) = 359 nm (4.5), 381 nm (4.5). MS (MALDI-TOF): *m/z* (%) = 6.75.234 (100) [M]$^-$. Anal. calcd. for $C_{42}H_{33}N_3O_6$: C 74.65%, H 4.92%, N 6.22%, found: C 74.20%, H 5.07%, N 5.75%.

General procedure C (GPC) for the synthesis of triptycenemonoaroylenimidazoles 6a-c



A mixture of triptycenenaphthalendiimide **5a-c** and $SnCl_2 \cdot 2H_2O$ was dissolved in EtOAc (4 mL) and heated at 85°C for 12 h under argon. After cooling to room temperature, the reaction mixture was diluted with DCM (50 mL), an aqueous $NaHCO_3$-solution (10%, 50.0 mL) was added and the mixture was extracted with DCM (2x 20 mL). The combined organic extract was dried over Na_2SO_4 and the solvent was removed by rotary evaporation. The crude product was then purified by flash column chromatography on silica gel.

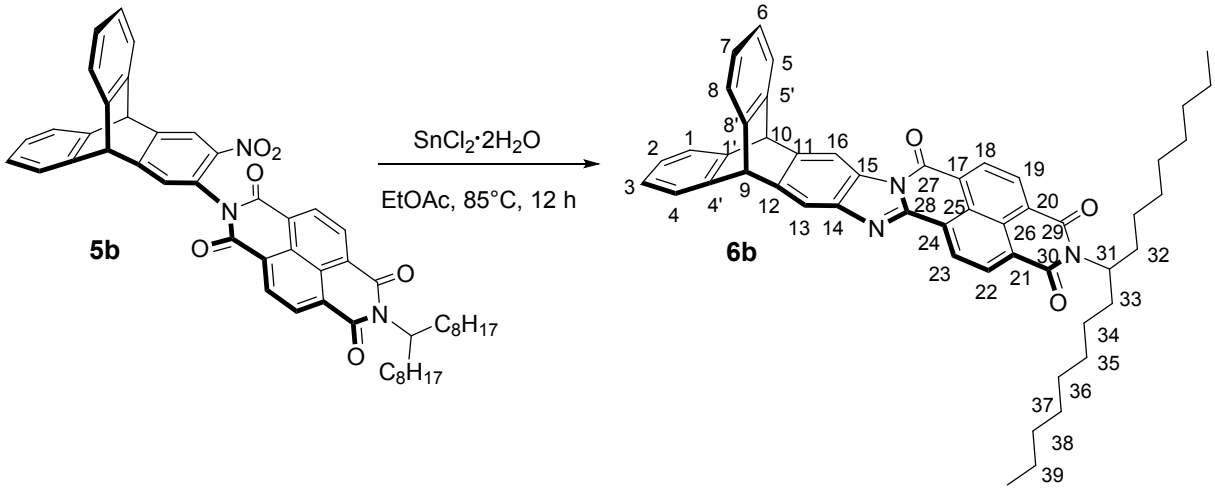
Synthesis of 12-[2,6-di(propan-2-yl)phenyl]-5,12,19-triazadecacyclo[21.6.6.2^{7,10}.0^{2,22}.0^{4,20}.0^{5,18}.0^{8,17}.0^{9,14}.0^{24,29}.0^{30,35}]heptatriaconta-2(22),3,7,9,14,16,18,20,24,26,28,30,32,34,36-pentadecaene-6,11,13-trione 6a



According to GPC a mixture of **5a** (150 mg, 207 µmol) and $SnCl_2 \cdot 2H_2O$ (421 mg, 1.87 mmol) dissolved in ethylacetate (4 mL) was reacted. Purification by column chromatography on SiO_2 (PE/ DCM 1:1, $R_f = 0$, then DCM ($R_f = 0.7$), followed by precipitation with pentane out of a chloroform solution gave the desired product **6a** as reddish solid (58 mg, 85 µmol, 41%). M.p.: >400 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.95-8.91 ppm (m, 2H, Ar-*H*-19,22), 8.85 (d, *J* = 7.6 Hz, 2H, Ar-*H*-23), 8.81 (d, *J* = 7.7 Hz, 2H, Ar-*H*-18), 8.58 (s, 1H, Ar-*H*-13), 7.89 (s, 1H, Ar-*H*-16), 7.52-7.49 (m, 1H, *H*-35), 7.48-7.47 (m, 4H, Ar-*H*-1, 4, 5, 8), 7.35 (d, J = 7.8 Hz, 2H, H-34), 7.10-6.99 (m, 4H, Ar-*H*-2, 3, 6, 7), 5.66 (s, 1H, bridgehead-*H*-10), 5.62 (s, 1H, bridgehead -*H*-9), 2.71 (dt, *J* = 13.6 Hz, 6.8 Hz, -C*H*-CH_3), 1.16 (d, J = 6.8 Hz, -CH_3). ^{13}C NMR (151 MHz, $CDCl_3$): δ = 163.2 ppm (*C*-O-29), 163.1 (*C*-O-30), 159.3 (*C*-O-27), 147.7 (*C*-28), 145.8 (Ar-*C*-33), 145.3 (Ar-C_q-1'5'), 144.9 (Ar-C_q-4',8'), 144.8 (*C*-14), 144.6 (Ar-C_q-11), 141.8 (Ar-C_q-12), 132.4 (Ar-*C*-18,19,22,23), 131.6 (Ar-*C*-18,19,22,23), 131.4 (Ar-*C*-18,19,22,23), 130.1 (Ar-*C*-18,19,22,23), 127.7 (Ar-*C*-15), 126.5 (Ar-*C*-35), 125.8 (Ar-*C*-2,3,6,7), 124.4 (Ar-*C*-1,5,34), 124.1 (*C*-4,8), 116.1 (Ar-*C*-13), 111.8 (Ar-C-16), 54.6 (bridgehead -*C*-9), 54.5 (bridgehead -*C*-10), 29.4 (*C*H-CH_3), 24.2 (-*C*H_3). IR (ATR): $\tilde{\nu}$ = 3067 cm^{-1} (w), 2962 (m), 2928 (w), 2869 (w), 1709 (s), 1673 (vs), 1618 (w), 1599 (m), 1577 (m), 1546 (w), 1508 (w), 1459 (m), 1435 (s), 1400 (m), 1378 (s), 1354 (s), 1337 (vs), 1309 (m), 1272 (m), 1243 (s), 1192 (s), 1154 (m), 1126 (w), 1056 (w), 1024 (w), 989 (m), 939 (w), 899 (w), 879 (m), 835 (w), 801 (m), 789 (w), 765 (s), 756 (m), 741 (s), 724 (m), 701 (w), 644 (vw), 628 (m), 617 (w). UV/VIS (DCM): λ_{abs} (lg ε) = 324 nm (4.4), 372 nm (3.9), 476 nm (4.0). Fluorescence (DCM): λ_{em} (λ_{ex}) = 624 nm (450). CV (DCM, NBu_4OCl_4): $E^{red1}_{1/2}$ = -1.19 V (Fc),

$E^{red1}_{1/2}$ = -1.70 V (Fc). MS (MALDI): *m/z* (%) = 675.251 (100) $[M]^-$. Anal. calcd. for $C_{46}H_{33}N_3O_3 \cdot \frac{1}{4} CH_2Cl_2$: C 79.70%, H 4.84%, N 6.03%, found: C 79.42%, H 5.26%, N 5.83%.

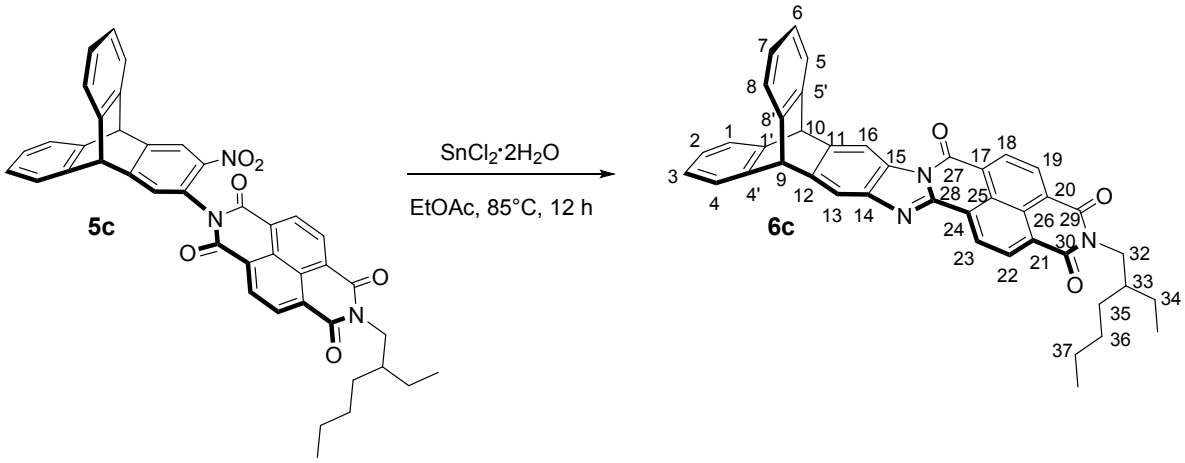
Synthesis of 12-(heptadecan-9-yl)-5,12,19-triazadecacyclo[21.6.6.2^{7,10}.0^{2,22}.0^{4,20}.0^{5,18}.0^{8,17}.0^{9,14}.0^{24,29}.0^{30,35}]heptatriaconta-2(22),3,7,9,14,16,18,20,24,26,28,30,32,34,36-pentadecaene-6,11,13-trione 6b



According to GPC a mixture of **5b** (200 mg, 249 µmol) and $SnCl_2 \cdot 2H_2O$ (253 mg, 1.12 mmol) dissolved in ethylacetate (4 mL) was reacted. Purification by column chromatography on SiO_2 (PE/ DCM 2:1, R_f = 0, then DCM (R_f = 0.9) gave **6b** as reddish solid (96 mg, 127 µmol, 51%). M.p.: 245 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.79-8.75 ppm (m, 2H, Ar-*H*-22,19), 7.68-7.64 (m, 2H, Ar-*H*-18,23), 8.52 (s, 1H, Ar-*H*-16), 7.82 (s, 1H, Ar-*H*-13), 7.53-7.36 (m, 4H, Ar-*H*-1, 4, 5, 8), 7.22-7.04 (m, 4H, Ar-*H*-2, 3, 6, 7), 5.64 (s, 1H, bridgehead-*H*-10), 5.60 (s, 1H, bridgehead -*H*-9), 5.23-5.09 (m, 1H, *H*-31), 2.25-2.20 (m, 2H, *H*-32/33), 1.88-1.84 (m, 2H, *H*-32/33), 1.34-1.21 (m, 24H, -CH_2), 0.82 (t, *J* = 6.9 Hz, 6H, -CH_3). ^{13}C NMR (151 MHz, $CDCl_3$): δ = 164.3 ppm (*C*-O-29), 163.2 (*C*-O-30), 159.4 (*C*-O-27), 147.8 (*C*-28), 145.1 (Ar-C_q-1'5'), 145.0 (Ar-C_q-4',8'), 144.8 (*C*-14), 144.4 (Ar-C_q-11), 141.8 (Ar-C_q-12), 132.2 (Ar-*C*-18,19,22,23), 131.4 (Ar-*C*-18,19,22,23), 131.3 (Ar-*C*-18,19,22,23), 129.7 (*C*-15), 127.7 (Ar-C_q), 127.2 (C_q), 126.4 (Ar-*C*-1,5), 125.8 (Ar-*C*-2,3,6,7), 125.6 (Ar-C_q), 124.0 (*C*-4,8), 116.0 (Ar-*C*-13), 111.8 (Ar-C-16), 55.3 (C-31), 54.5 (bridgehead -*C*-9), 54.4 (bridgehead -*C*-10), 32.5 (*C*-32/33), 32.0 (*C*-34), 29.7 (*C*-35), 29.7 (*C*-36), 29.4 (C-37), 27.1 (C-38), 22.8 (C-39), 14.3 (-*C*H_3). IR (ATR): $\tilde{\nu}$ = 2955 cm^{-1} (m), 2924 (s), 2854 (m), 1703 (s), 1666 (vs), 1617 (w), 1601 (w), 1577 (m), 1551 (w), 1509 (w), 1459 (m), 1436 (m), 1407 (m), 1377 (m), 1354 (m), 1335 (vs), 1309 (m), 1245 (s), 1198 (m), 1174 (m), 1155 (w), 1101 (s), 1023 (m), 987 (m), 879 (m), 803 (s), 766 (s), 757 (m), 741 (s), 659 (vw), 645 (vw), 628 (m), 618 (w). UV/VIS (DCM): λ_{abs}

(lg ε) = 324 nm (4.7), 372 nm (4.2), 476 nm (4.3). Fluorescence (DCM): λ_{em} (λ_{ex}) = 620 nm (450). MS (MALDI): *m/z* (%) = 753.394 (100) $[M]^-$. Anal. calcd. for $C_{51}H_{51}N_3O_3 \cdot \frac{1}{7} CH_2Cl_2$: C 80.18%, H 6.75%, N 5.48%, found: C 80.47%, H 6.93%, N 5.42%.

Synthesis of 12-(2-ethylhexyl)-5,12,19-triazadecacyclo[21.6.6.2^{7,10}.0^{2,22}.0^{4,20}.0^{5,18}.0^{8,17}.0^{9,14}.0^{24,29}.0^{30,35}]heptatriaconta-2(22),3,7,9,14,16,18,20,24,26,28,30,32,34,36-pentadecaene-6,11,13-trione 6c



According to GPC a mixture of **5c** (100 mg, 148 µmol) and $SnCl_2 \cdot 2H_2O$ (300 mg, 1.33 mmol) dissolved in ethylacetate (4 mL) was reacted. Purification by column chromatography on SiO_2 (PE/ DCM 1:1, R_f = 0, then DCM (R_f = 0.8), followed by precipitation with diethylether out of a chloroform-solution gave after filtration and washing with methanol **6c** as reddish solid (53 mg, 84 µmol, 56%). M.p.: 290 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.85-8.84 ppm (dd, *J* = 10.1, 7.7 Hz, 2H, Ar-*H*-19,22), 8.77-8.55 (dd, *J* = 16.8, 7.7 Hz, 2H, Ar-*H*-16,23), 8.54 (s, 1H, Ar-*H*-16), 7.86 (s, 1H, Ar-*H*-13), 7.52-7.42 (m, 4H, Ar-*H*-1, 4, 5, 8), 7.10-6.98 (m, 4H, Ar-*H*-2, 3, 6, 7), 5.64 (s, 1H, bridgehead-*H*-10), 5.60 (s, 1H, bridgehead -*H*-9), 4.19-4.10 (m, 2H, *H*-32), 1.96-1.93 (m, 1H, *H*-33), 1.39-1.30 (m, 8H, *H*-34-37), 0.95-0.86 (m, 6H, -C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.5 ppm (*C*-O-29), 163.3 (*C*-O-30), 159.3 (*C*-O-27), 147.8 (*C*-28), 145.2 (Ar-C_q-1'5'), 145.0 (Ar-C_q-4',8'), 144.9 (*C*-14), 144.5 (Ar-C_q-11), 141.9 (Ar-C_q-12), 131.9 (Ar-*C*-18,19,22,23), 131.3 (Ar-*C*-18,19,22,23), 131.0 (Ar-*C*-18,19,22,23), 129.7 (*C*-15), 127.8 (Ar-C_q), 127.6 (Ar-C_q), 127.4 (Ar-C_q), 126.4 (Ar-*C*-1,5), 125.8 (Ar-*C*-2,3,6,7), 124.4 (Ar-C_q), 124.0 (Ar-*C*-4,8), 122.0 (*C*-2), 116.1 (Ar-*C*-13), 111.8 (Ar-C-16), 54.6 (bridgehead -*C*-9), 54.5 (bridgehead -*C*-10), 44.8 (*C*-32), 38.2 (*C*-33), 30.9 (*C*-35), 28.9 (*C*-36), 24.3 (*C*-34), 23.2 (*C*-37), 14.3 (-*C*H$_3$), 10.8 (-*C*H$_3$). IR (ATR): $\tilde{\nu}$ = 2958 cm^{-1} (m), 2929 (m), 2873 (m), 2858 (m), 1704 (vs), 1665 (vs), 1615 (m), 1599), 1577 (m), 1548 (m), 1509 (m), 1460 (s), 1438 (s), 1405 (m), 1377 (s), 1355 (s), 1335 (vs), 1307 (s), 1271 (m), 1242 (s), 1199 (m), 1182 (m), 1157

(m), 1094 (m), 990 (m), 941 (w), 880 (m), 828 (w), 808 (w), 787 (w), 765 (s), 756 (m), 742 (s), 727 (w), 664 (vw), 646 (vw), 628 (m), 617 (w). UV/VIS (DCM): λ_{abs} (lg ε) = 323 nm (4.5), 372 nm (4.0), 476 nm (4.1). Fluorescence (DCM): λ_{em} (λ_{ex}) = 620 nm (450). MS (MALDI): *m/z* (%) = 627.254 (100) $[M]^-$. Anal. calcd. for $C_{42}H_{33}N_3O_3 \cdot \frac{1}{7} CH_2Cl_2$: C 79.11%, H 5.24%, N 6.57%, found: C 79.35%, H 5.51%, N 6.67%.

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

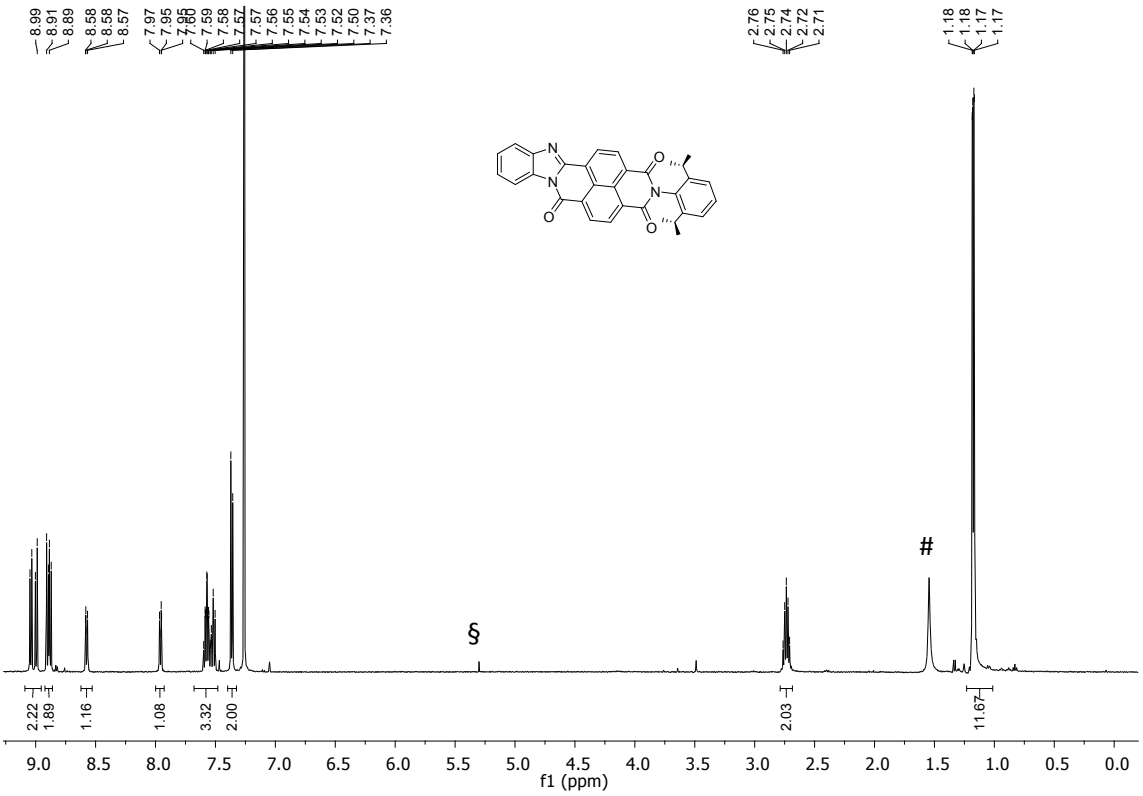


Figure S1: ^{1}H NMR spectrum of **3a** in $CDCl_3$ (500 MHz, 25 °C). Residual solvent signals: #H_2O, § DCM.

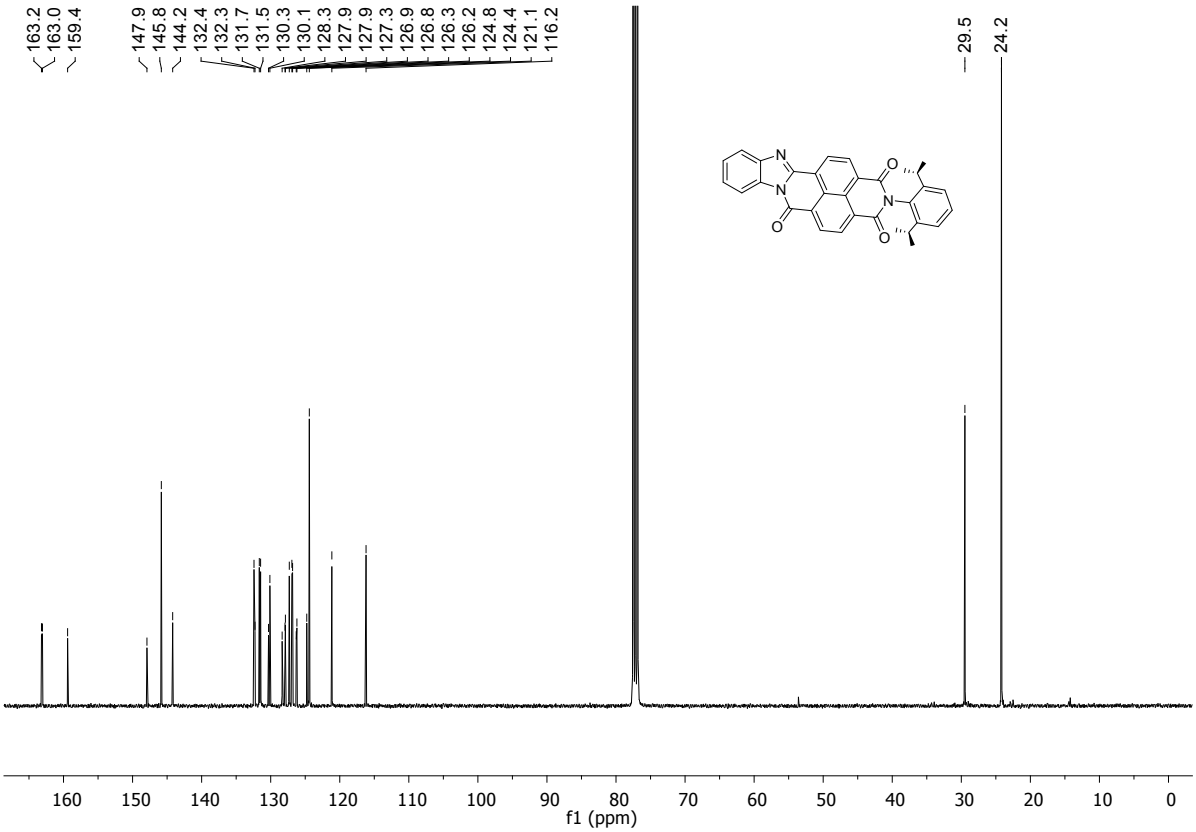


Figure S2: ^{13}C NMR spectrum of **3a** in $CDCl_3$ (101 MHz, 25 °C).

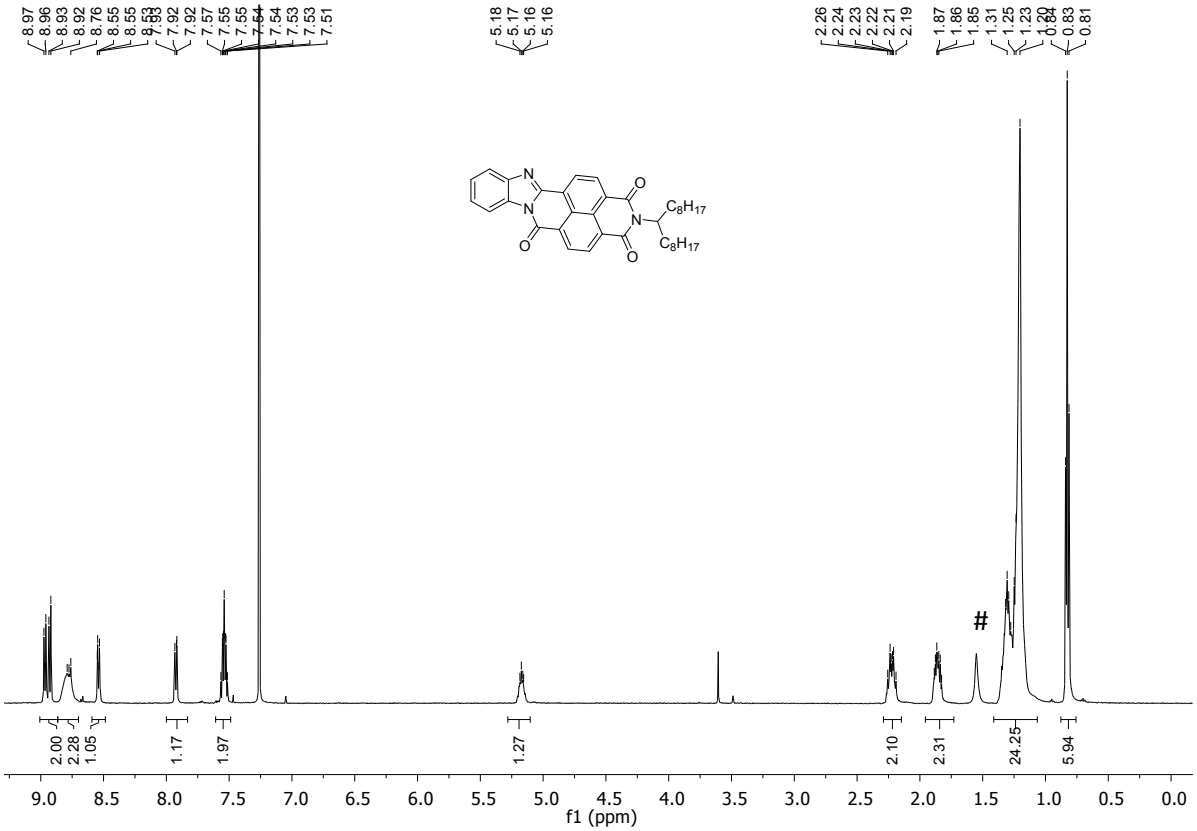


Figure S3: ^{1}H NMR spectrum of **3b** in $CDCl_3$ (500 MHz, 25 °C). Residual solvent signals: $\#H_2O$.

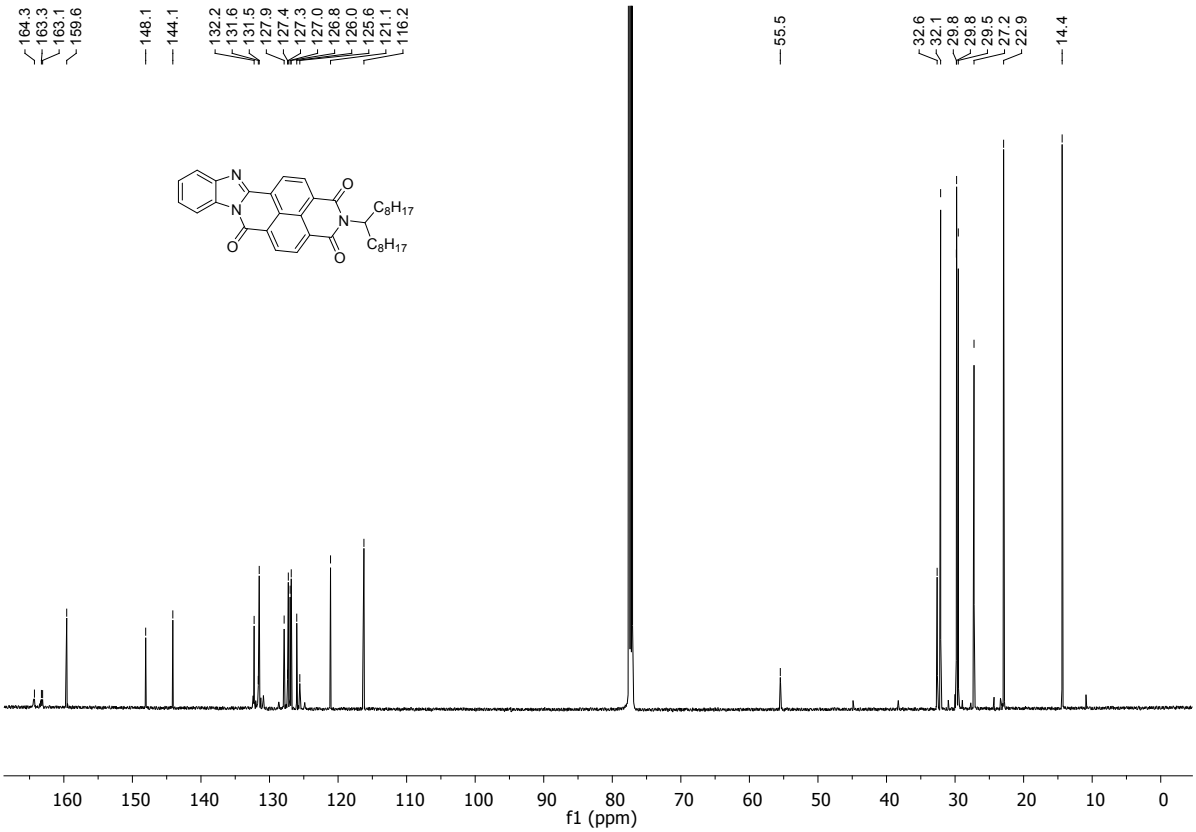


Figure S4: ^{13}C NMR spectrum of **3b** in $CDCl_3$ (151 MHz, 25 °C).

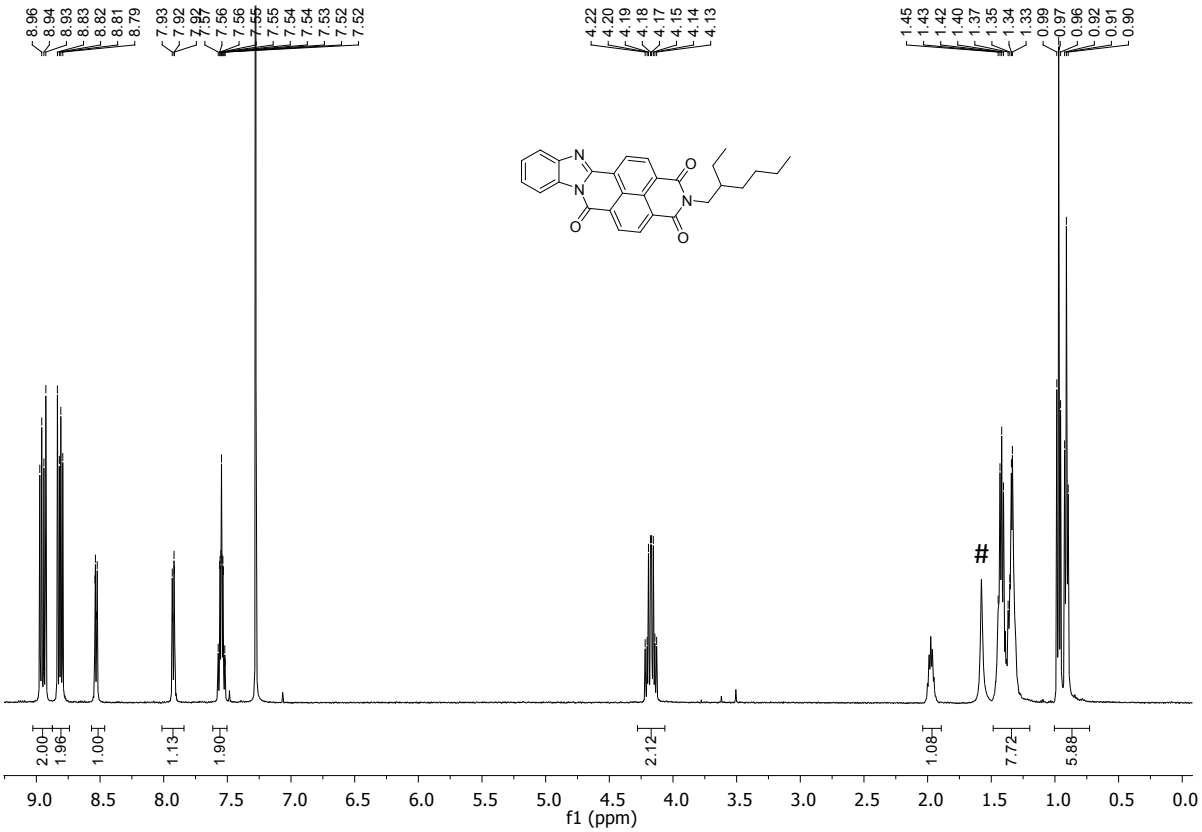


Figure S5: ^{1}H NMR spectrum of **3c** in $CDCl_3$ (500 MHz, 25 °C). Residual solvent signals: #H_2O, § DCM.

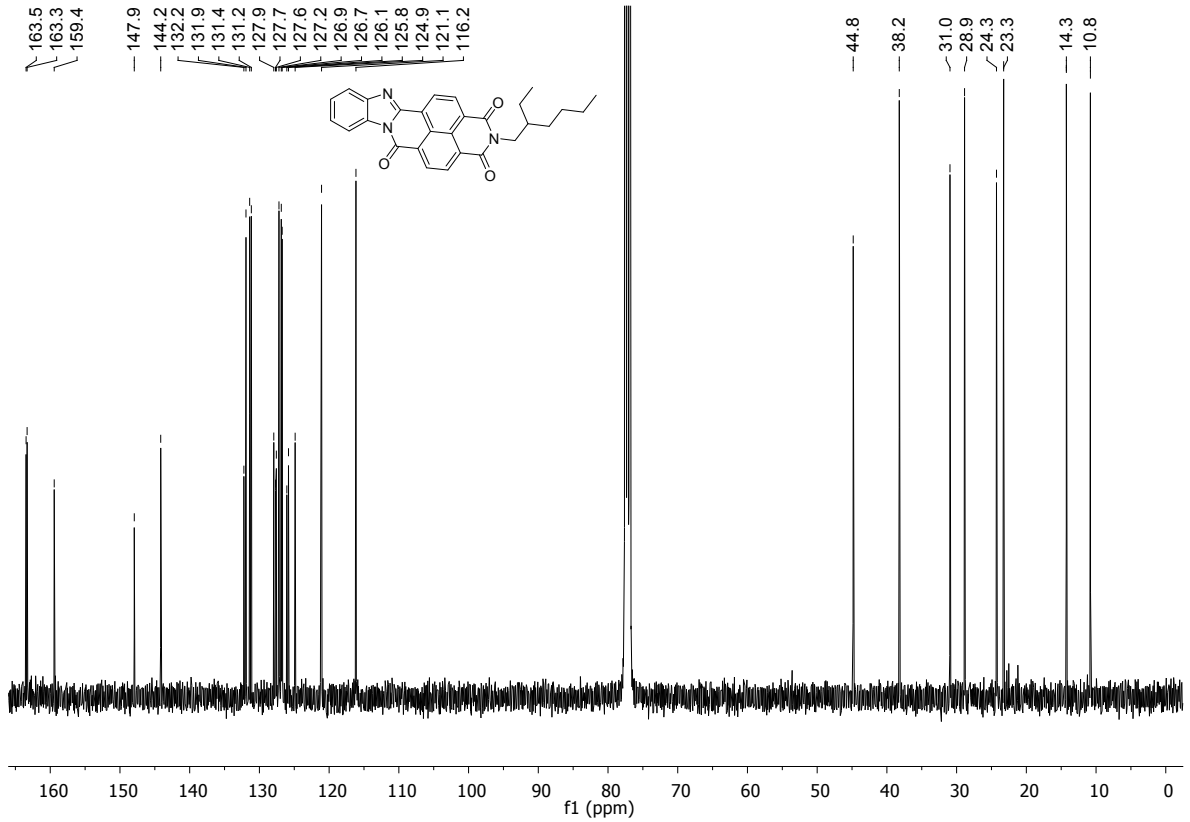


Figure S6: ^{13}C NMR spectrum of **3c** in $CDCl_3$ (101 MHz, 25 °C).

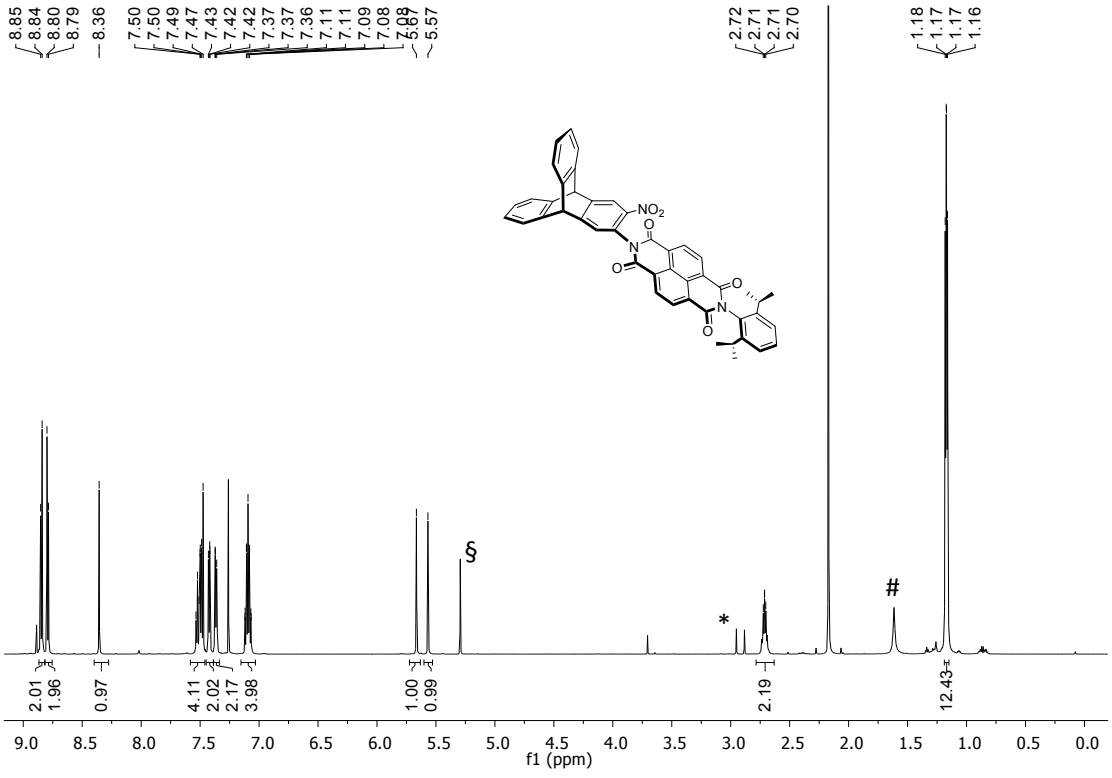


Figure S7: ^{1}H NMR spectrum of **5a** in $CDCl_3$ (600 MHz, 25 °C). Residual solvent signals: #H_2O, § DCM, *DMF.

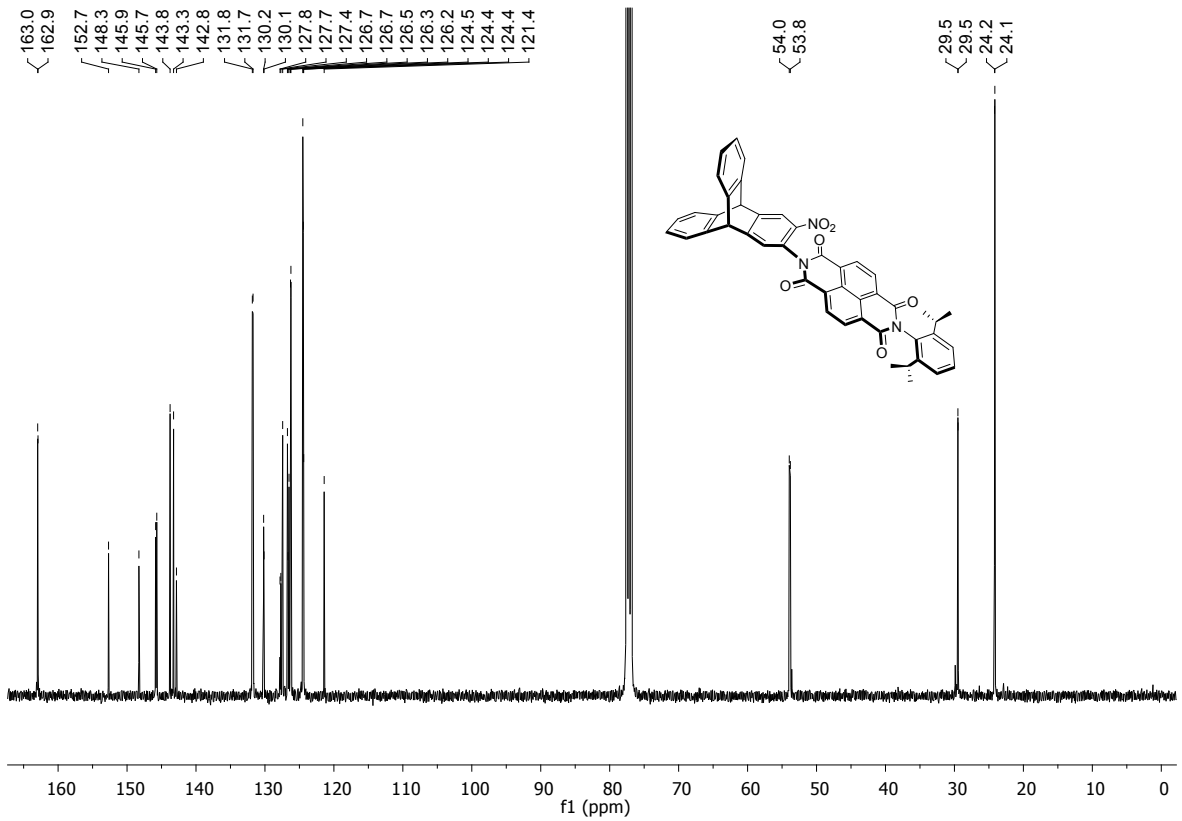


Figure S8: ^{13}C NMR spectrum of **5a** in $CDCl_3$ (101 MHz, 25 °C).

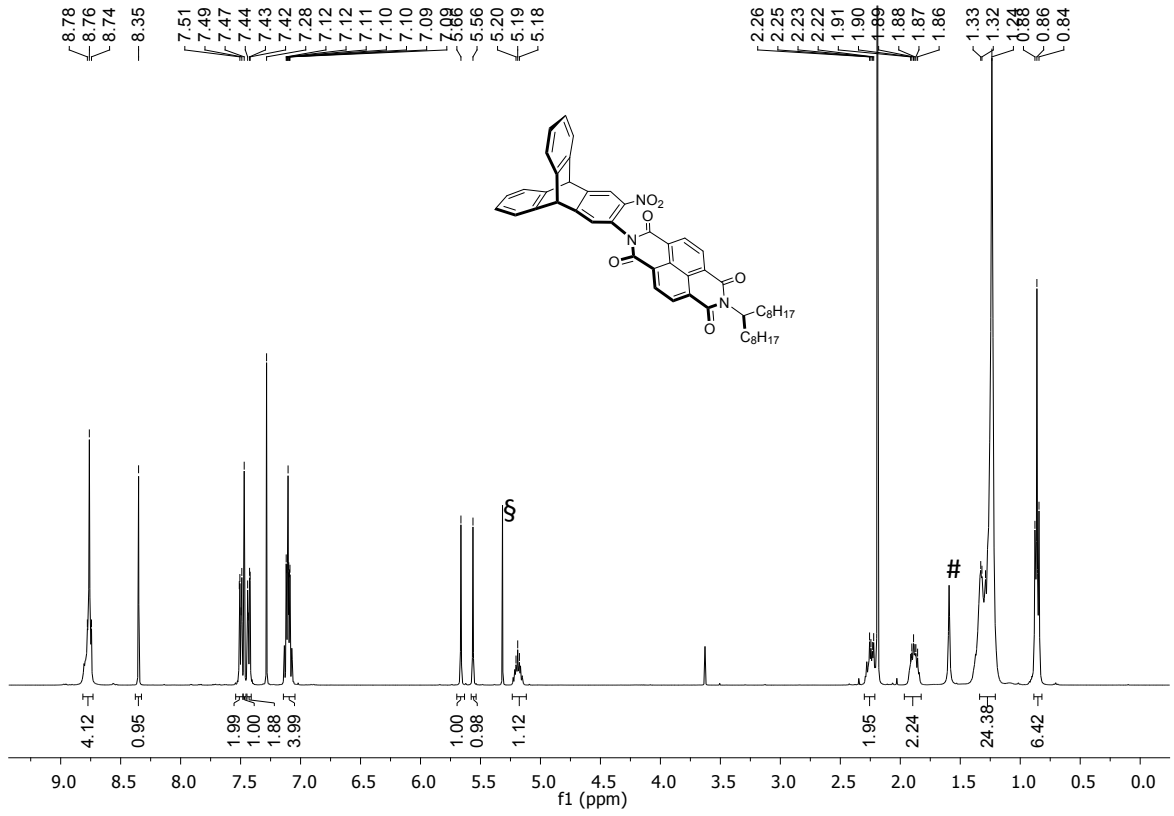


Figure S9: ^{1}H NMR spectrum of **5b** in $CDCl_3$ (400 MHz, 25 °C). Residual solvent signals: #H_2O, § DCM.

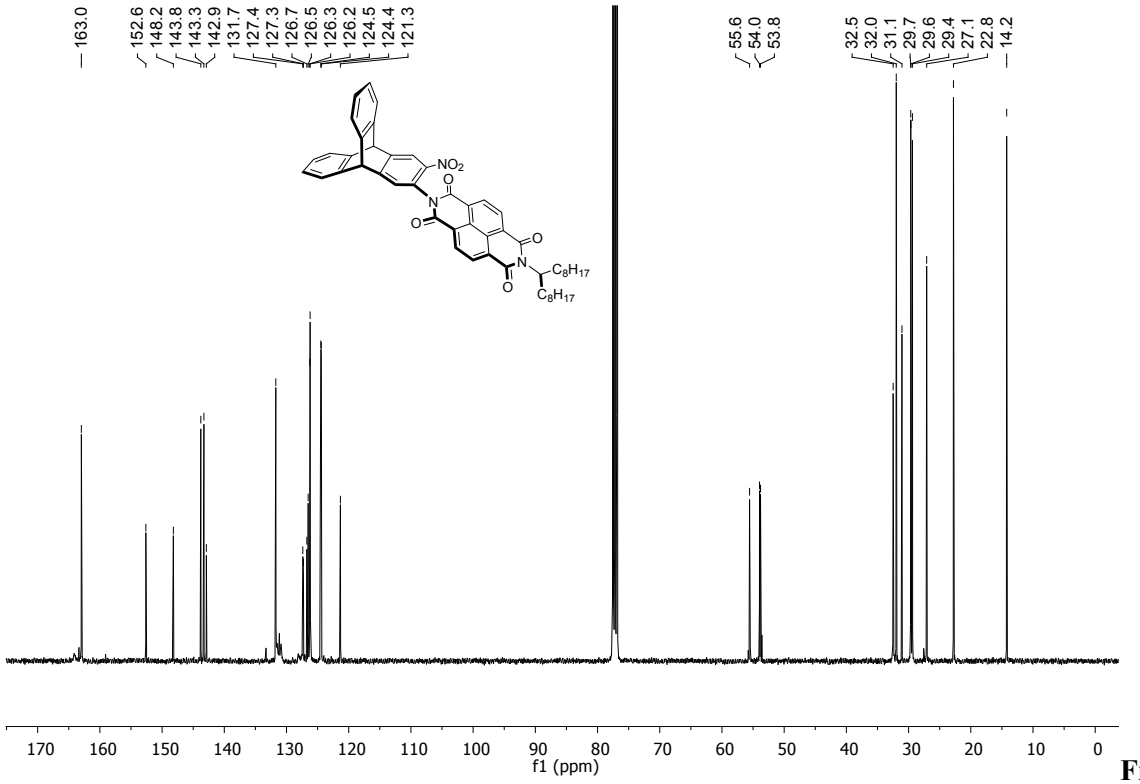


Figure S10: ^{13}C NMR spectrum of **5b** in $CDCl_3$ (101 MHz, 25 °C).

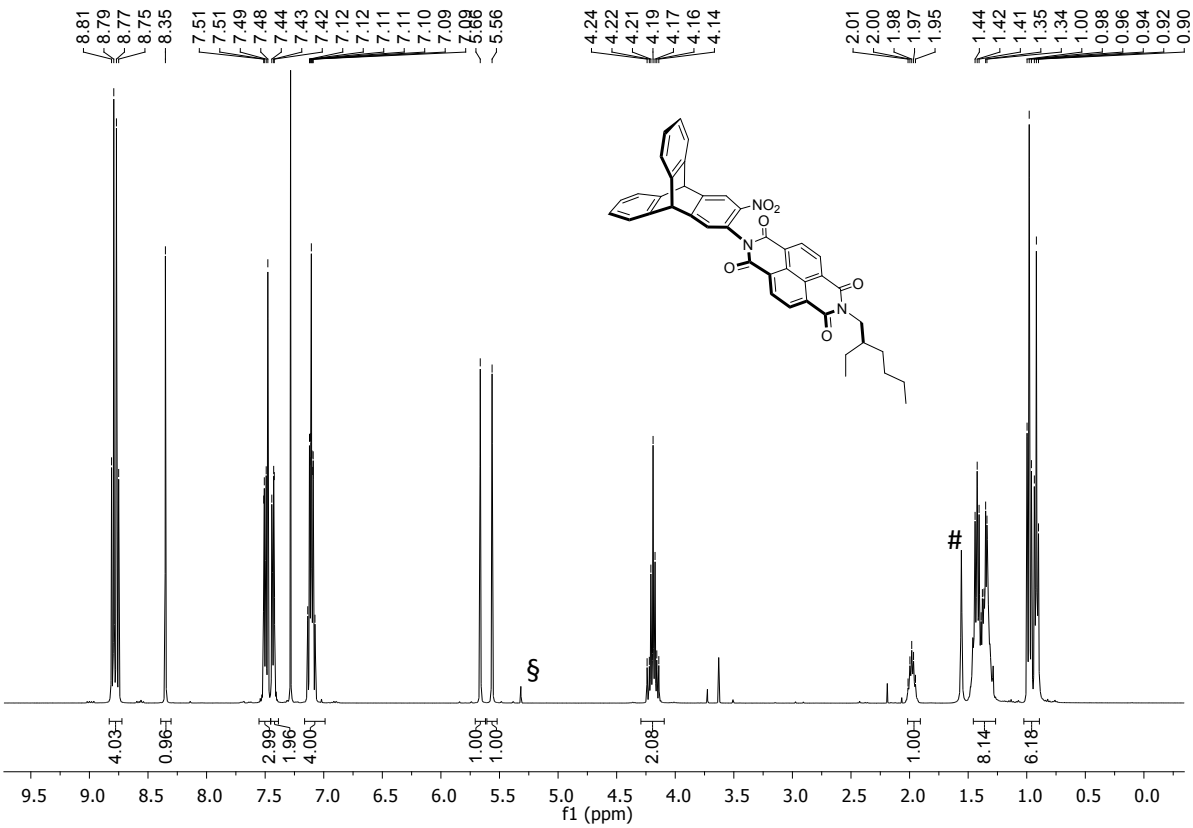


Figure S11: ^{1}H NMR spectrum of **5c** in $CDCl_3$ (400 MHz, 25 °C). Residual solvent signals: #H_2O, § DCM.

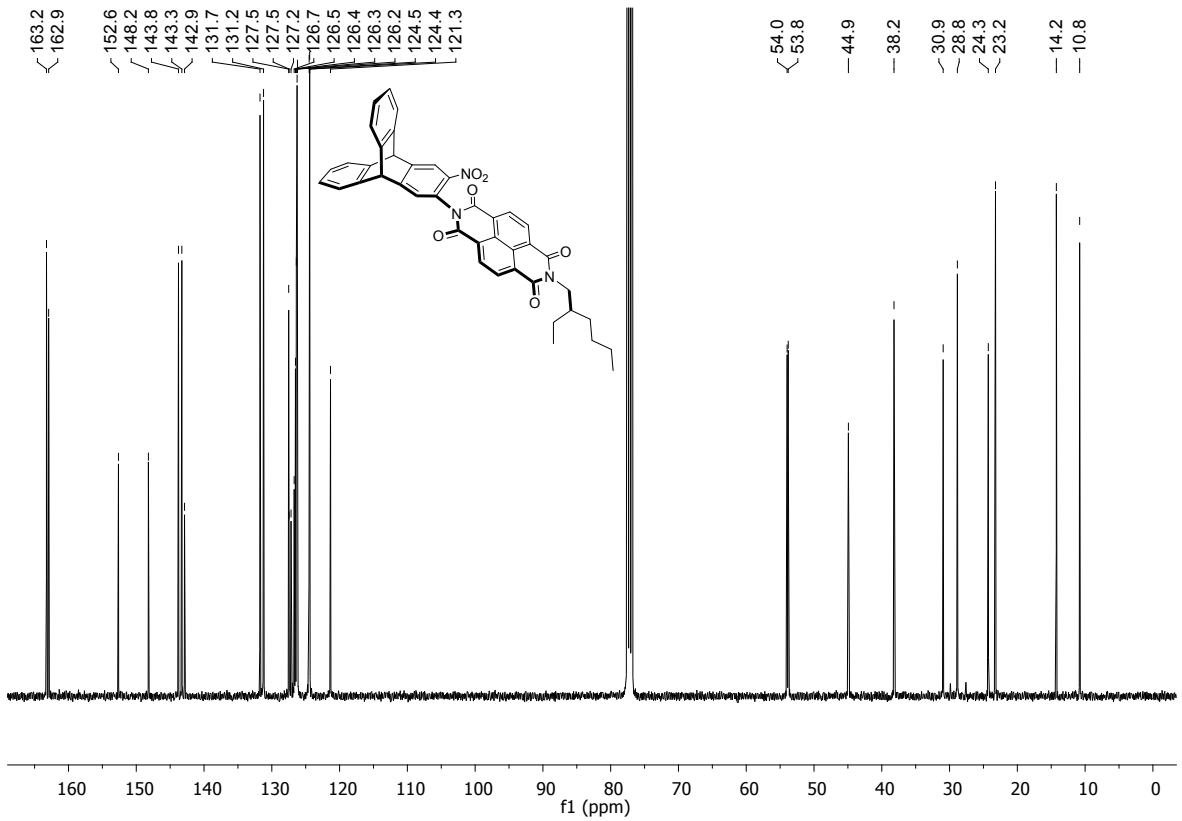


Figure S12: ^{13}C NMR spectrum of **5c** in $CDCl_3$ (101 MHz, 25 °C).

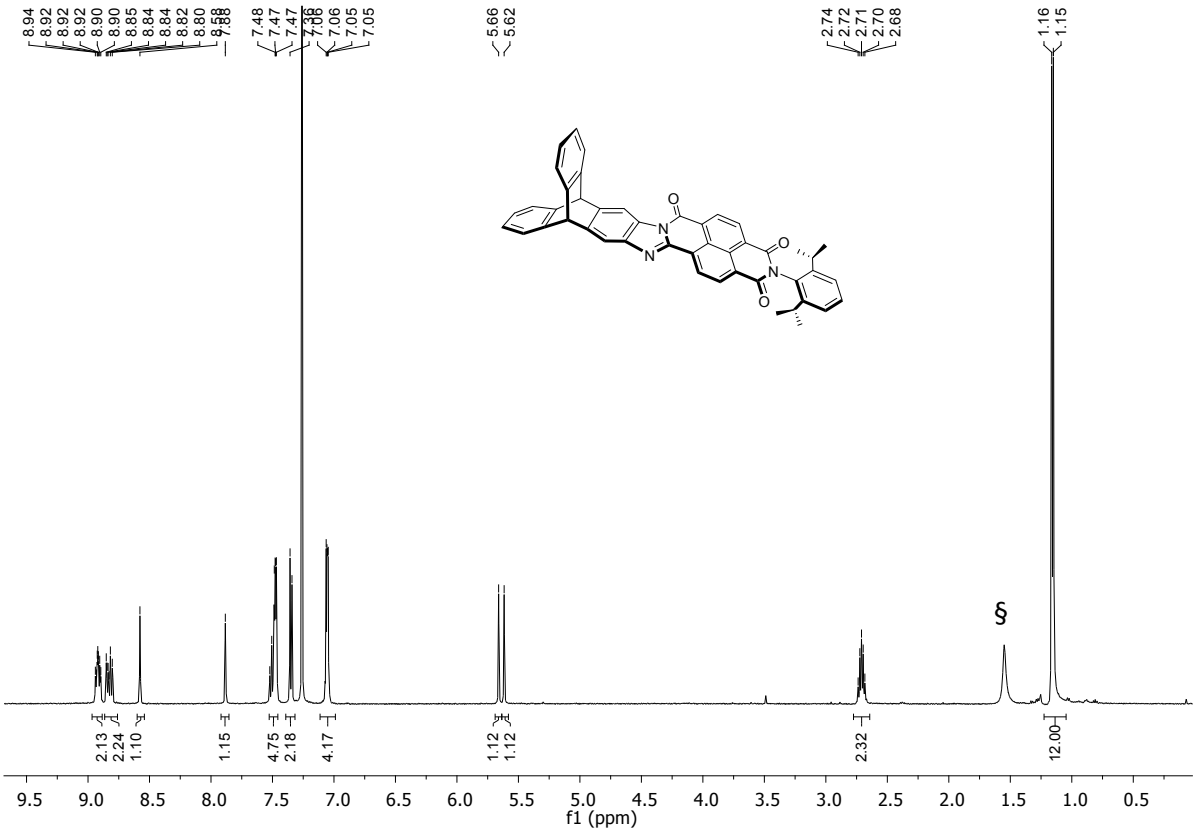


Figure S13: ^{1}H NMR spectrum of **6a** in $CDCl_3$ (500 MHz, 25 °C). Residual solvent signals: § H_2O.

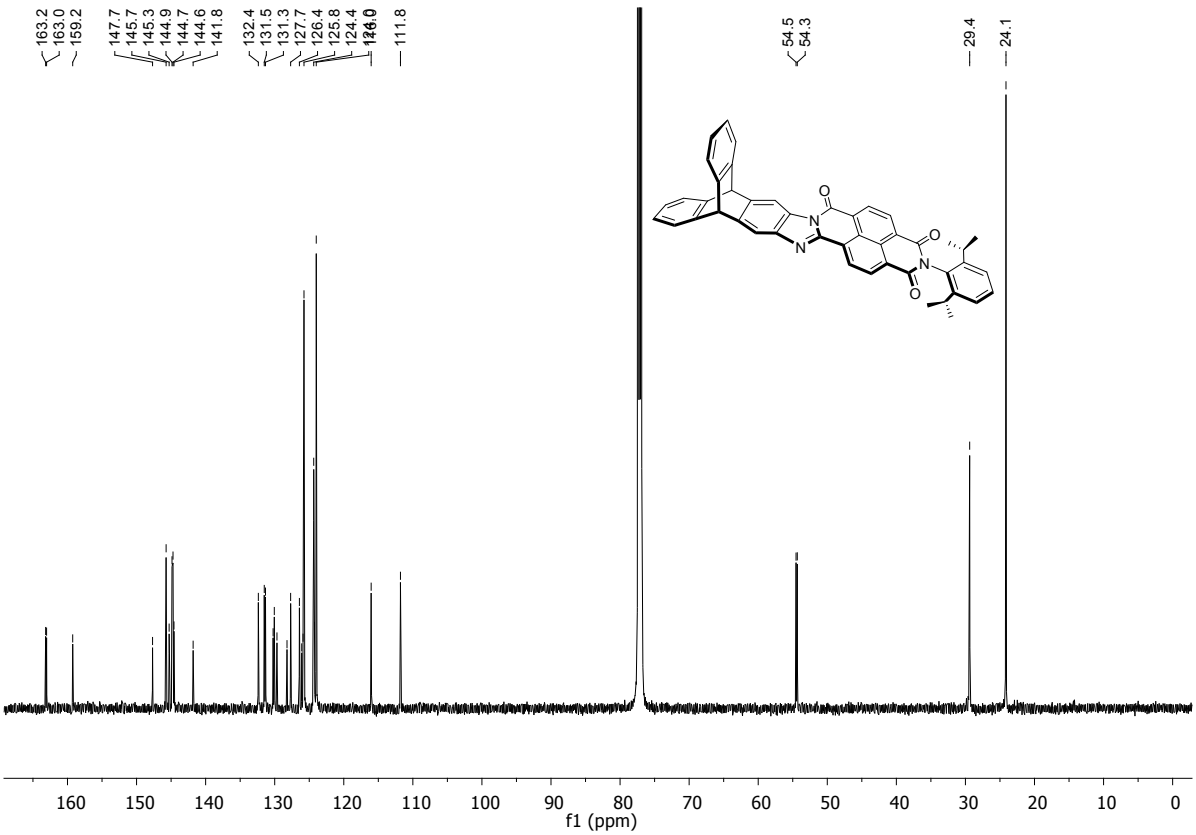


Figure S14: ^{13}C NMR spectrum of **6a** in $CDCl_3$ (101 MHz, 25 °C).

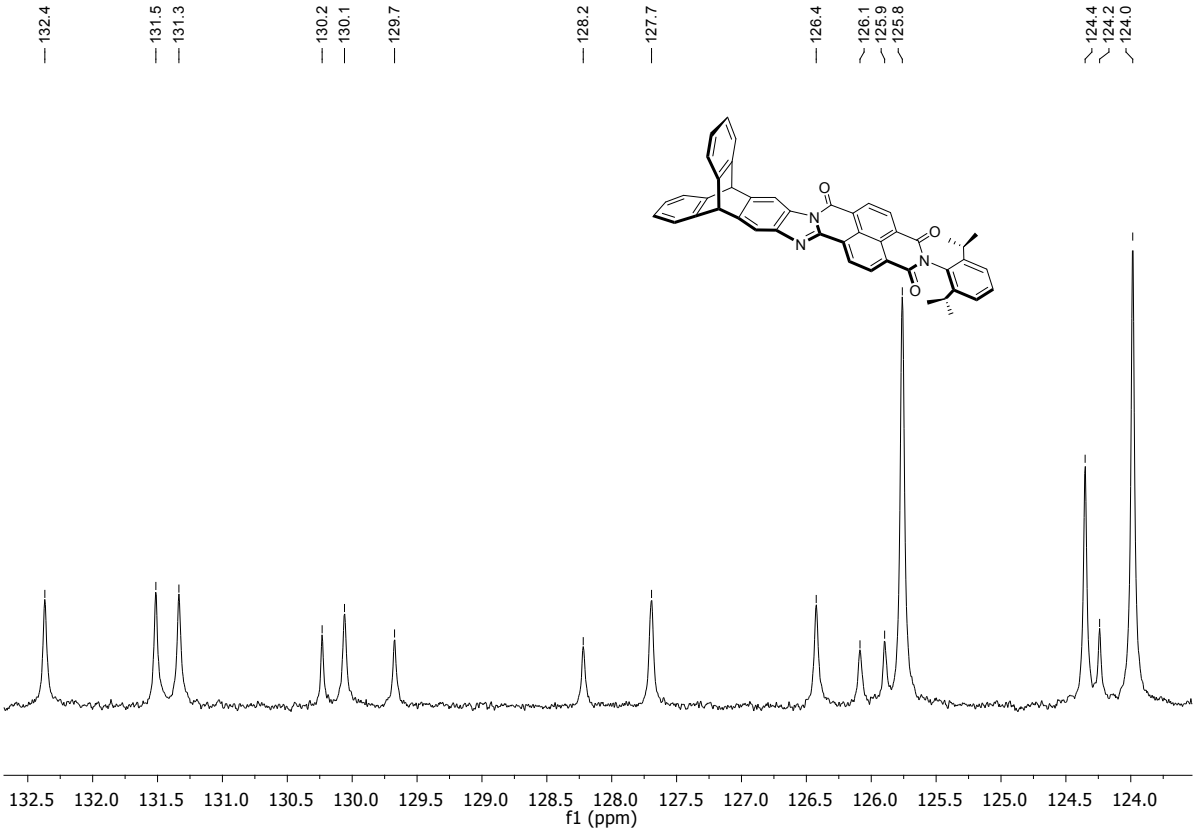


Figure S15: ^{13}C NMR spectrum zoom into the aromatic region of **6a** in $CDCl_3$ (101 MHz, 25 °C), overlapping of signals.

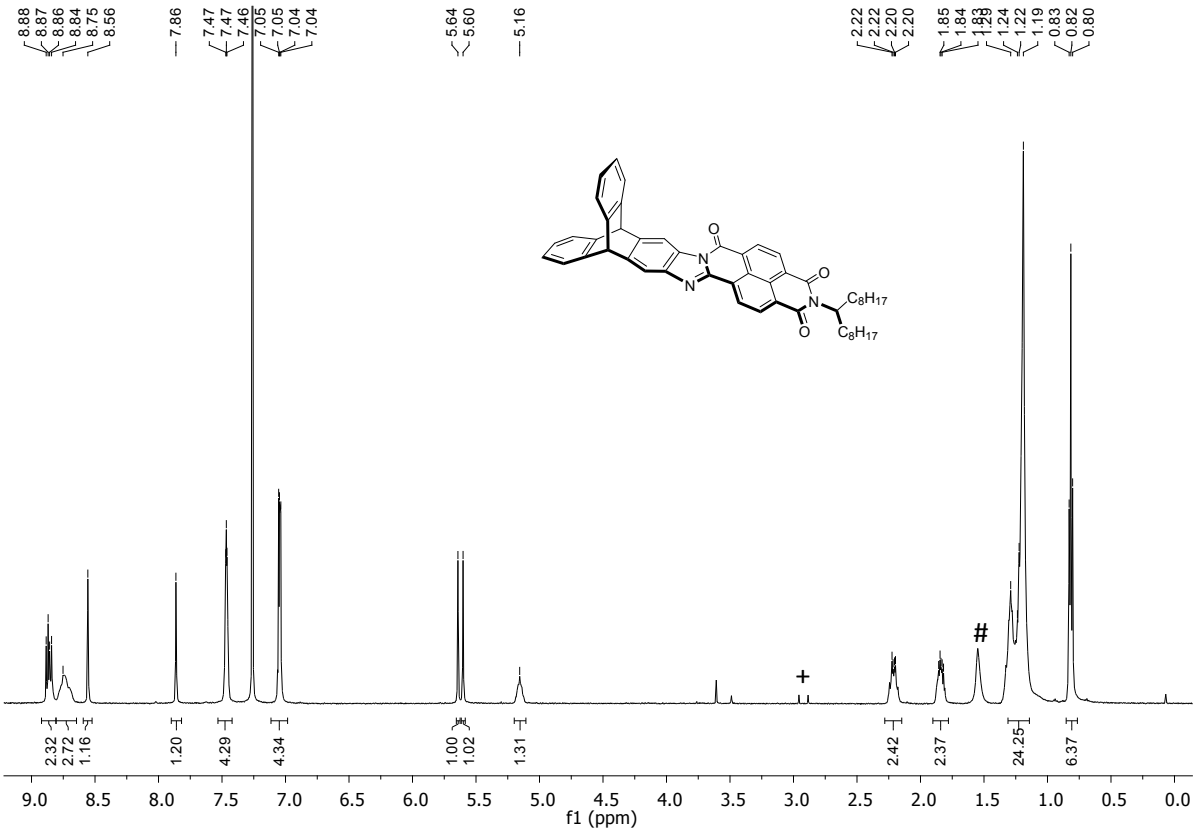


Figure S16: ^{1}H NMR spectrum of **6b** in $CDCl_3$ (500 MHz, 25 °C). Residual solvent signals: #H_2O, + DMF.

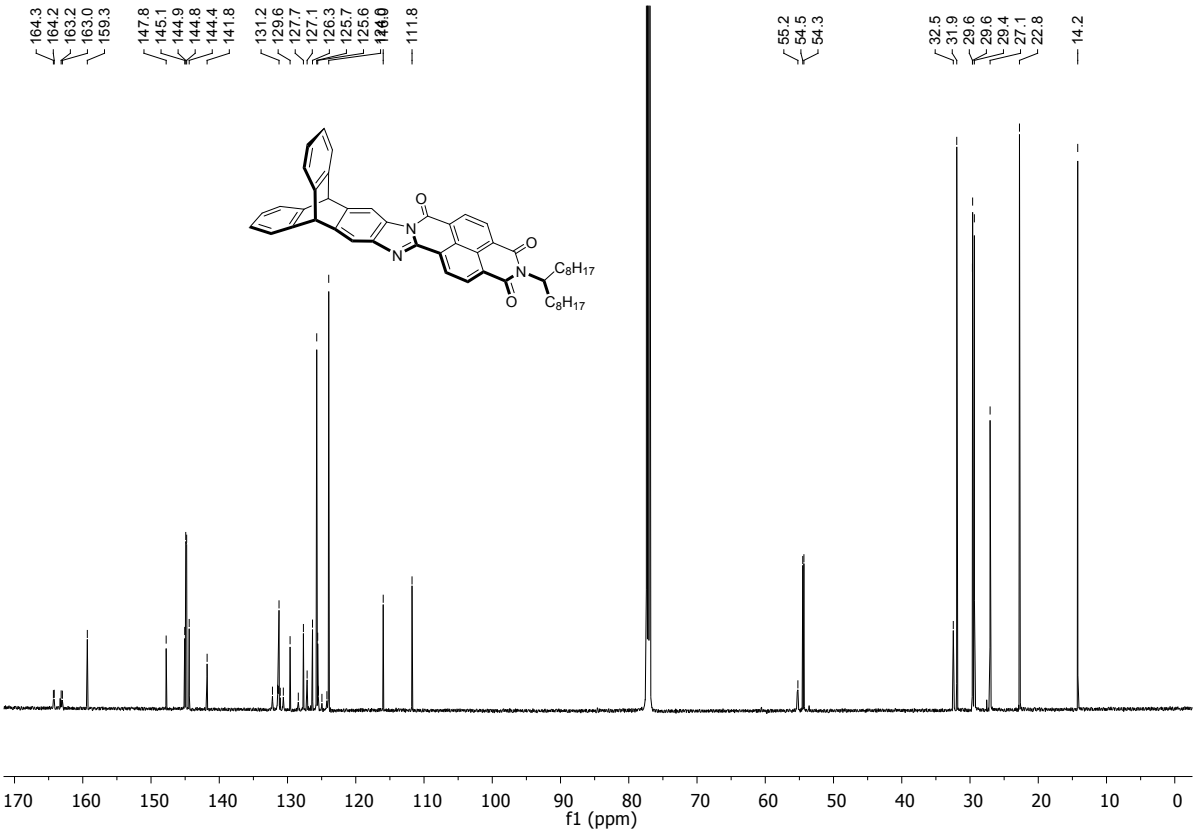


Figure S17: ^{13}C NMR spectrum of **6b** in $CDCl_3$ (101 MHz, 25 °C).

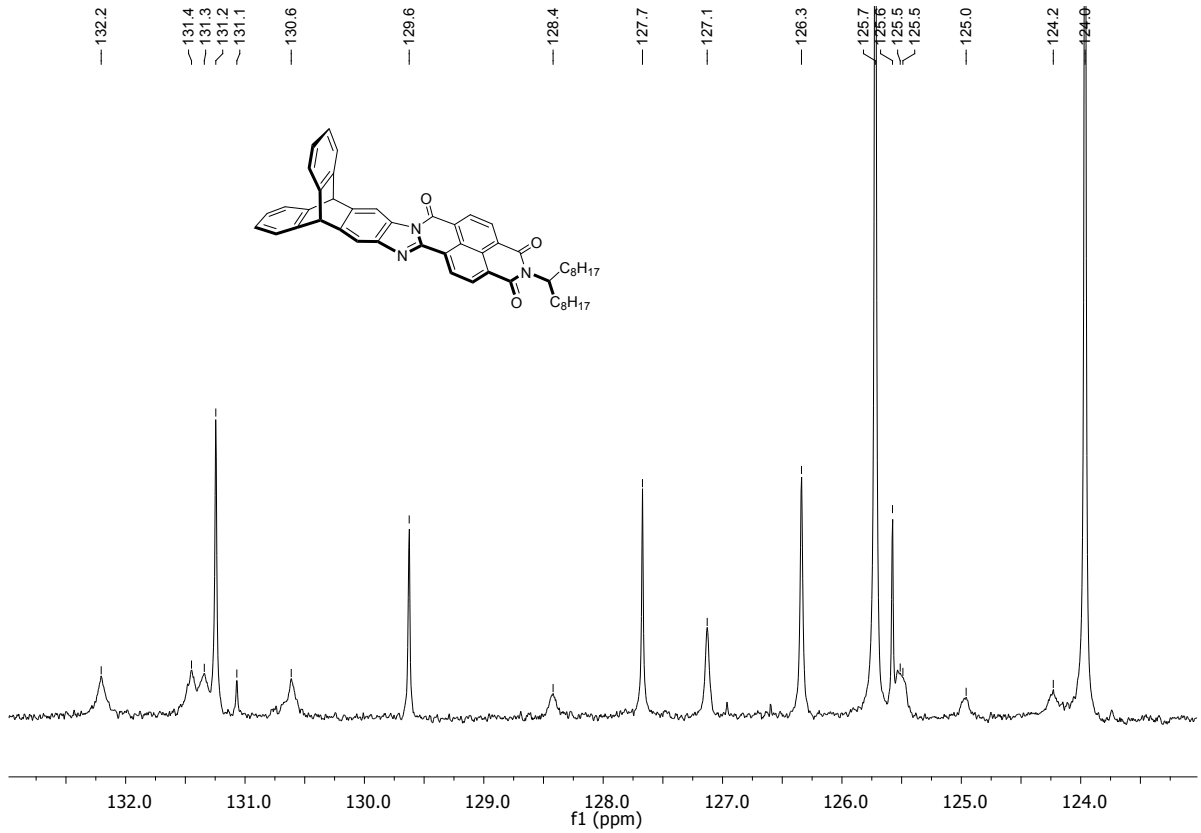


Figure S18: ^{13}C NMR spectrum-zoom of the aromatic region of **6b** in $CDCl_3$ (101 MHz, 25 °C). The 2-heptadecanyl-substituent on the imid-*N* leads to sterical hindrance.

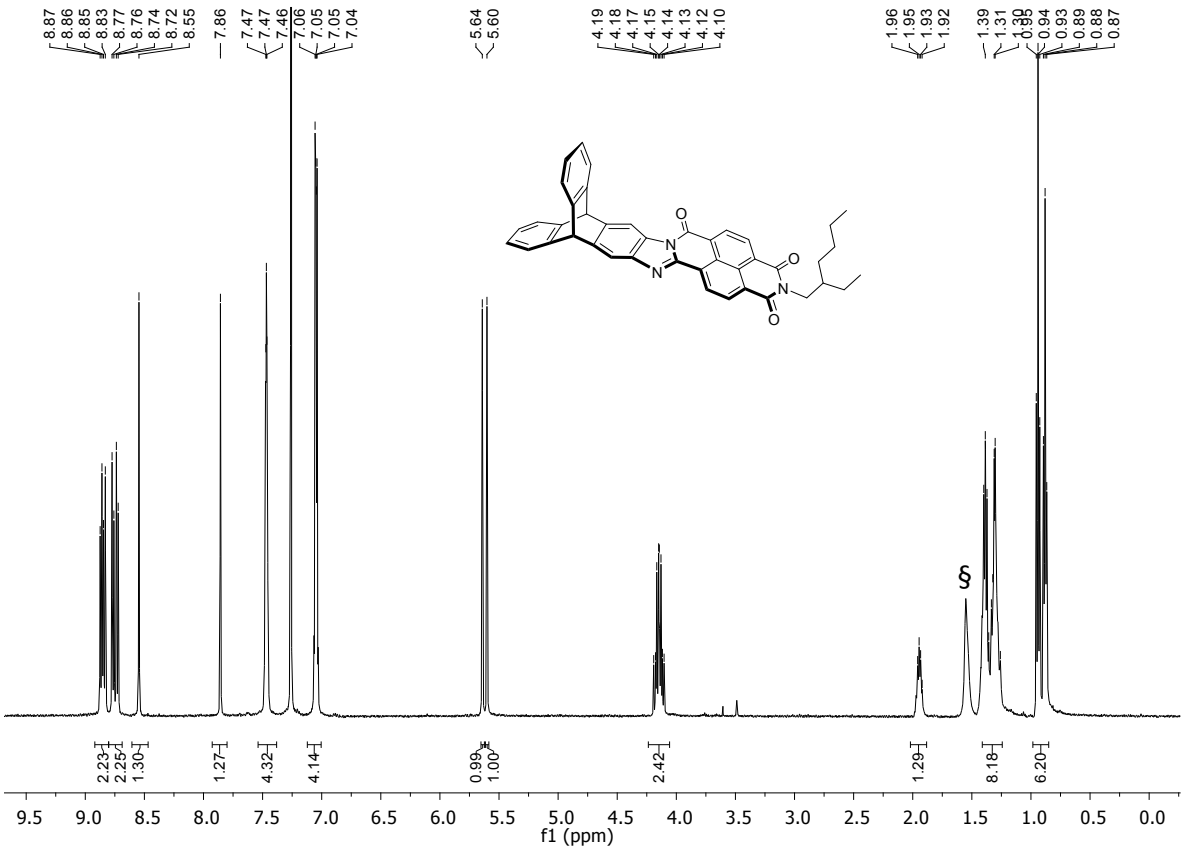


Figure S19: ^{1}H NMR spectrum of **6c** in $CDCl_3$ (500 MHz, 25 °C). Residual solvent signals: § H_2O.

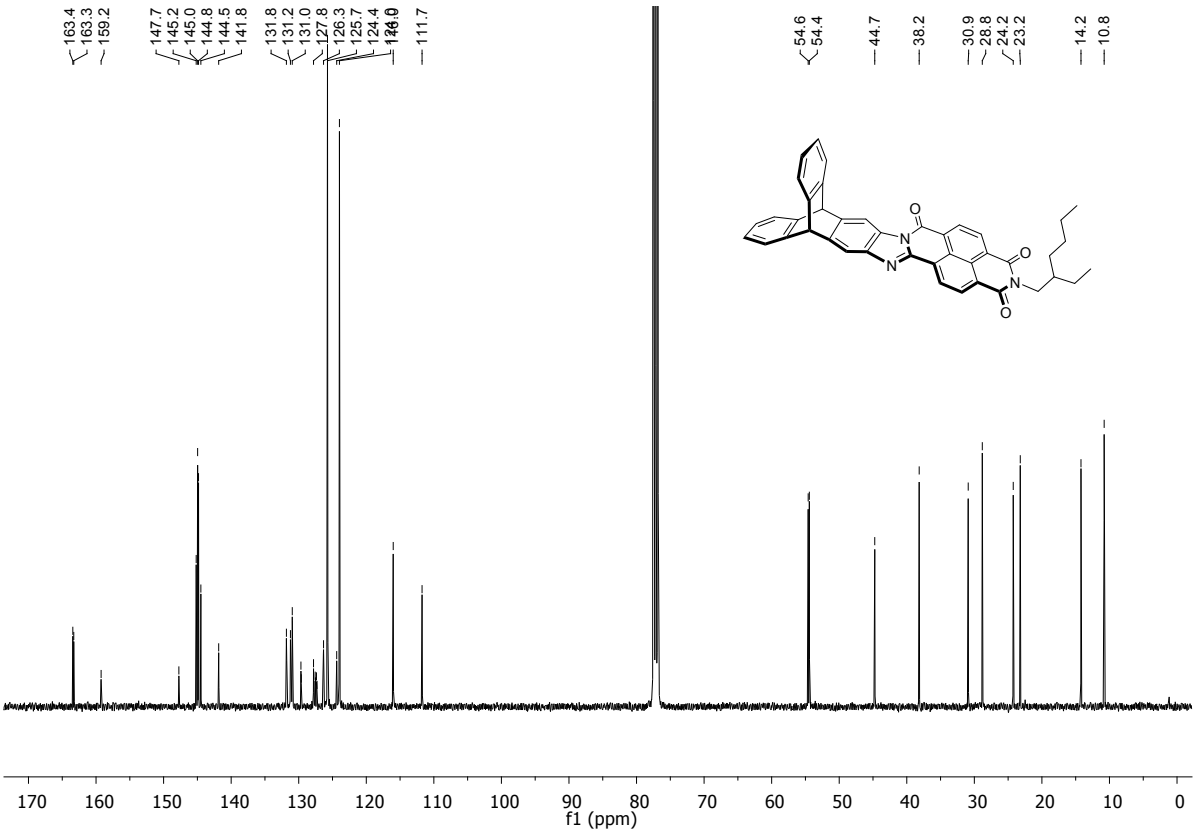


Figure S20: ^{13}C NMR spectrum of **6c** in $CDCl_3$ (101 MHz, 25 °C).

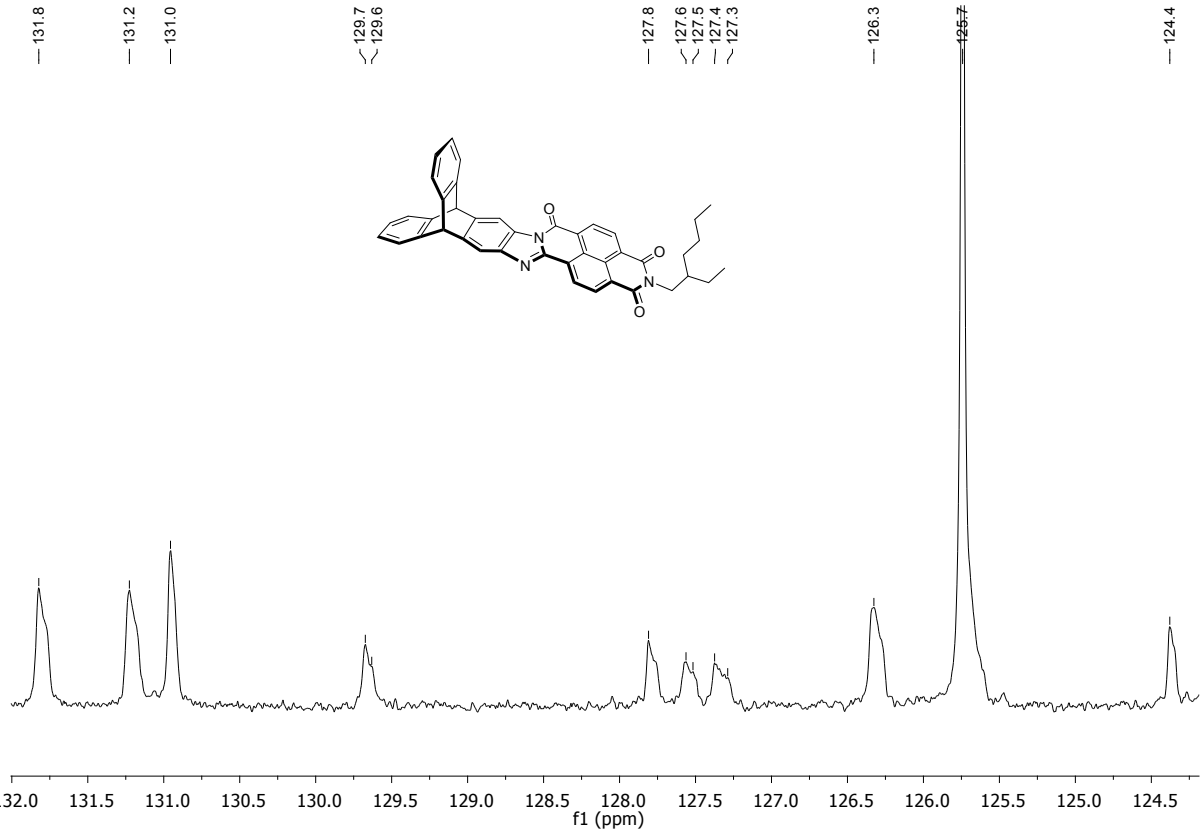


Figure S21: ^{13}C NMR spectrum-zoom of the aromatic region of **6b** in $CDCl_3$ (101 MHz, 25 °C), overlapping of signals.

4. Mass spectra of the new compounds

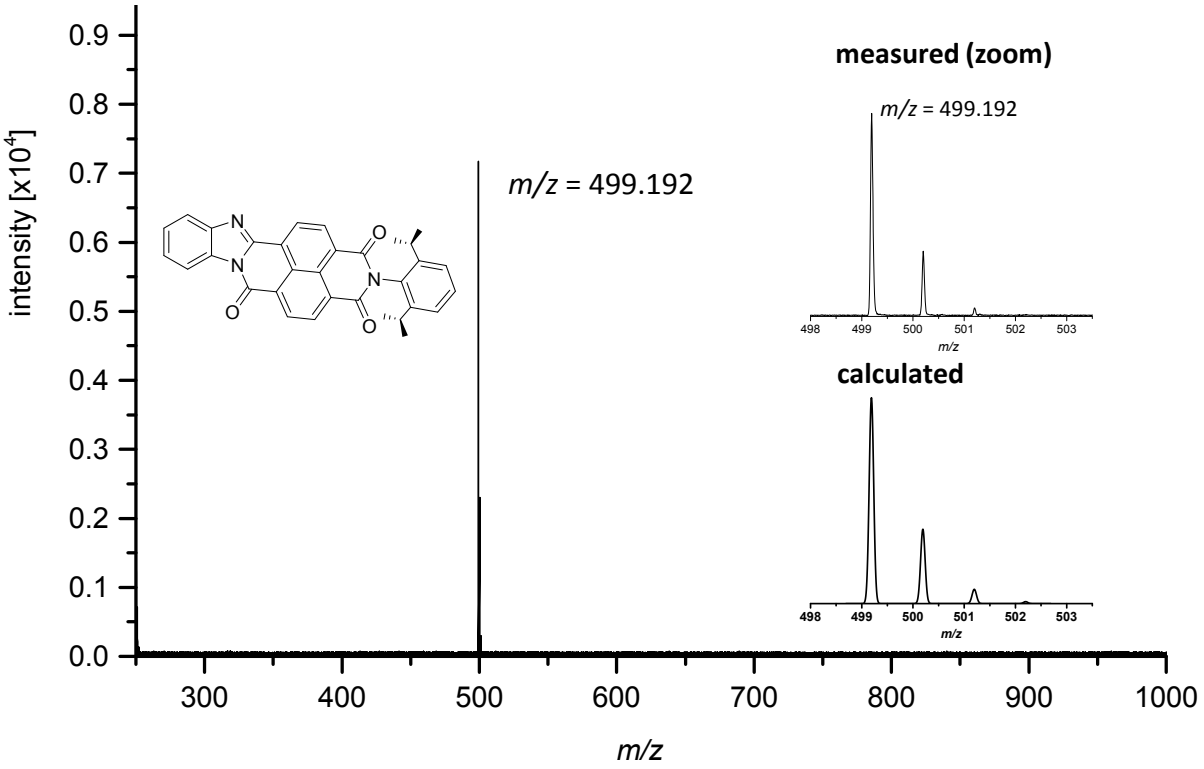


Figure S22: Mass spectrum (MALDI-TOF) of **3a**.

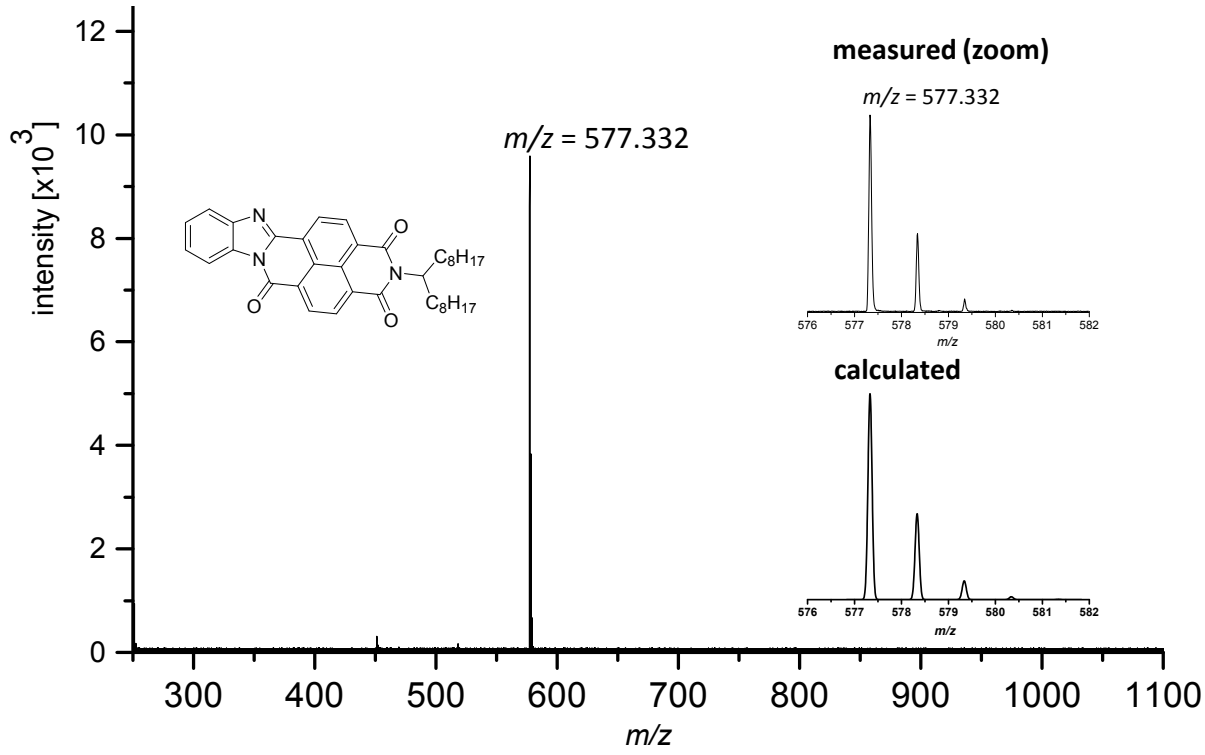


Figure S23: Mass spectrum (MALDI-TOF) of **3b**.

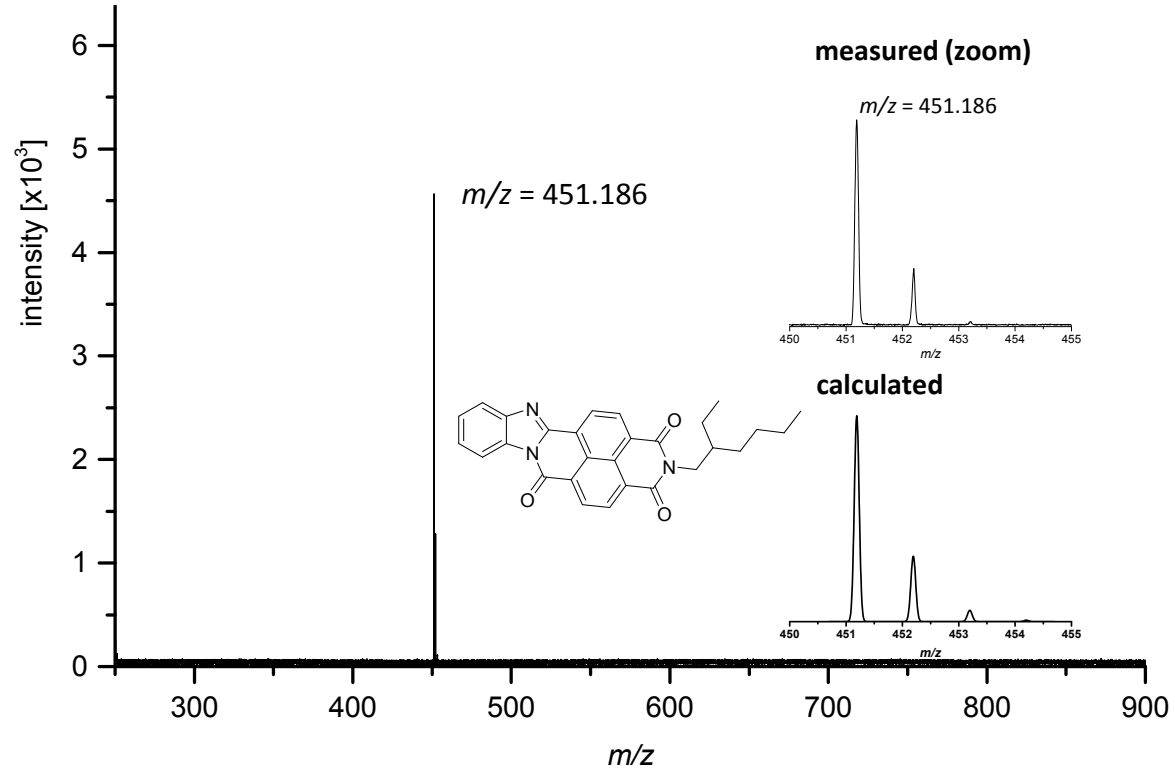


Figure S24: Mass spectrum (MALDI-TOF) of **3c**.

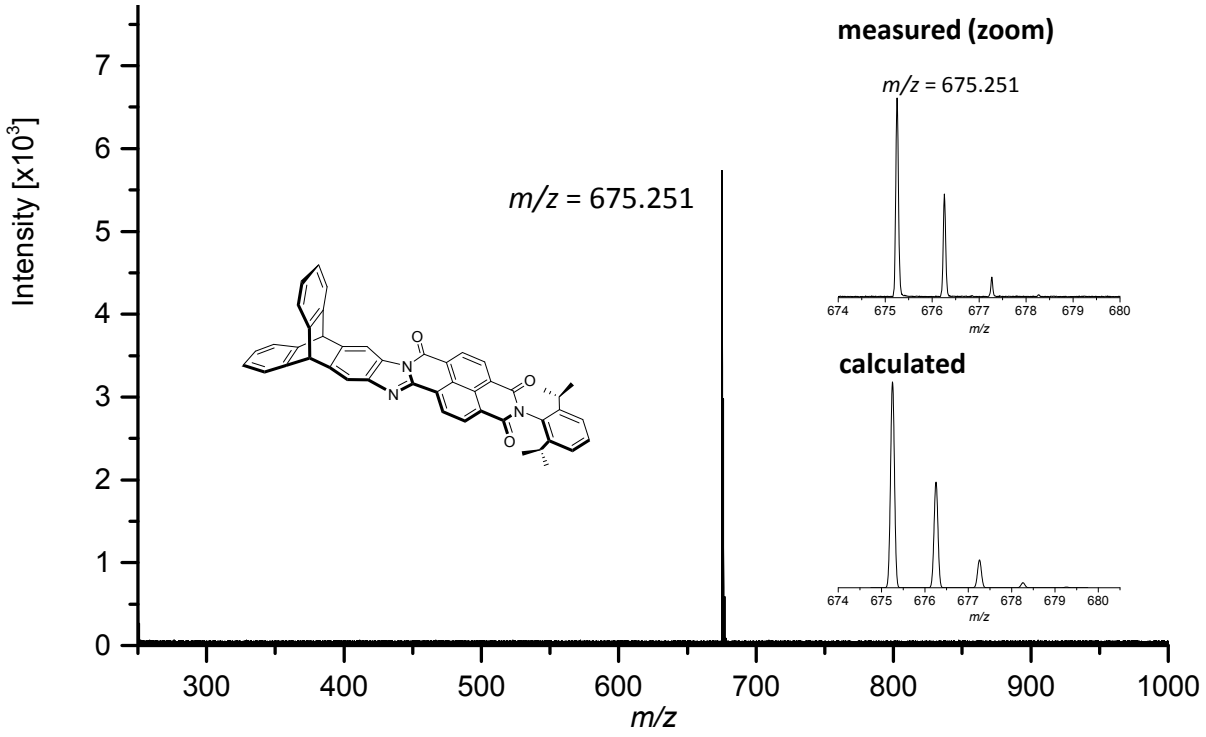


Figure S25: Mass spectrum (HR-MALDI) of **6a**.

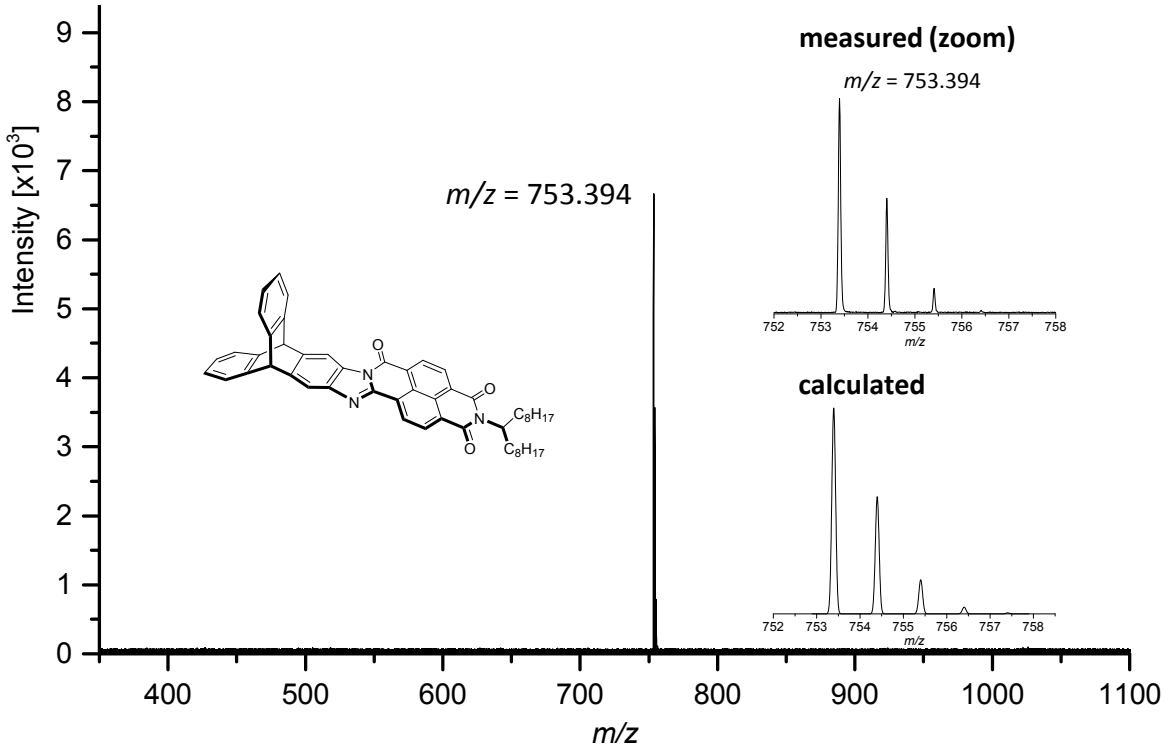


Figure S26: Mass spectrum (HR-MALDI) of **6b**.

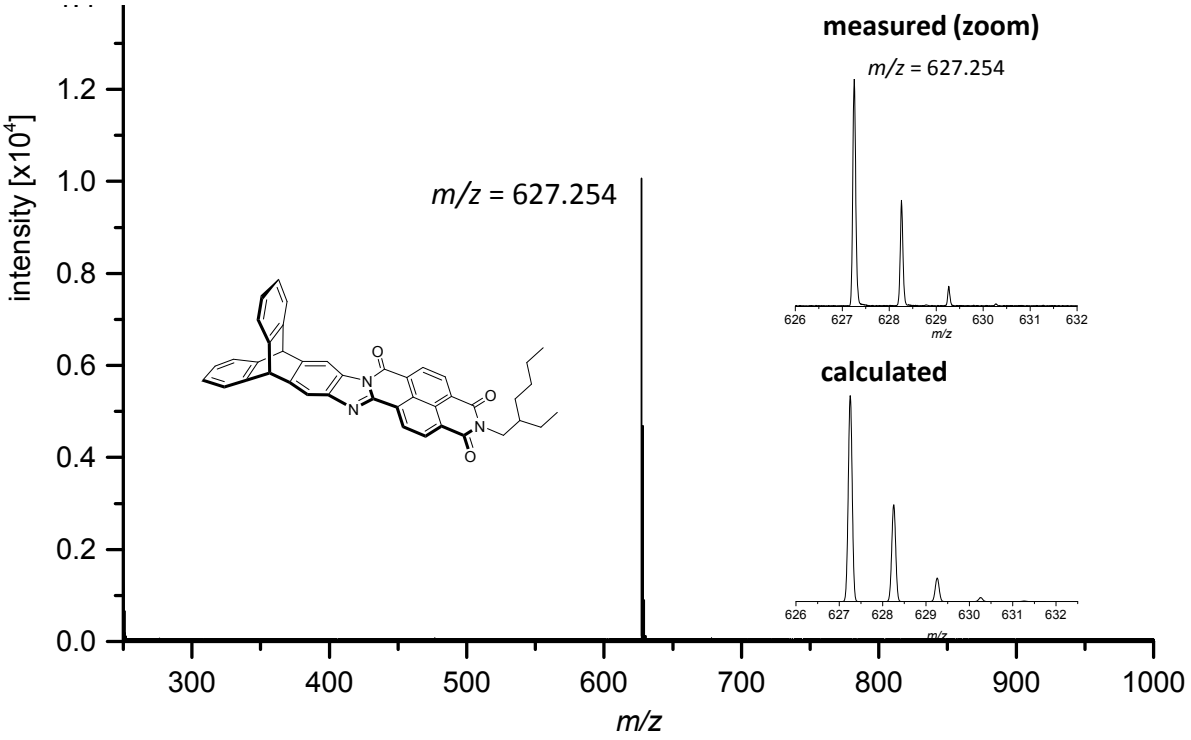


Figure S27: Mass spectrum (HR-MALDI) of **6c**.

5. Mobility measurements

In order to measure the electron mobility of the synthesized compounds **3a-c** and **6a-c**, space-charge limited current (SCLC) measurements were performed. Hence, devices with a unipolar architecture (Figure S22(c)) were fabricated. For the bottom electron transporting layer (ETL), ZnO with 2% Cs doping was used and spin coated at 2000 rpm for 50 sec. For the top ETL a BCP layer was spin coated at 4000 rpm on top of the charge carrier layer, which consisted of the compounds (**3a-c** and **6a-c**). On top a 80 nm Ag-layer was evaporated. The concentrations used were chosen according to the maximum solubility. For **3a-c** a concentration of 4 mg/ml and for **6a-c** a concentration of 5mg/ml was used, dissolved in chloroform.

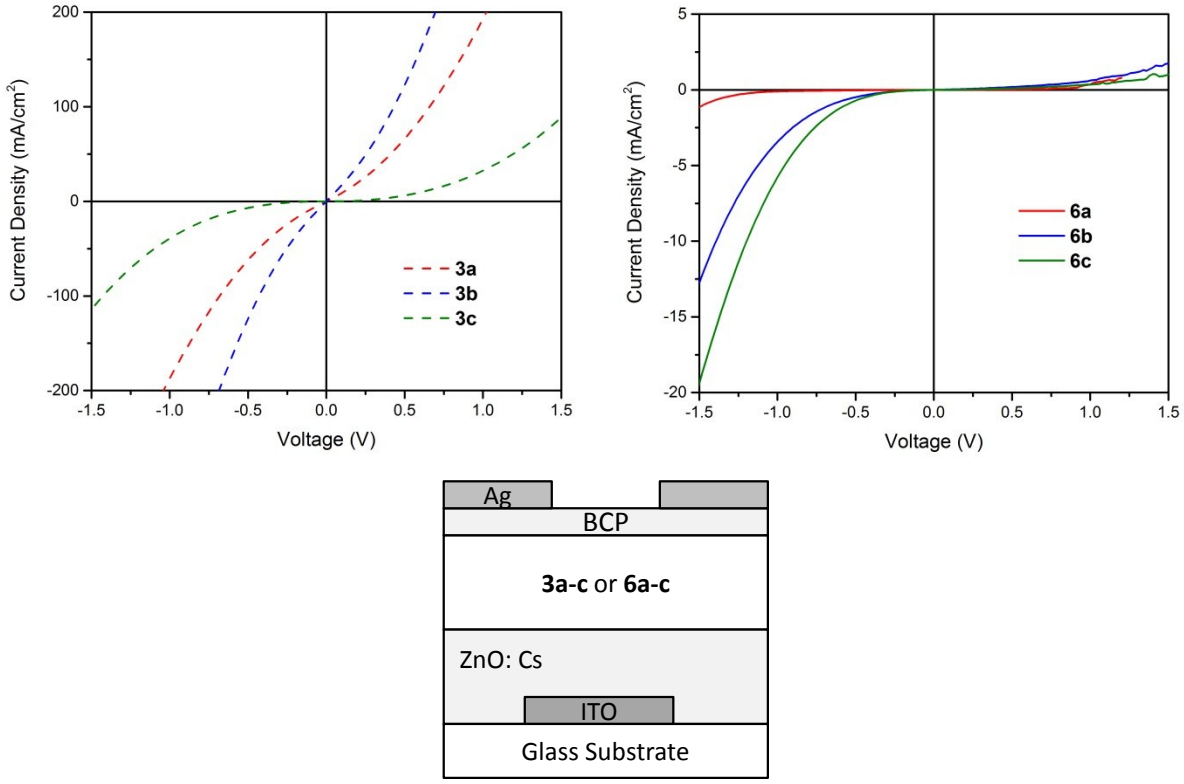


Figure S28: Representative DJV measurements for **3a-c** (top left) and **6a-c** (top right). Bottom: Architecture with two ETL layers which was used to measure the electron mobility.

The corresponding space charge limited current is known as the Mott-Gurney law and is given by[S5]

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

where ε_r, ε_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 [cm²/Vs]
3a	$(6.0 \pm 2.2) \cdot 10^{-7}$
3b	$(1.4 \pm 0.3) \cdot 10^{-7}$
3c	$(2.6 \pm 1.5) \cdot 10^{-6}$
6a	$(7.8 \pm 2.8) \cdot 10^{-8}$
6b	$(1.9 \pm 0.2) \cdot 10^{-7}$
6c	$(4.0 \pm 0.4) \cdot 10^{-7}$

The relative permittivity ε_r is estimated to be 3, the active layer thickness L lies between 4 to 25 nm and the ratio $\frac{J}{V^2}$ can be estimated from Figure S22. As the layer thickness is very thin and thus difficult to measure with the profilometer used, the systematic error on the result can exceed the statistic error stated in the table above.

6. PLQE measurements

PL and PLQE measurements were carried out following the method of de Mello et al.[S6] 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 S23) and the calculated PLQE values (Table S2) both show that the PL of the donor materials is clearly quenched by the acceptor molecules **3a-c** and **6a-c**.

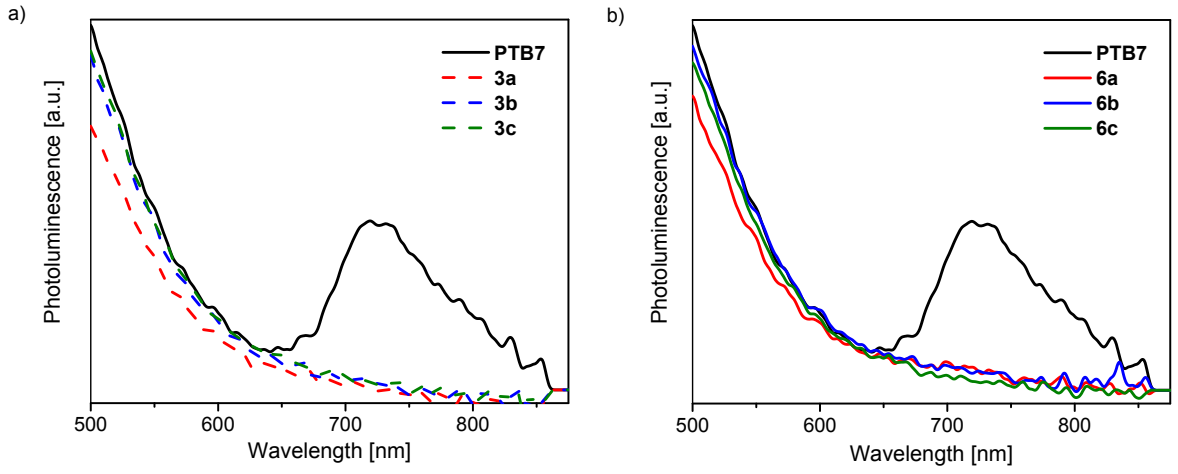


Figure S29: On-axis PL measurements of (a) PTB7 and PTB7: **3a-c** blends and (b) PTB7 and PTB7: **6a-c** blends for the optimal values.

Table S2: Results of photoluminescence measurements for different blend compounds. In both cases the PL of the donor molecule, PTB7, is quenched by the acceptor molecule **3a-c** or **6a-c.**

Blend compound	PLQE [%]
PTB7	2.3082
PTB7:**3a**	$-4.5348 \cdot 10^{-2}$
PTB7:**3b**	$8.3763 \cdot 10^{-2}$
PTB7:**3c**	$5.5688 \cdot 10^{-2}$
PTB7:**6a**	$6.6853 \cdot 10^{-2}$
PTB7:**6b**	$2.9520 \cdot 10^{-1}$
PTB7:**6c**	$-4.9090 \cdot 10^{-2}$

7. Fabrication of solar cells

a. Cleaning the substrates

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

b. Architecture

Inverted architecture devices (Figure S25) were used for all investigations.

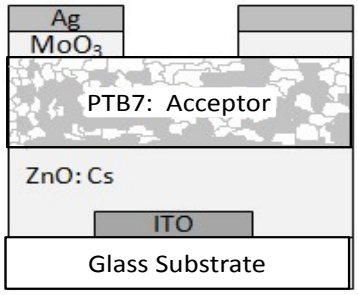


Figure S30: Inverted architecture: The ZnO, which was doped with 2% Cs, is used as the ETL and the MoO_3 as the HTL. The electrodes are ITO and Ag. The active layer is a blend of compound **3a-c** or **6a-c** and PTB7.

As an electron transport layer (ETL), ZnO with 2% Cs doping was used and spin coated at 2000 rpm for 50 sec. The solution of **3a-c**, **6a-c** and PTB7 were prepared in a nitrogen filled glovebox and dissolved in chloroform. The thickness was 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.

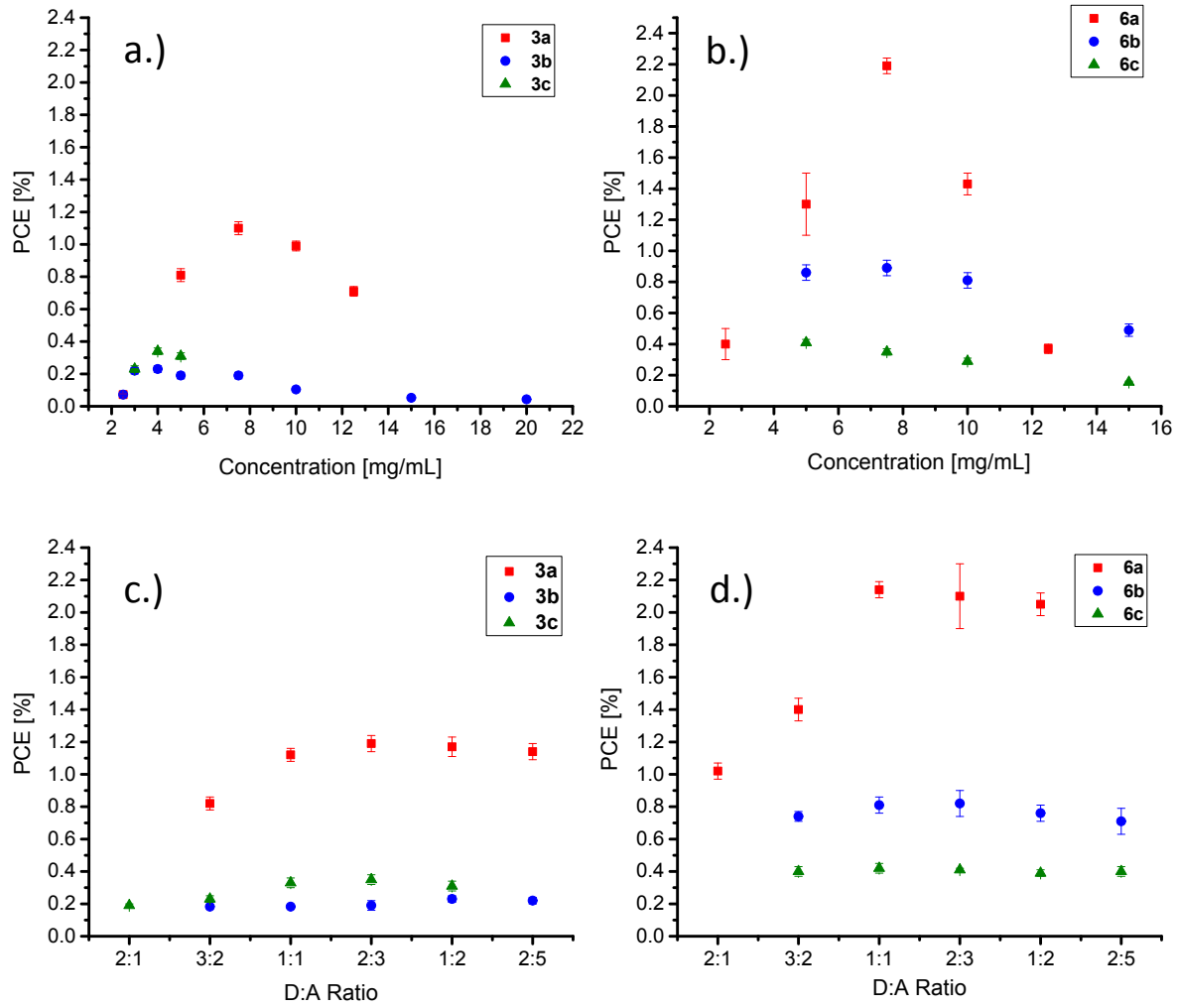


Figure S31: Optimization of SC-measurements with PTB7 as donor. **The listed concentrations referred to the separated donor- and acceptor-solutions which are mixed in the different ratios.** A.) As acceptors are compounds **3a-c** used, D/A-ratio 1:1, different concentrations. B.) As acceptors are compounds **6a-c** used, D/A-ratio 1:1, different concentrations. C.) Best concentration out of A.) is used by changing D/A ratios: **3a**: 7.5 mg/mL; **3b**: 5 mg/mL; **3c**: 4 mg/mL. D.) Best concentration out of B.) is used by changing D/A ratios: **6a**: 7.5 mg/mL; **6b**: 5 mg/mL; **6c**: 5 mg/mL.

Table S3: Photovoltaic performance for **3a**, D/A-ratio 1:1 by different concentrations.

Concentration [mg/mL]	V_{OC} [V]	J_{SC} [mA/cm^2]	FF [%]	PCE [%]	PCE^{max} [%]
2.5	0.25 ± 0.02	-0.96 ± 0.05	29.6 ± 0.5	0.072 ± 0.005	0.0785
5	0.816 ± 0.006	-3.61 ± 0.09	27.6 ± 0.3	0.81 ± 0.04	0.858
7.5	0.822 ± 0.004	-3.5 ± 0.09	38.2 ± 0.5	1.10 ± 0.04	1.152[a]
10	0.818 ± 0.004	-3.35 ± 0.05	36.1 ± 0.5	0.99 ± 0.03	1.036
12.5	0.807 ± 0.005	-2.7 ± 0.09	32.5 ± 0.4	0.71 ± 0.03	0.761

[a]corresponds to a layer thickness of: (51 ± 3) nm.

Table S4: Photovoltaic performance for **3a**, concentration: 7.5 mg/mL (turned out to be the best), different D/A- ratios.

D/A-ratio	V_{OC} [V]	J_{SC} [mA/cm^2]	FF [%]	PCE [%]	PCE^{max} [%]
3:1	0.811 ± 0.008	-2.96 ± 0.07	34.1 ± 0.5	0.82 ± 0.04	0.861
1:1	0.822 ± 0.005	-3.5 ± 0.2	38.6 ± 0.4	1.12 ± 0.04	1.156
2:3	0.823 ± 0.006	-3.6 ± 0.2	40.1 ± 0.6	1.19 ± 0.05	1.253
1:2	0.829 ± 0.007	-3.4 ± 0.2	42.0 ± 0.6	1.17 ± 0.06	1.242
2:5	0.832 ± 0.004	-3.2 ± 0.2	42.3 ± 0.5	1.14 ± 0.05	1.212

Table S5: Photovoltaic performance for **3b**, D/A-ratio 1:1 by different concentrations.

Concentration [mg/mL]	V_{OC} [V]	J_{SC} [mA/cm^2]	FF [%]	PCE [%]	PCE^{max} [%]
2.5	0.25 ± 0.02	-0.96 ± 0.05	29.6 ± 0.5	0.072 ± 0.005	0.0785
3	0.719 ± 0.006	-1.03 ± 0.07	27.6 ± 0.3	0.22 ± 0.02	0.247
4	0.785 ± 0.009	-1.01 ± 0.05	28.8 ± 0.6	0.23 ± 0.02	0.255
5	0.793 ± 0.009	-0.85 ± 0.04	27.7 ± 0.8	0.19 ± 0.02	0.203[a]
7.5	0.80 ± 0.02	-0.83 ± 0.06	28.3 ± 0.6	0.19 ± 0.02	0.222
10	0.82 ± 0.02	-0.47 ± 0.03	26.8 ± 0.3	0.104 ± 0.009	0.1196
15	0.80 ± 0.02	-0.237 ± 0.007	27.5 ± 0.2	0.052 ± 0.003	0.0547
20	0.81 ± 0.02	-0.18 ± 0.02	29.1 ± 0.6	0.043 ± 0.005	0.0495

[a] corresponds to a layer thickness of: (24 ± 3) nm.

Table S6: Photovoltaic performance for **3b**, concentration: 4 mg/mL, different D/A- ratios.

D/A ratio	V_{OC} [V]	J_{SC} [mA/cm^2]	FF [%]	PCE [%]	PCE^{max} [%]
3:2	0.74 ± 0.04	-0.82 ± 0.02	26.2 ± 0.6	0.16 ± 0.02	0.172
1:1	0.75 ± 0.03	-0.89 ± 0.03	27.3 ± 0.8	0.183 ± 0.009	0.1959
2:3	0.6 ± 0.2	-0.93 ± 0.04	28.4 ± 0.9	0.15 ± 0.05	0.222
1:2	0.40 ± 0.03	-0.95 ± 0.01	29.5 ± 0.5	0.112 ± 0.007	0.1191
2:5	0.53 ± 0.03	-0.95 ± 0.03	30.6 ± 0.1	0.153 ± 0.002	0.1547

Table S7: Photovoltaic performance for **3b**, concentration: 5 mg/mL (turned out to be the best), different D/A- ratios.

D/A ratio	V_{OC} [V]	J_{SC} [mA/cm^2]	FF [%]	PCE [%]	PCE^{max} [%]
3:2	0.77 ± 0.02	-0.86 ± 0.02	27.5 ± 0.7	0.183 ± 0.008	0.1957
1:1	0.76 ± 0.03	-0.89 ± 0.04	27.1 ± 0.5	0.183 ± 0.009	0.192
2:3	0.7 ± 0.2	-0.99 ± 0.03	28 ± 2	0.19 ± 0.03	0.236
1:2	0.78 ± 0.03	-1.0 ± 0.03	28.8 ± 0.8	0.23 ± 0.02	0.241
2:5	0.79 ± 0.02	-0.96 ± 0.043	28.8 ± 0.6	0.22 ± 0.02	0.24

Table S8: Photovoltaic performance for **3c**, D/A-ratio 1:1 by different concentrations.

Concentration [mg/mL]	V_{OC} [V]	J_{SC} [mA/cm^2]	FF [%]	PCE [%]	PCE^{max} [%]
3	0.733 ± 0.009	-1.0 ± 0.03	32.1 ± 0.6	0.23 ± 0.02	0.258[a]
4	0.81 ± 0.02	-1.34 ± 0.06	31.5 ± 0.8	0.34 ± 0.02	0.376[b]
5	0.83 ± 0.01	-1.23 ± 0.03	30.4 ± 0.5	0.31 ± 0.02	0.326[c]

[a] corresponds to a layer thickness of: (8 ± 3) nm, [b] corresponds to a layer thickness of: (22 ± 3) nm, [c] corresponds to a layer thickness of: (24 ± 3) nm.

Table S9: Photovoltaic performance for **3c**, concentration: 4 mg/mL (turned out to be the best), different D/A- ratios.

D/A ratio	V_{OC} [V]	J_{SC} [mA/cm^2]	FF [%]	PCE [%]	PCE^{max} [%]
2:1	0.76 ± 0.04	-0.88 ± 0.04	27.9 ± 0.7	0.19 ± 0.01	0.2
3:2	0.76 ± 0.02	-1.04 ± 0.04	28.9 ± 0.8	0.23 ± 0.02	0.246
1:1	0.79 ± 0.01	-1.28 ± 0.08	32.2 ± 0.7	0.33 ± 0.03	0.355
2:3	0.81 ± 0.02	-1.27 ± 0.09	33.9 ± 0.9	0.35 ± 0.03	0.394
1:2	0.80 ± 0.02	-1.15 ± 0.05	34 ± 1	0.31 ± 0.03	0.371

Table S10: Photovoltaic performance for **6a**, D/A-ratio 1:1 by different concentrations.

Concentration [mg/mL]	V_{OC} [V]	J_{SC} [mA/cm^2]	FF [%]	PCE [%]	PCE^{max} [%]
2.5	0.6 ± 0.1	-2.0 ± 0.1	36 ± 3	0.4 ± 0.1	0.50[a]
5	0.80 ± 0.04	-4.28 ± 0.06	39 ± 3	1.3 ± 0.2	1.50[b]
7.5	0.874 ± 0.003	-5.6 ± 0.2	41.7 ± 0.3	2.04 ± 0.04	2.266[c]
10	0.868 ± 0.004	-4.8 ± 0.2	34.0 ± 0.5	1.43 ± 0.07	1.50
12.5	0.71 ± 0.02	-1.7 ± 0.2	30.4 ± 0.4	0.37 ± 0.03	0.4

[a] corresponds to a layer thickness of: (29 ± 1) nm, [b] corresponds to a layer thickness of: (69 ± 5) nm, [c] corresponds to a layer thickness of: (126 ± 2) nm.

Table S11: Photovoltaic performance for **6a**, concentration: 7.5 mg/mL (turned out to be the best), different D/A- ratios.

D/A ratio	V_{OC} [V]	J_{SC} [mA/cm^2]	FF [%]	PCE [%]	PCE^{max} [%]
2:1	0.933 ± 0.005	-3.2 ± 0.2	34.5 ± 0.8	1.02 ± 0.05	1.099
3:2	0.937 ± 0.007	-3.9 ± 0.2	38.3 ± 0.7	0.40 ± 0.07	1.487
1:1	0.893 ± 0.004	-5.6 ± 0.2	42.73 ± 0.05	2.14 ± 0.05	2.185
2:3	0.88 ± 0.02	-5.5 ± 0.3	43 ± 2	2.1 ± 0.2	2.35
1:2	0.889 ± 0.005	-5.1 ± 0.2	45.1 ± 0.8	2.05 ± 0.07	2.166

Table S12: Photovoltaic performance for **6b**, D/A-ratio 1:1 by different concentrations

Concentration [mg/mL]	V_{OC} [V]	J_{SC} [mA/cm^2]	FF [%]	PCE [%]	PCE^{max} [%]
5	0.931 ± 0.009	-2.5 ± 0.09	37.0 ± 0.6	0.86 ± 0.05	0.923[a]
10	0.960 ± 0.007	-2.4 ± 0.2	34.8 ± 0.5	0.81 ± 0.05	0.877[b]
15	0.94 ± 0.02	-1.65 ± 0.08	31.4 ± 0.5	0.49 ± 0.04	0.537[c]

[a] corresponds to a layer thickness of: (20 ± 4) nm, [b] corresponds to a layer thickness of: (73 ± 2) nm, [c] corresponds to a layer thickness of: (125 ± 4) nm.

Table S13: Photovoltaic performance for **6b**, concentration: 5 mg/mL (turned to be the best), different D/A- ratios.

D/A ratio	V_{OC} [V]	J_{SC} [mA/cm^2]	FF [%]	PCE [%]	PCE^{max} [%]
3:2	0.910 ± 0.008	-2.37 ± 0.05	34.5 ± 0.4	0.74 ± 0.03	0.788
1:1	0.923 ± 0.007	-2.38 ± 0.08	37 ± 0.05	0.81 ± 0.05	0.881
2:3	0.92 ± 0.02	-2.4 ± 0.1	38 ± 0.08	0.82 ± 0.08	0.924
1:2	0.92 ± 0.02	-2.22 ± 0.05	37 ± 0.05	0.76 ± 0.05	0.833
2:5	0.92 ± 0.03	-2.05 ± 0.09	37 ± 0.08	0.71 ± 0.08	0.83

Table S14: Photovoltaic performance for **6c**, D/A-ratio 1:1 by different concentrations

Concentration [mg/mL]	V_{OC} [V]	J_{SC} [mA/cm^2]	FF [%]	PCE [%]	PCE^{max} [%]
5	0.89 ± 0.02	-1.59 ± 0.03	28.8 ± 0.7	0.41 ± 0.02	0.443[a]
10	0.90 ± 0.02	-1.06 ± 0.04	30.2 ± 0.7	0.29 ± 0.02	0.311[b]
15	0.873 ± 0.008	-0.58 ± 0.02	30.4 ± 0.2	0.155 ± 0.006	0.1667[c]

[a] corresponds to a layer thickness of: (10 ± 1) nm, [b] corresponds to a layer thickness of: (31 ± 1) nm, [c] corresponds to a layer thickness of: (53 ± 2) nm.

Table S15: Photovoltaic performance for **6c**, concentration: 5 mg/mL (turned out to be the best), different D/A- ratios.

D/A ratio	V_{OC} [V]	J_{SC} [mA/cm^2]	FF [%]	PCE [%]	PCE^{max} [%]
3:2	0.87 ± 0.02	-1.56 ± 0.04	29.4 ± 0.8	0.40 ± 0.03	0.426
1:1	0.87 ± 0.02	-1.6 ± 0.04	30 ± 1	0.42 ± 0.03	0.447
2:3	0.88 ± 0.02	-1.6 ± 0.04	29.2 ± 0.5	0.41 ± 0.01	0.429
1:2	0.874 ± 0.009	-1.52 ± 0.04	29.6 ± 0.7	0.39 ± 0.02	0.41
2:5	0.88 ± 0.03	-1.51 ± 0.04	29.9 ± 0.9	0.40 ± 0.03	0.436

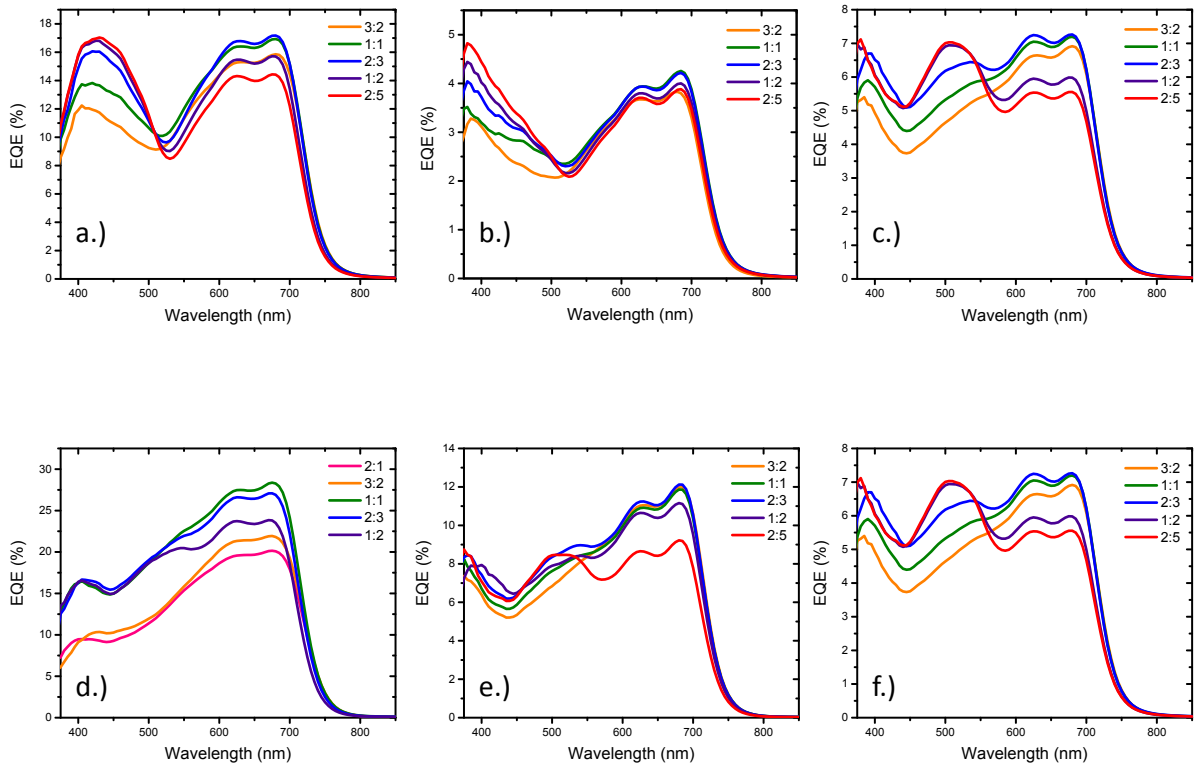


Figure S32: EQE-plots of all devices: a) **3a**; b) **3b**; c) **3c**; d) **6a**; e) **6b**; f) **6c**. Ratios given are D:A.

8. AFM Measurements

The AFM measurements were performed on the active layer of the best solar cell, shown in Figure S27. While the layers are overall very smooth, the domain size changes according to the different solubilities, implying different phase separations. For **6a-c**, the largest domains are found for **6a**, which has the lowest solubility. Correspondingly, the smallest domains are found for **6b**, which has the highest solubility. Surprisingly, this behavior is reversed for **3a-c**. Here, the biggest domains can be found for the molecule with the highest solubility and vice versa. **3b**, which exhibits the highest solubility and the largest domains, also performs worse in comparison to **3a** and **3c**.

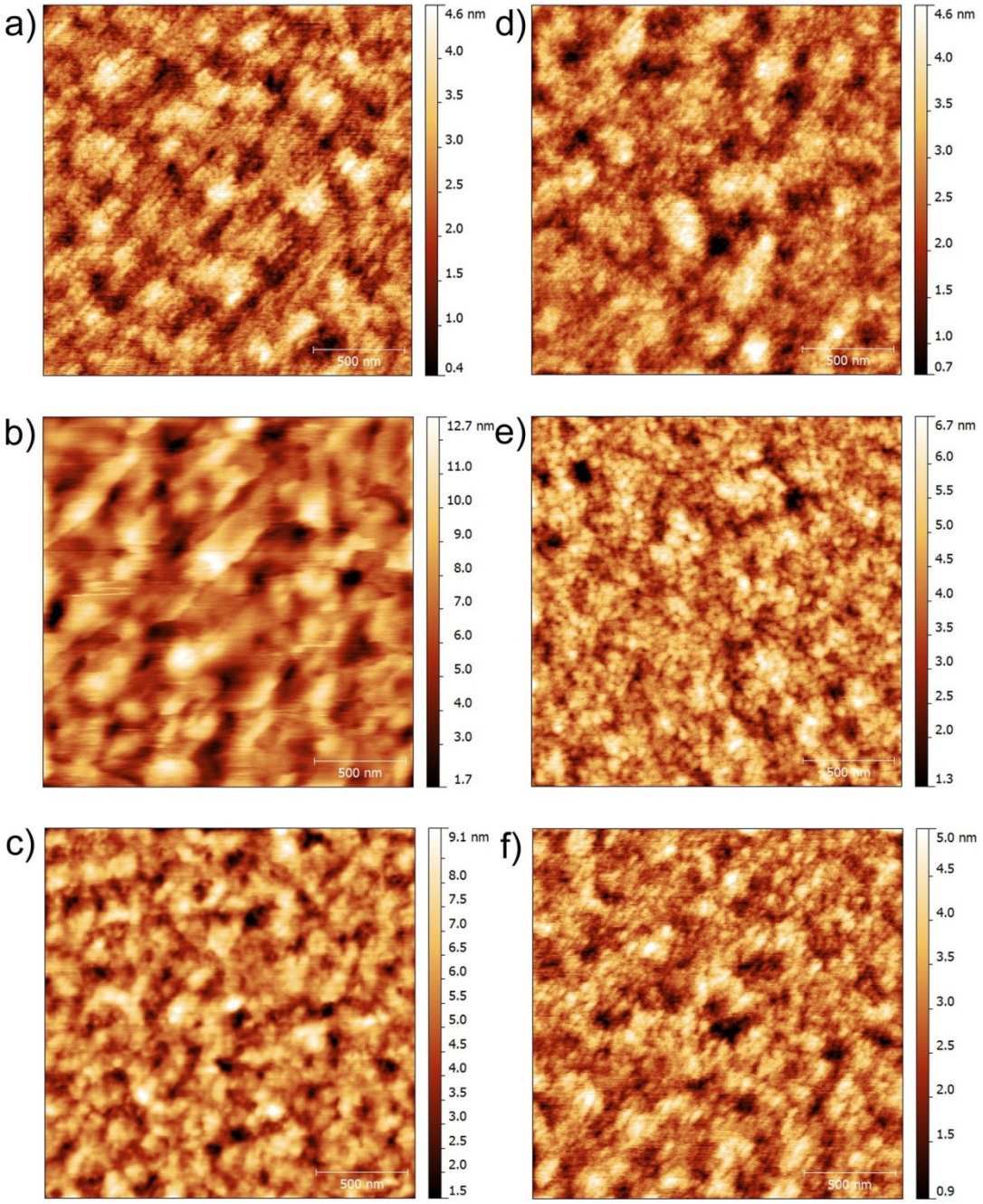


Figure S33: AFM pictures of best photovoltaic devices with PTB7 as donor: Left: a.) **3a** with *D/A* 2:3, 7.5 mg/mL, b.) **3b** with *D/A* 1:2, 5 mg/mL; c.) **3c** with *D/A* 2:3, 4 mg/mL. Right: d.) **6a** with *D/A* 1:1, 7.5 mg/mL, e.) **6b** with *D/A* 2:3, 5 mg/mL and f.) **6c** with *D/A* 1:1, 5 mg/mL.

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