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Supporting Information

Supramolecular Organization of Dye Molecules in Zeolite L Channels: Synthesis, Properties, and Composite Materials

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SUPPLEMENTARY MATERIAL

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SI1 Experimental

SI1.1 Materials and Chemicals.

Cesium exchanged nano-sized ZL (NZL-40) was obtained from Clariant GmbH, while barrel-shaped ZL was prepared according to a procedure that is described below. Clariant GmbH provided a purified sample of Hostasol Red GG (HR). tb-DXP was synthesized according to a newly developed procedure based on previously published works.[1,2] A detailed description of this procedure will be published in a separate paper. The other chemicals used in this study were obtained from their respective suppliers and used without further purification: aluminum hydroxide (ABCR, dried gel, >99%); Aerosil OX-50 (Degussa); potassium hydroxide (Fluka, purum p.a. >85%); potassium nitrate (Fluka, puriss p.a. ≥99%); 1-ethyl-3-methylimidazolium bromide (IMZ^+, Fluka, ≥97%); 1,4-bis(4-methyl-5-phenyl-2-oxazolyl)benzene (DMPOPOP) (Sigma); 1-butanol (Sigma-Aldrich, puriss p.a.); acetonitrile (Honeywell, gradient grade for HPLC,); dichloromethane (DCM) (Fluka, puriss, p.a.); toluene (Thommen-Furler AG, technical grade); branched poly-ethyleneimine (Sigma-Aldrich, Mw=600-800); ethanol (Honeywell, p.a.); immersion oil (Sigma, for microscopy); base-coat nail varnish (Lady Manhattan Cosmetics, Pro Shine Base Coat). Hydrofluoric acid (Sigma-Aldrich, technical 40% - 45%) was diluted to ca. 4% with doubly distilled water before use.

SI1.2 Synthesis of dyes

SI1.2.1 General Consideration

Chemicals and solvents. Unless otherwise indicated, all reagents were obtained from commercial suppliers (Fluka, Sigma-Aldrich) and were used without further purification. Deuterated solvents such as dichloromethane, acetonitrile, acetone, methanol, DMSO and chloroform, were obtained from Cambridge Isotope Laboratories. Tetrahydrofurane and toluene from Armar Chemicals. The deuterated chloroform was dried and neutralized on basic Alox before use. DIAD (diisopropyl azodicarboxylate) and quinoline were distilled before use. Zinc acetate was dried under vacuum. Water was taken from a milliQ system.

Characterization.

Thin layer chromatography (TLC) was done using aluminium sheets coated with silica gel 60 F254 from Fluka. Silica gel column chromatography was carried out with silica gel (32-63, 60 Å) from Brunschwig.

NMR spectra were measured and recorded with a Bruker Ultrashield 300 (^{1}H: 300 MHz and ^{13}C: 75.45 MHz) spectrometer, a Bruker Avance DPX 360 (^{1}H: 360 MHz and ^{13}C: 90.55 MHz) or a Bruker Avance DRX 500 (^{1}H: 500MHz and ^{13}C: 125.77 MHz) using $CDCl_3$, CD_2Cl_2, CD_3CN, acetone-d6, THF-d8 or CD_3OD as solvents. Chemical shifts are given in ppm, calibrated on the residual solvent peak (7.27 and 77.16 ppm for $CDCl_3$, 1.94 and 1.30 ppm for CD_3CN respectively for ^{1}H and ^{13}C), coupling constants "J" are expressed in Hertz (multiplicity: s = singlet, d = doublet, dd = double x doublet, t = triplet, dt = double x triplet, q = quadruplet, quint = quintet, sext = sextet, m = multiplet).

ESI-MS and -HRMS mass spectra were determined by Bruker FTMS 4.7T BioAPEXII or on a Thermo Fisher LTQ Orbitrap XL using Nano Electrospray Ionization (NSI).

UV-vis spectra were measured on a Cary 100 Bio spectrometer, a Perkin-Elmer Lambda 40 or a Perkin-Lambda 25 spectrophotometer with a slit width of 1 nm and a scan speed of 120 nm/min. Luminescence spectra were obtained from an LS50B (Perkin-Elmer) by using a slit width of 7.5 nm for oil−glass sandwiches (OGS) and of 2.5 nm for liquid samples. The scan speed was 120 nm/min. Both spectrometers were equipped with a custom-built sample holder for the OGS samples.[3]

For the final double condensation step in the PDI synthesis, a round bottom, heavy wall, pressure rated flask complete with a solid PTFE screw plug seal from Ace glass was used.

SI1.2.2.1 Synthesis of PDIs with commercially available amines

The corresponding PDIs were prepared by applying a simple condensation reaction in which anthra[2,1,9-*def*:6,5,10-d'ef']diisochromene-1,3,8,10-tetraone (**1**) was treated with appropriate commercially available amines in quinoline or imidazole as solvent and zinc acetate as catalyst at

180 – 230 ^{0}C for several hours under an Argon atmosphere. The reaction condition and the observed yield for the amines: 4-tert-butyl-aniline, 2,4,6-trimethyl-aniline, 4-butyl-aniline, 2,6-diethyl-aniline, and 2,6-di-isopropylaniline are given in Table SI1. The workup procedure (purification by chromatography on silica gel; CH_2Cl_2/MeOH 2%) gives the pure dyes in 8.3% to 95%.

Table SI1: Reaction conditions for the synthesis of dyes with commercially available amines.

Abbreviation	(**1**) (mmol)	Amine (mmol)	Catalyst	Solvent	Reaction Temperature / (°C)	Reaction time (h)	Yield (%)
tb-XP	0.39 g (1.0)	2.00 g (13.4)	Diethanol-amine 0.01 g	–	180	6	77.7
m-DXP	3.97 g (10.1)	5.00 g (37.0)	$Zn(OAc)_2$ 1.70 g	Quinoline 22.7 ml	230	4	73.0
b-XP	3.60 g (9.2)	5.00 g (33.5)	$Zn(OAc)_2$ 1.55 g	Quinoline 20.5 ml	230	4	95.0
DEXP	1.00 g (2.55)	1.64 g (11.0)	$Zn(OAc)_2$ 0.43 g	Quinoline 8.0 ml	220	24	47.0
DIXP	1.0 g (2.55)	1.88 g (10.6)	–	Imidazole 7.5 g	190	24	8.3

tb-XP:

^{1}H NMR (500 MHz. $CDCl_3$, ppm): δ 8.78-8.70 (q, J = 16 Hz, 8 H), δ 7.60-7.52 (t, J = 20 Hz, 8 H), δ 1.41 (s, 18 H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): the solubility was too poor to get the ^{13}C NMR data. HRMS (m/z): $[M]^-$ Calcd for $C_{44}H_{34}N_2O_4$, 654.25; Found 654.2511.

m-DXP:

^{1}H NMR (500 MHz. $CDCl_3$, ppm): δ 8.71-8.80 (q, J = 15 Hz, 8 H), δ 7.06 (s, 4 H), δ 2.37 (s, 12 H), δ 2.14 (s, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 162.85, 138.77, 135.07, 131.99, 130.90, 130.16, 129.48, 126.82, 123.47, 23.35, 21.21, 17.85. HRMS (m/z): $[M]^-$ Calcd for $C_{42}H_{30}N_2O_4$, 626.2210, Found: 626.2215.

b-XP:

^{1}H NMR (500 MHz. $CDCl_3$, ppm): δ 8.69-8.77 (q, J = 15 Hz, 8 H), δ 7.37-7.39 (d, J = 10, 8 H), δ 2.71-2.75 (t, J = 10 Hz, 4 H), δ 1.66-1.74 (p, J = 10 Hz, 4 H), δ 1.39-1.47 (p, J = 10 Hz, 6 H), δ

0.96-1.00 (p, J = 10 Hz, 4 H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): the solubility is too poor to get the ^{13}C NMR data. HRMS (m/z): $[M]^-$ Calcd for $C_{44}H_{34}N_2O_4$, 654.25; Found 654.2544.

DEXP:

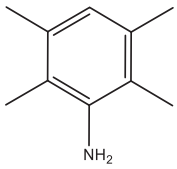
^{1}H NMR (500 MHz. $CDCl_3$, ppm): δ 8.72-8.80 (q, J = 15 Hz, 8 H), δ 7.42-7.45 (p, J = 10 Hz, 6 H), δ 2.46-2.52 (q, J = 10 Hz, 12 H), δ 1.15-1.19 (t, J = 10, 8 H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): the solubility is too poor to get the ^{13}C NMR data. HRMS (m/z): $[M]^-$ Calcd for $C_{44}H_{34}N_2O_4$, 654.22; Found 654.2521.

DIXP:

^{1}H NMR (500 MHz. $CDCl_3$, ppm): δ 8.76-8.83 (q, J = 10 Hz, 8 H), δ 7.12-7.20 (p, J = 9 Hz, 6 H), δ 2.21 (s, 12 H), δ 2.16 (s, 12 H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 162.46, 135.63, 134.81, 133.84, 131.48, 129.86, 128.51, 128.19, 126.52, 123.22, 123.10, 17.37. HRMS (m/z): $[M]^-$ Calcd for $C_{48}H_{42}N_2O_4$, 710.27; Found 710.3152.

SI1.2.2.2 Synthesis of PDIs with non-commercially available amines

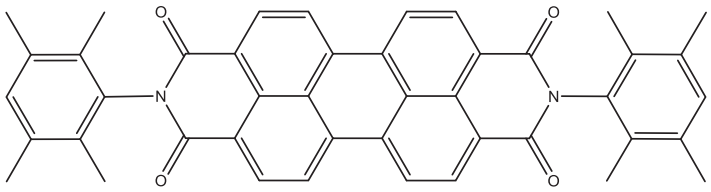
2,3,5,6-Tetramethylbenzenamine (3):



2,3,5,6-Tetramethyl-3-nitrobenzene **(2)** (860 mg, 4.79 mmol) was dissolved in absolute ethanol (12.5 ml) and water (3.3 ml) was added. To the resultant mixture was added $CaCl_2$•$2H_2O$ (497 mg, 4.47 mmol) followed by zinc powder (4.13 g, 63.3 mmol), and the mixture was vigorously stirred at 75°C for 16 h. The mixture was then cooled to rt, filtered through Celite, the solvent was removed in vacuum. The residue was dissolved in Et_2O (50 ml), extracted with water (50 ml), the organic phase was dried (Na_2SO_4), filtered and the solvent was removed in vacuum. The residue was purified by flash chromatography on silica gel (hexane/EtOAc 9:1) to yield **(3)** as a solid (485 mg, 67%).

The analytical data were identical to those published in literature [4].

***N,N'*-Bis(2,3,5,6-tetramethylphenyl)-3,4,9,10-perylenetetracarboxylic diimide (dm-DXP):**



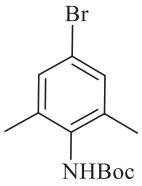
Compound **dm-DXP** was prepared according to the procedure described for **tB-DXP**, starting from perylene-3,4,9,10-tetracarboxylic dianhydride **(1)**, (312 mg, 0.79 mmol), compound **(3)** (475 mg, 3.18 mmol), $Zn(OAc)_2$ (144 mg, 0.79 mmol), and quinoline (30 ml), which gave a red solid (165 mg, 32%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.79 (d, *J* = 8.0 Hz, 4H, perylene), 8.73 (d, *J* = 8.1 Hz, 4H, perylene), 7.12 (s, 2H, phenyl), 2.32 (s, 12H, 4×CH_3), 2.04 (s, 12H, 4×CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ 162.93(4C, 4×C=O), 135.06, 134.63, 133.33, 132.44, 131.98, 130.91, 130.16, 126.83, 123.48, 123.32, 20.13 (4C, 4×CH_3), 14.32 (4C, 4×CH_3).

HRMS-NSI)m/z): $[M+H]^+$ Calcd for $C_{44}H_{35}N_2O_4$, 655.2591; Found 655.2593.

(4-Bromo-2,6-dimethylphenyl)carbamic acid *tert*-butyl ester (5):



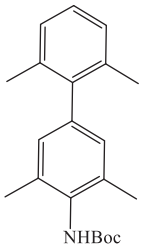
To a solution of 4-bromo-2,6-dimethylaniline (**(4)**, 5 g, 24.9 mmol) in absolute ethanol (30 ml) was added di-*tert*-butyl dicarbonate (8.18 g, 37.4 mmol) and the reaction mixture was stirred at r.t. for 24 h. TLC (hexane/ethyl acetate 8:2) revealed unreacted **(4)**, therefore more di-*tert*-butyl dicarbonate (4.70 g, 21.5 mmol) was added and the reaction mixture was stirred at r.t. for 24 h. The solvent was removed in vacuum and the residue was purified by flash chromatography on silica gel (hexane/EtOAc 9:1) to yield **(5)** (7.47 g, quant.) as a colorless crystalline solid. Due to the dynamic conformation of the carbamate group, some ^{1}H NMR peaks were very broad, and some ^{13}C NMR peaks were of a low intensity.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (s, 2H, phenyl), 5.82 (bs, 1H, NH), 2.23 (s, 6H, 2×CH_3), 1.48 (s, 9H, *t*Bu).

^{13}C NMR (75 MHz, $CDCl_3$) δ 137.97 (2C, C_q), 130.84 (2C), 120.23 (1C, C_q), 28.27 (2C, 2×CH_3), 18.20 (3C, 3×CH_3, *t*Bu).

HRMS-NSI (m/z): $[M+H]^+$ Calcd for $C_{13}H_{19}BrNO_2$, 300.0595; Found, 300.0594.

***N*- (2', 3, 5, 6'-Tetramethyl-1, 1'-biphenyl)- 4'-yl carbamic acid *tert*-butyl ester (7):**



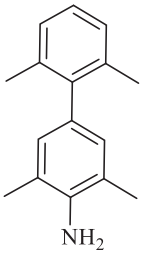
A solution of $Pd(OAc)_2$ (116 mg, 5.16×10^{-4} mol) and triphenylphosphine (416 mg, 1.58 mmol) in dry, degassed THF (40 ml) was stirred at rt under argon for 30 min. Compound **(5)** (3.38 g, 11 mmol) and 2,6-dimethylphenylboronic acid **(6)**, 1.68 g, 11.2 mmol) were added, followed by aqueous K_2CO_3 solution (20 ml, 1.15 M, 2.1 eq). The resultant black mixture was stirred at 80 °C under argon for 24 h. The mixture was diluted with Et_2O (150 ml), washed with water (1×100 ml), dried (Na_2SO_4), filtered and the solvent was removed in vacuum. The residue was purified by flash chromatography on silica gel (hexane/EtOAc 9:1) yielding **(7)** (3.27 g, 91%) as a colorless crystalline solid. According to NMR, the product was slightly contaminated with compound **(5)** due to having a very similar R_f value. However, after Boc cleavage in the next step, the resultant anilines could be better separated by flash chromatography.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10 (m, 3H, biphenyl), 6.86 (s, 2H, biphenyl), 5.92 (bs, 1H, NH), 2.30 (s, 6H, 2×CH_3), 2.05 (s, 6H, 2×CH_3), 1.54 (s, 9H, tBu).

^{13}C NMR (75 MHz, $CDCl_3$) δ 153.83 (1C, C_q, C=O), 141.47, 139.64, 137.96, 136.00, 135.81, 132.49, 130.82, 128.63, 127.14, 126.85, 120.20, 79.82 (1C, C_q, *t*-Bu), 28.25 (2C, 2×CH_3), 20.84 (2C, 2×CH_3), 18.43 (3C, 3×CH_3, *t*-Bu).

HRMS-NSI (m/z): $[M+H]^+$ Calcd for $C_{21}H_{28}NO_2$, 326.2115; Found, 326.2117.

4-Amino-2', 3, 5, 6'-tetramethyl-1, 1'-biphenyl (8):



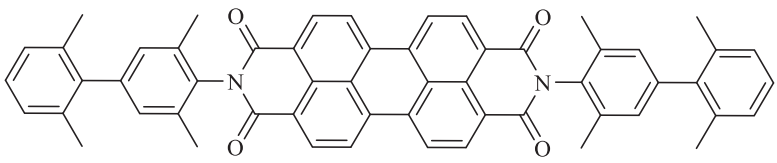
Compound **(7)** (3.27 g, 10 mmol) was dissolved in dioxane (40 ml) and HCl/dioxane (4 M, 20 ml) was added, followed by water (30 ml). The mixture was heated to 90 °C for 1 h, after which TLC (hexane/EtOAc 9:1) revealed no starting material. The mixture was cooled (ice bath), saturated Na_2CO_3 (200 ml) was added and the mixture stirred for 20 min. The mixture was extracted with DCM (300 ml) and the aqueous layer discarded. After drying (Na_2SO_4) and filtration, the solvent was removed in vacuum. The residue was purified by flash chromatography on silica gel (hexane/EtOAc 9:1), yielding **(8)** (725 mg, 32%) as a colorless solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (m, 3H, biphenyl), 6.73 (s, 2H, biphenyl), 3.93 (bs, 2H, NH_2), 2.24 (s, 6H, 2×CH_3), 2.06 (s, 6H, 2×CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.28, 141.07, 136.63, 130.77, 128.84, 127.13, 126.49, 121.66, 21.05 (2C, 2×CH_3), 17.75 (2C, 2×CH_3).

HRMS-NSI (m/z): $[M+H]^+$ Calcd for $C_{16}H_{20}N$, 226.1590; Found, 226.1588.

***N*,*N'*-Bis(2',3,5,6'-tetramethyl-1,1'-biphen-4-yl)-3,4,9,10-perylenetetracarboxylic diimide (dmp-DXP):**



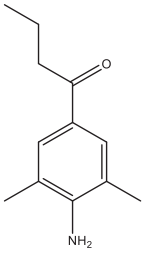
Compound **dmp-DXP** was prepared according to the procedure described for **tB-DXP**, starting from perylene-3,4,9,10-tetracarboxylic dianhydride **(1)**, 400 mg, 1.02 mmol), compound **(8)** (459 mg, 2.04 mmol), $Zn(OAc)_2$ (217 mg, 1.18 mmol), and quinoline (30 ml), which gave a red solid (105 mg, 13%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.82 (d, *J* = 8.0 Hz, 4H, perylene), 8.77 (d, *J* = 8.1 Hz, 4H, perylene), 7.15 (m, 6H, 2×biphenyl), 7.04 (s, 4H, 2×biphenyl), 2.21 (s, 12H, 4×CH3), 2.16 (s, 12H, 4×CH3).

^{13}C NMR (75 MHz, $CDCl_3$) δ 162.77 (4C, 4×C=O), 141.61, 141.31, 136.17, 135.58, 135.11, 132.21, 131.94, 130.22, 129.12, 127.23, 127.06, 126.88, 123.56, 123.43, 21.00 (4C, 4×CH_3), 18.05 (4C, 4×CH_3).

HRMS-NSI (m/z): $[M+H]^+$ Calcd for $C_{56}H_{43}N_2O_4$ 807.3217; Found 807.3235.

1-(4-Amino-3,5-dimethylphenyl)-1-butanone (10):



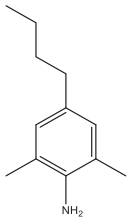
A mixture of 2,6-dimethylaniline **(9)**, 2 g, 16.5 mmol) and butyric acid (2.30 g, 26.1 mmol) in polyphosphoric acid (ca 50 ml) was heated to 175 °C with stirring for 2 h. The mixture was cooled to 60 °C and $HCl_{aq.}$ (1 M, 50 ml) was added (caution: highly exothermic). The mixture was stirred for 1.5 h, allowing reaching r.t. Then water (500 ml) was added and the mixture was extracted with DCM (500 ml). The organic phase was washed with water (1×500 ml), dried (Na_2SO_4), filtered and the solvent was removed in vacuum. The residue was purified by flash chromatography on silica gel (hexane/EtOAc 7:3) to yield **(10)** (1.05 g, 33%) as an oil which crystallized upon storage.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (s, 2H, phenyl), 4.06 (bs, 2H, NH_2), 2.84 (t, *J* = 7.4 Hz, 2H, CH_2CO), 2.19 (s, 6H, 2×CH_3), 1.73 (sex, *J* = 7.4 Hz, 2H, $CH_3CH_2CH_2CO$), 0.98 (t, *J* = 7.4 Hz, 3H, 2×$CH_3CH_2CH_2CH_2$).

^{13}C NMR (75 MHz, $CDCl_3$) δ 199.30 (1C, C_q), 147.55 (1C, C_q), 129.10 (2C), 127.13 (1C, C_q), 120.42 (2C, C_q), 39.93 (1C, CH_2), 18.41 (1C, CH_2), 17.53 (2C, 2×CH_3), 14.01 (1C, CH_3).

HRMS-NSI (m/z): $[M+H]^+$ Calcd for $C_{12}H_{18}ON$, 192.1383; Found, 192.1381.

4-Butyl-2,6-dimethylbenzenamine (11):



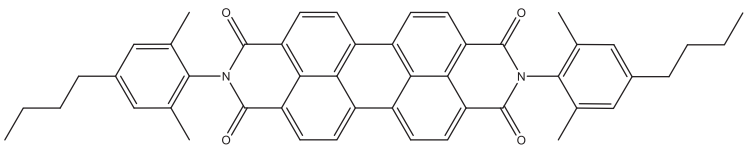
Compound **(10)** (896 mg, 4.68 mmol) was dissolved in CF_3CO_2H (10 ml) and triethylsilane (5 ml, 31.3 mmol) was added. The mixture was stirred at r.t. for 2 h. The solvent was removed in vacuum and the residue was dissolved in DCM (50 ml), washed with saturated $NaHCO_3$ (1×50 ml), dried (Na_2SO_4), filtered and the solvent was removed in vacuum. The residue was purified by flash chromatography on silica gel (hexane/EtOAc 9:1) to yield **(11)** (700 mg, 85%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.79 (s, 2H, phenyl), 3.59 (bs, 2H, NH_2), 2.48 (t, *J* = 7.6 Hz, 2H, CH_2, benzyl), 2.19 (s, 6H, 2×CH_3), 1.55 (m, 2H, $CH_3CH_2CH_2CH_2$), 1.36 (m, 2H, $CH_3CH_2CH_2CH_2$), 0.93 (t, *J* = 7.3 Hz, 1H, 2× $CH_3CH_2CH_2CH_2$).

^{13}C NMR (75 MHz, $CDCl_3$) δ 140.34 (1C, C_q), 132.53 (1C, C_q), 128.22 (2C), 121.74 (1C, C_q), 34.82 (1C, CH_2), 34.21 (1C, CH_2), 22.47(1C, CH_2), 17.65 (1C, CH_3), 14.01 (1C, CH_3).

HRMS-NSI (m/z): $[M+H]^+$ Calcd for $C_{12}H_{20}ON$, 178.1590; Found, 178.1592.

***N,N'*-Bis(4-butyl-2,6-dimethylphenyl)-3,4,9,10-perylenetetracarboxylic diimide (b-DXP):**



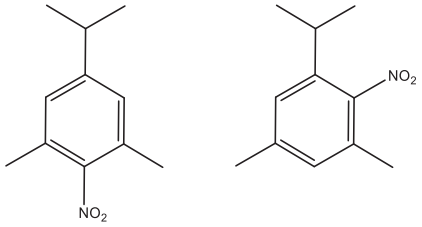
Synthesised as described for **tb-DXP**. Yield = 19%.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.77 (dd, *J* = 8 Hz, 8H, perylene), 7.06 (s, 4H, phenyl), 2.63 (m, 4H, 2×CH_2, benzyl) , 2.14 (s, 12H, 4×CH_3), 1.67 (m, 4H, 2×$CH_3CH_2CH_2CH_2$), 1.42 (m, 4H, 2×$CH_3CH_2CH_2CH_2$), 0.97 (t, *J* = 7.3 Hz, 6H, 2×$CH_3CH_2CH_2CH_2$).

^{13}C NMR (75 MHz, $CDCl_3$) δ 162.82 (4C, 2×C=O), 135.05 (4C, C_q), 131.94 (4C), 128.71 (4C), 123.52, 123.30 (4C), 117.48, 35.39, 33.34, 22.56, 17.91 (4C, 4×CH_3), 13.99.

HRMS-NSI (m/z): $[M+H]^+$ Calcd for $C_{48}H_{43}N_2O_4$, 711.3217; Found, 711.3229.

2,6(4)-Dimethyl-4(6)-isopropyl-1-nitrobenzene (13/14):



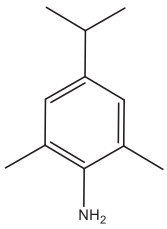
Fuming nitric acid (1.8 ml, 40.2 mmol), Ac_2O (1 ml, 10.6 mmol) and acetic acid (2 ml) were combined (CAUTION: EXOTHERMIC) in a dropping funnel, and the resultant soution was added dropwise to a solution of 5-isopropyl-m-xylene **(12)** (3.44 g, 23.2 mmol) in Ac_2O (5 ml, 53 mmol) kept at 0 °C. After 30 min, the ice bath was removed and the mixture was stirred for 1.5 h. The reaction mixture was then quenched by the addition of ice and extracted with Et_2O (2×100 ml). The organic phase was washed with $NaOH_{aq.}$ (0.2 M, 500 ml), brine, dried (Na_2SO_4), filtered and the solvent was removed in vacuum. The residue was purified by flash chromatography on silica gel (hexane/EtOAc 1:0→95:5) to yield **(13/14)** (4.38 g, 71%, mixture of 2 regioisomers) as an oil. Due to the low boiling point of the product, the hexane from the column was not fully removed on high vacuum. This did not hamper the next step.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05-6.91 (m, 2H, 2×CH, phenyl), 2.87 (septet, *J* = 6.8 Hz, 1H, CH, *i*-propyl), 2.34-2.25 (m, 6H, 2×CH_3, phenyl), 1.31-1.23 (m, 6H, 2×CH_3, *i*-propyl).

^{1}H NMR (75 MHz, $CDCl_3$) δ 151.11 (1C, CNO_2), 140.15, 139.58, 129.63, 129.19, 128.64, 126.90, 124.68, 33.86, 28.87, 23.73, 23.69, 21.30, 17.68, 17.22.

HRMS-NSI (m/z): $[M+H]^+$ Calcd for $C_{11}H_{16}O_2N$, 194.1176; Found, 194.1169.

2,6-Dimethyl-4-isopropylaniline (15):



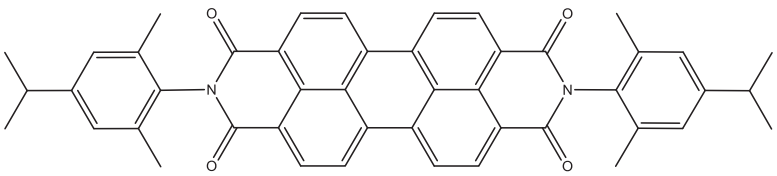
Compound **(13/14)** (4.36 g, 22.6 mmol) was dissolved in absolute ethanol (57 ml) and water (15.2 ml) was added. To the resultant mixture was added $CaCl_2$ •$2H_2O$ (2.30 g, 15.6 mmol) followed by zinc powder (19.1 g, 292 mmol), and the mixture was vigorously stirred at 75 °C for 16 h. The mixture was then cooled to r.t., filtered through Celite, the solvent was removed in vacuo. The residue was purified by flash chromatography on silica gel (hexane/EtOAc 95:5→9:1) to yield **(15)** as an oil (442 mg, 12%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.84 (s, 2H, phenyl), 3.48 (bs, 2H, NH_2), 2.79 (septet, *J* = 6.9 Hz, 1H, CH, *i*-propyl), 2.20 (s, 6H, phenyl$(CH_3)_2$), 1.23 (d, *J* = 6.9 Hz, 6H, 2×CH_3, *i*-propyl).

^{13}C NMR (75 MHz, $CDCl_3$) δ 140.57 (1C, C_q), 138.65 (1C, C_q), 126.25, 121.80 (2C, 2×C_q), 33.34 (1C, CH), 24.45 (2C, 2×CH_3), 17.81 (2C, 2×CH_3).

HRMS-NSI (m/z): $[M+H]^+$ Calcd for $C_{11}H_{16}N$, 162.1277; Found, 162.1283.

***N*,*N'*-Bis(4-*iso*-propyl-2,6-dimethylphenyl)-3,4,9,10-perylenetetracarboxylic diimide (ip-DXP):**



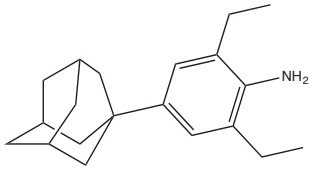
A mixture of perylene-3,4,9,10-tetracarboxylic dianhydride **(1)**, 596 mg, 1.52 mmol), compound **(15)** (744 mg, 4.56 mmol), $Zn(OAc)_2$ (276 mg, 1.50 mmol) in quinoline (60 ml) were stirred vigorously at 240 °C for 2 d. The resultant mixture was poured onto $HCl_{aq.}$ (2 M, 500 ml). The precipitate was filtered, washed with $HCl_{aq.}$ (1 M, 500 ml) then water (500 ml), dried under high vacuum and chromatographed on silica gel using chloroform as eluent to give **ip-DXP** (77 mg, 7%) as a red solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.81-8.71 (m, 4H, H-2, 5, 8, 11, perylene), 7.09 (s, 4H, phenyl), 2.93 (septet, *J* = 7 Hz, 2H, 2×CH, *i*-propyl), 2.15 (s, 12H, 4×CH_3, phenyl), 1.30 (d, *J* = 6.9 Hz, 12H, 4×CH_3, *i*-propyl).

^{13}C NMR (75 MHz, $CDCl_3$) δ 162.83 (4C, 4×C=O), 149.26 (2C, 2×C-N), 135.05, 134.95, 131.93, 126.80, 123.53, 123.30, 33.81, 23.93, 23.17, 18.00.

HRMS-NSI (m/z): $[M+H]^+$ Calcd for $C_{46}H_{39}N_2O_4$, 683.2904; Found 683.2906.

4-((1*r*,3*R*,5*S*)-Adamantan-1-yl)-2,6-diethylaniline (19):

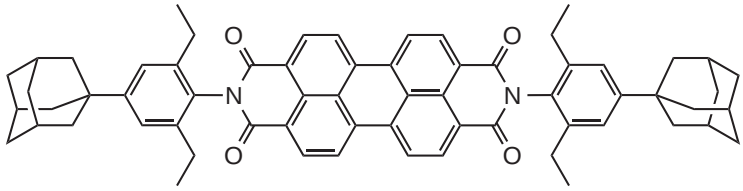


A mixture of **(17)** 2.08 g (13.9 mmol) and **(18)** 3 g (13.9 mmol) were heated at 200 ^{0}C for 4 h. The mixture was then cooled to rt. The residue was dissolved in Et_2O (50 ml), extracted with water (50 ml), the organic phase was dried (Na_2SO_4), filtered and the solvent was removed in vacuum. The yield of **(19)** was 1.9 g (48%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.90 (s, 2H, aromatic protons), 3.52 (s, broad, 2H, amine), 2.47 (q, 4H, ethyl), 2.00 (s, 3H, adamantane), 1.83 (s, 6H, adamantane), 1.67 (m, 6H, adamantane), 1.19 (t, 6H, ethyl).

MS (m/z): Calcd for $C_{20}H_{29}N$, 283.23; Found 283.18.

***N,N'*-Bis(4-((1*r*,3*R*,5*S*)-adamantan-1-yl)-2,6-diethylphenyl-3,4,9,10-perylenetetracarboxylic diimide (ADE-XP):**



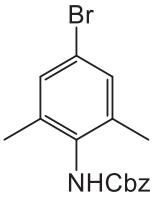
ADE-XP

A mixture of perylene-3,4,9,10-tetracarboxylic dianhydride (**1**, 1 g, 2.5 mmol), compound **(19)** (3.18 mg, 11.0 mmol), $Zn(OAc)_2$ (430 mg, 2.34 mmol) in quinoline (8 ml) were stirred vigorously at 220 °C for 24 h. The resultant mixture was poured onto $HCl_{aq.}$ (2 M, 50 ml) and 60 ml EtOH and stirred for 3h. The precipitate was filtered, washed with EtOH and dried under high vacuum and chromatographed on silica gel using dichloromethane/2% MeOH as eluent to give **ADE-XP** (300 mg, 13%) as a red solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.82 (q, 8H, aromatic protons perylene), 7.32 (s, 4H, aromatic protons), 2.53 (q, 8H, ethyl), 2.20 (s, 6H, adamantane), 2.07 (s, 12H, adamantane), 1.87 (s, 12H, adamantane), 1.22 (t, 12H, ethyl).

HRMS-NSI (m/z): $[M+H]^+$ Calcd for $C_{64}H_{62}N_2O_4$, 922.4715; Found 922.4711.

(4-Bromo-2,6-dimethylphenyl)carbamic acid benzyl ester (20):



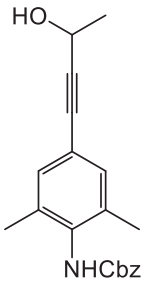
4-Bromo-2,6-dimethylaniline **(4)**, 2.5 g, 12.5 mmol) was dissolved in dry THF (50 ml) and $NaHCO_3$ (1.15 g, 13.7 mmol) was added. The mixture was cooled to 0 °C and benzyl chloroformate (1.97 ml, 13.7 mmol) was added. The reaction mixture was allowed to reach rt, and was thus stirred for 8 h. The solvent was removed in vacuum and the residue was purified by flash chromatography on silica gel (hexane/EtOAc 9:1→7:3) to yield **(20)** (6.5 g, 78%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (m, 5H, C_6H_5), 7.23 (s, 2H, C_6H_2), 5.99 (bs, 1H, NH), 5.19 (s, 2H, CH_2), 2.22 (s, 6H, 2×CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ 154.26 (1C, C_q, C=O), 138.16, 136.36, 132.90, 131.14, 128.70, 128.41, 128.26, 120.84, 67.40 (1C, CH_2), 18.30.

HRMS-NSI (m/z): $[M+H]^+$ Calcd for $C_{16}H_{17}BrNO_2$, 334.0437; Found, 334.0447.

***N*-[4-(3-Hydroxy-1-butyn-1-yl)-2,6-dimethylphenyl]carbamic acid benzyl ester (21):**



Compound **(20)** (10 g, 29.9 mmol) was dissolved in THF-Et_3N (3:2, 100 ml) and the solution was degased by 4 vacuum-argon backfill cycles. 3-butyn-1-ol (4.24 ml, 54.1 mmol) was added, followed by $Pd[Ph_3P]_4$ (200 mg, 1.73 mmol) and CuI (40 mg, 0.21 mmol), and the resultant mixture was stirred in a closed Schlenk flask at 75 °C for 16 h. More 3-butyn-1-ol (2 ml, 25.5 mmol) was then added, and the mixture was stirred at 55 °C for an additional 16 h. The solvent was removed in vacuo and the residue was dissolved in DCM (100 ml), washed with water (250 ml) and then brine (250 ml), dried (Na_2SO_4), filtered, and the solvent was removed in vacuum.

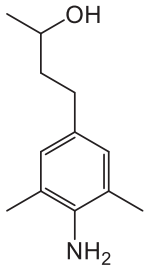
The residue was purified by flash chromatography on silica gel (hexane/EtOAc 6:4) to yield **(21)** (1.6 g, 16%) as a colorless solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (m, 5H, phenyl, Cbz), 7.15 (s, 2H, Ar, aniline), 6.07 (bs, 1H, NH), 5.19 (s, 2H, CH_2), 4.74 (m, 1H, CH), 2.21 (s, 6H, 2×CH_3, aniline), 1.87 rotamers, 1.54 (d, J = 8.6 Hz, 3H, C*H*$_3$CHOH).

^{13}C NMR (75 MHz, $CDCl_3$) δ 135.86, 131.45, 128.55, 128.24, 121.33, 83.68, 67.24 (1C, CH_2), 58.86 (1C, COH), 58.67, 24.41, 23.92, 18.19 (2C, 2×CH_3) rotamers.

HRMS-NSI (m/z): $[M+H]^+$ Calcd for $C_{13}H_{19}BrNO_2$, 300.0595; Found, 300.0594.

4-(3-Hydroxybut-1-yl)-2,6-dimethylaniline (22):



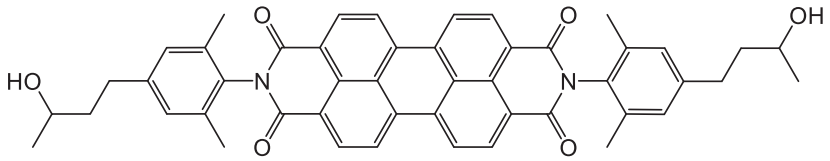
Compound **(21** (420 mg, 1.29 mmol) was dissolved in methanol (20 ml) and Pd/C (10%, 170 mg) was added. The mixture was vigorously stirred under a hydrogen atmosphere (balloon) for 16 h. The mixture was filtered through Celite, the solvent was removed in vacuum, and the residue was redissolved in methanol (20 ml), Pd/C (10%, 170 mg) was added, and the mixture was vigorously stirred under a hydrogen H_2 atmosphere (balloon) for another 16 h. The mixture was filtered through Celite, the solvent was removed in vacuum and the residue was purified by flash chromatography on silica gel (hexane/EtOAc 7:3→1:1) to yield **(22)** (6.5 g, 78%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.82 (s, 2H, phenyl), 3.83 (m, 1H, $CH_2CH_2C(CH_3)$*H*OH), 2.58 (m, 2H, CH_2C*H*$_2$C(CH$_3$)HOH), 2.19 (s, 6H, 2×CH_3), 1.73 (m, 2H, C*H*$_2$CH$_2$C(CH$_3$)HOH), 1.23 (d, 3H, C(C*H*$_3$)HOH).

^{13}C NMR (75 MHz, $CDCl_3$) δ 140.35, 131.37, 128.03, 121.75, 67.34 (1C, CHOH), 41.18, 31.12, 23.35, 17.47.

HRMS-NSI (m/z): $[M+H]^+$ Calcd for $C_{12}H_{20}NO$, 194.1539; Found 194.1542.

***N,N'*-Bis[4-(3-hydroxybut-1-yl)-2,6-dimethylphenyl]-3,4,9,10-perylenetetracarboxylic diimide (23):**

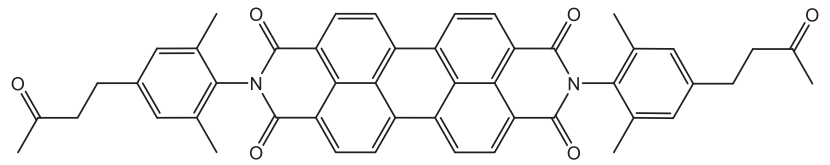


A mixture of perylene-3,4,9,10-tetracarboxylic dianhydride **(1)**, 175 mg, 0.45 mmol), compound **(22)**, 180 mg, 0.93 mmol), $Zn(OAc)_2$ (40 mg, 0.22 mmol), imidazole (10 g) was degassed by 3 vacuum-argon backfill cycles. The resultant mixture was stirred at 240 °C under argon for 48 h. The resultant mixture was poured onto $HCl_{aq.}$ (2 M, 400 ml), filtered, dried in air overnight and chromatographed on silica gel using DCM/MeOH (1:0→97:3, stepwise gradient) as eluent to give **(23)** (40 mg, 12%) as a red solid. Due to the extremely low solubility of the compound, we could not obtain a good quality ^{1}H-NMR spectrum, and we were not able to record a ^{13}C-NMR spectrum.

^{1}H NMR (300 MHz, MeOD-$CDCl_3$) δ 8.75 (m, 8H, perylene), 7.06 (s, 4H, 2×phenyl), 3.84 (m, 4H, 2×$CH_2CH_2C(CH_3)$*H*OH), 2.70 (m, 4H, 2×CH_2C*H*$_2$C(CH_3)HOH), 2.11 (s, 12H, 4×CH_3), 1.79 (m, 4H, 2×C*H*$_2CH_2C(CH_3)$HOH), 1.22 (m, 14H, 2×C(C*H*$_3$)HOH + impurity).

HRMS-NSI (m/z): $[M+H]^+$ Calcd for $C_{48}H_{43}N_2O_6$, 743.3116; Found 743.3134.

***N,N'*-Bis[4-(3-oxobut-1-yl)-2,6-dimethylphenyl]-3,4,9,10-perylenetetracarboxylic diimide (bone-DXP):**



Compound **(23)** (40 mg, 53.8 μmol) was dissolved in DCM and PCC (0.56 mmol) was added. The mixture was stirred at r.t. while being monitored by TLC (DCM/MeOH 95:5) for the disappearance of the starting material, which took approximately 2 h. The solvent was removed

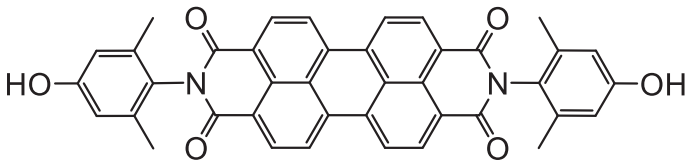
in vacuo, and the residue chromatographed on silica gel using DCM/MeOH (1:0→99:1) as eluent to give **bone-DXP** (10 mg, 25%) as a red solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.78 (m, 8H, perylene), 7.07 (s, 4H, phenyl), 2.92-2.84 (m, 8H, 2×C*H*$_2$C*H*$_2$C=O(CH_3)), 2.20 (s, 6H, 2×C=O(C*H*$_3$)), 2.14 (s, 12H, 4×CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ 207.63 (2C, 2 × C=O), 162.55 (4C, 4 × C=O, imide), 141.96, 141.50, 136.98, 135.23, 134.86, 131.96, 131.77, 131.37, 129.93, 128.61, 126.60, 123.91, 123.14, 77.22, 77.00, 76.80, 76.37, 44.79 (2C, 2 × CH_2), 29.89 (2C, 2×C=O(*C*H_3)), 29.46, 29.05 (2C, 2 × CH_2), 17.68 (4C, 4×CH_3).

HRMS-NSI (m/z): $[M+H]^+$ Calcd for $C_{48}H_{39}N_2O_6$, 739.2803; Found 739.2816.

***N,N'*-Bis(4-hydroxy-2,6-dimethylphenyl)-3,4,9,10-perylenetetracarboxylic diimide (25):**



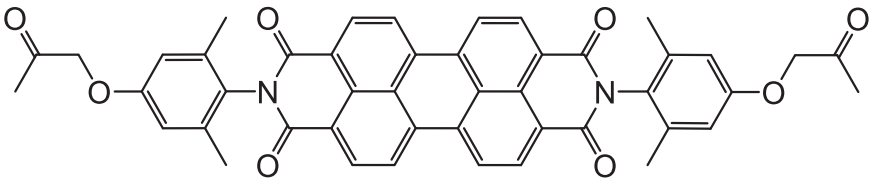
A mixture of perylene-3,4,9,10-tetracarboxylic dianhydride **(1),** 228 mg, 0.58 mmol), 4-hydroxy-2,6-dimethylaniline**(24)**, 320 mg, 2.33 mmol), $Zn(OAc)_2$ (106 mg, 0.58 mmol), quinoline (20 ml) was degassed by 3 vacuum-argon backfill cycles. The resultant mixture was stirred at 250 °C under argon for 48 h. The mixture was poured onto $HCl_{aq.}$ (2 M, 400 ml), filtered, dried in air overnight and chromatographed on silica gel using DCM/MeOH (1:0→95:5, stepwise gradient) as eluent to give **(25)** (223 mg, 60%) as a red solid.

^{1}H NMR (300 MHz, DMSO-d_6) δ 9.51 (s, 2H, 2×OH), 8.44 (d, *J* = 8.2 Hz, 4H, perylene), 8.33 (d, *J* = 7.9 Hz, 4H, perylene), 6.65 (s, 4H, phenyl), 2.04 (s, 12H, 4×CH_3).

^{13}C NMR (75 MHz, DMSO-d_6) δ 162.20 (4C, 4 × C=O), 157.01, 136.36, 133.85, 130.97, 128.67, 125.36, 125.08, 123.80, 122.31, 114.74, 17.68 (4C, 4×CH_3).

HRMS-NSI (m/z): $[M+H]^+$ Calcd for $C_{40}H_{27}N_2O_6$, 631.1864; Found 631.1863.

***N,N'*-Bis[4-(2-oxopropoxy)-2,6-dimethylphenyl]-3,4,9,10-perylenetetracarboxylic diimide (o-bone-DXP):**



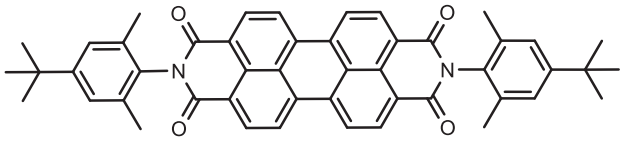
Compound **(25)** (80 mg, 0.13 mmol) was dissolved in DMF (5 ml) and K_2CO_3 (35 mg), KI (20 mg) and chloroacetone (60 µl, 0.76 mmol) were added. The mixture was heated to 80 °C for 12 h under argon. The solvent was removed in vacuum. The residue was purified by flash chromatography on silica gel using DCM/MeOH (1:0→99:1) as eluent to give a red solid, which was dissolved in DCM, precipitated with excess MeOH, filtered and dried to give **o-bone-DXP** (54 mg, 57%).

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.78 (d, J = 8.3 Hz, 4H, perylene), 8.52 (d, J = 7.9 Hz, 1H, perylene), 6.81 (s, 4H, phenyl), 4.88 (s, 4H, 2×OCH_2), 2.21 (s, 6H, 2×CH_3, phenyl), 2.07(s, 6H, 2×$COCH_3$).

^{13}C NMR (125 MHz Hz, $CDCl_3$): 162.92, 157.68, 137.27, 135.13, 132.06, 130.18, 127.40, 126.86, 123.45, 123.40, 114.54, 73.27, 29.70, 26.76, 18.23.

HRMS-NSI (m/z): $[M+H]^+$ Calcd for $C_{46}H_{35}N_2O_8$, 743.2388; Found 743.2396.

***N,N'*-Bis(4-*tert*-Butyl-2,6-dimethylphenyl)-3,4,9,10-perylenetetracarboxylic diimide (tb-DXP):**



A mixture of perylene-3,4,9,10-tetracarboxylic dianhydride **(1)**, 400 mg, 1.01 mmol), 4-*t*-butyl-2,6-dimethylaniline **(30)** (415 mg, 2.54 mmol), $Zn(OAc)_2$ (185 mg, 1.01 mmol), and quinoline (30 ml) were stirred vigorously at 240 °C for 2 d under argon. The resultant mixture was poured onto $HCl_{aq.}$ (1 M, 400 ml). The brown precipitate was filtered, washed with $HCl_{aq.}$ (1 M, 100 ml)

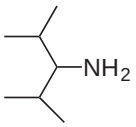
then water (100 ml), dried under high vacuum and chromatographed on silica gel using chloroform as eluent to give **tb-DXP** (403 mg, 56%) as a red solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.79 (d, *J* = 8.0 Hz, 4H, H-2, 5, 8, 11), 8.73 (d, *J* = 8.1 Hz, 4H, H-1, 6, 7, 12), 7.24 (s, 4H, phenyl), 2.17 (s, 12H, 4×CH_3), 1.35 (s, 18H, 2×*t*-butyl).

^{13}C NMR (75 MHz, $CDCl_3$): δ 162.82, 151.47, 135.04, 134.51, 131.94, 130.81, 125.77, 123.54, 123.30, 34.52, 31.40, 18.18.

HRMS-NSI (m/z): $[M+H]^+$ Calcd for $C_{48}H_{43}N_2O_4$, 711.3223; Found 711.3209.

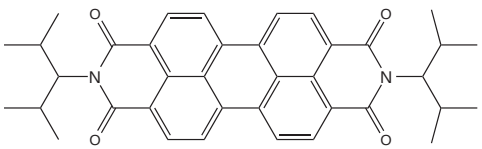
2,4-Dimethylpentan-3-amine (27):



2.88 g (25 mmol) of 2,4-dimethyl-3-pentanone **(26)**, 20 g (258 mmol) of NH_4OAc, and 1.12 g (17.8 mmol) of $NaBH_3CN$ were dissolved in 76 ml methanol and stirred at r.t. for 56h. The reaction was quenched by adding drop wise concentrated HCl (2 ml). The solution was then concentrated with a rotary evaporator. The solid thus obtained was dispersed in 250 ml of water and adjusted with KOH to pH 10. The obtained latex solution was extracted with 2x150 ml of $CHCl_3$. The pale yellow oil **(27)** (yield 83.6%) was obtained by concentrating the $CHCl_3$ fractions.

^{1}H NMR (360 MHz, $CDCl_3$): δ 2.15-2.18 (t, J =5 Hz, 1H, CNH), 1.65-1.73 (m, J = 6 Hz, 2H, isopropyl), 1.29 (s, broad, 2H, amine), 0.87-0.91 (dxd, J = 5 Hz, 12H).

2,9-Bis(2,4-dimethylpentan-3-yl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone (dmpa-XP):



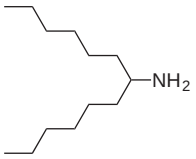
A mixture of **(1)** 0.44 g (1.1 mmol), **(27)** (0.3 g, 2,6 mmol), 6 g (0.088 mmol) imidazole were stirred under Argon at140^{0}C for 4 h. The cold reaction mixture was quenched by adding a solution of EtOH/water/HCl konz. (45 ml:50 ml:5 ml) and stirred for 6 h. The brown solid was filtered of and washed with water and dried in in a vacuum oven at 60^{0}C. The raw product was purified by chromatography (SiO_2; CH_2Cl_2/2% MeOH) Yield 46% on **dmpa-XP**.

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.70-8.65 (q, J = 10 Hz, 8H), 4.74-4.77 (t, J = 8 Hz, 2H), 2.67-2.77 (m, J = 6 Hz, 4H), 1.11-1.12 (d, J = 7, 12H), 0.93-0.95 (d, J = 7, 12H).

^{13}C NMR (125 MHz, $CDCl_3$, ppm), δ 165.17, 164.05, 134.57, 134.55, 134.52, 134.49, 131.99, 131.28, 129.57, 126.45, 123.82, 123.80, 123.21, 123.19, 123.05, 65.20, 29.15, 20.61, 21.82.

HRMS (m/z): $[M]^-$ Calcd for $C_{48}H_{42}N_2O_4$, 586.28; Found: 586.2839.

Tridecan-7-amine (29)

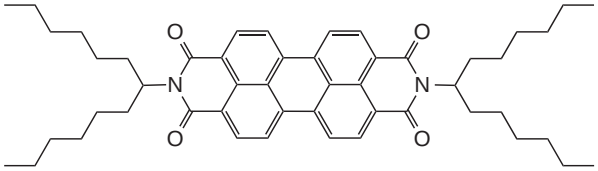


4.96 g (25 mmol) of 2,4-dimethyl-3-pentanone **(28)**, 20 g (258 mmol) of NH_4OAc, and 1.12 g (17.8 mmol) of $NaBH_3CN$ were dissolved in 76 ml methanol and stirred at r.t. for 56 h. The reaction was quenched by adding drop wise concentrated HCl (2 ml). The solution was then concentrated with a rotary evaporator. The solid thus obtained was dispersed in 250 ml of water and adjusted with KOH to pH 10. The obtained latex solution was extracted with 2x150 ml of $CHCl_3$. The pale yellow oil **(29)** (yield 82.3%) was obtained by concentrating the $CHCl_3$ fractions.

^{1}H NMR (360 MHz, $CDCl_3$): δ 3.05 (quint, J = 5 Hz, 1H), 1.67 (m, 4H), 1.34 (m, 16H), 0.93 (m, 6H).

MS (m/z): The correctness of compound (**29**) was proven by the analytics of the corresponding dye (tdc-XP).

2,9-Di(tridecan-7-yl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone (tdc-XP):



A mixture of **(1)** 1 g (2.5 mmol), **(29)** (1.2 g, 10.4 mmol), $Zn(AcO)_2$ (0.36 g, 1.97 mmol), and 5.09 g (0.075 mmol) imidazole were stirred under Argon at 190 ^{0}C for 4 h. The cold reaction mixture was quenched by adding a solution of EtOH/water/HCl konz. (45 ml:50 ml:5 ml) and was stirred for 6 h. The brown solid was filtered off and washed with water and dried in in a vacuum oven at 60 ^{0}C. The raw product was purified by chromatography (SiO_2; CH_2Cl_2/2% MeOH) Yield 73%.

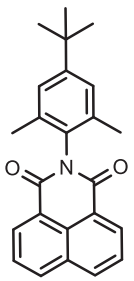
^{1}H NMR (360 MHz, $CDCl_3$, ppm): δ = 8.68-8.61 (q, J = 11 Hz, 8 H), 5.15-5.21 (q, 2 H), 2.21-2.28 (m, J = 5 Hz, 8 H), 1.83-1.89 (m, J = 4 Hz, 8 H), 1.20-1.36 (m, J = 5 Hz, 32 H), 0.81-0.84 (t, J = 7 Hz, 12 H).

^{13}C NMR (90 MHz, $CDCl_3$, ppm): 164.65, 163.56, 134.52, 131.89, 131.14, 129.61, 123.22, 123.02, 54.76, 32.37, 31.75, 30.92, 29.20, 26.92, 22.57, 14.03.

HRMS (MALDI-TOF) (m/z): [M^+] Calcd for $C_{50}H_{62}N_2O_4$, 754.47; Found: 754.4717.

SI1.2.2.3 Synthesis of TDIs

***N*-(4-*tert*-Butyl-2,6-dimethylphenyl)-1,8-naphthalimide (31):**



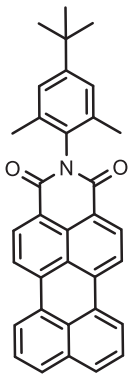
A mixture containing 1,8-naphthalic anhydride (2.23 g, 11.2 mmol) and 4-*t*-butyl-2,6-dimethylaniline **(30)**, 2 g, 11.2 mmol) in acetic acid (50 ml) was heated to 130 °C overnight. The resultant mixture was poured on ice and the precipitated solid was filtered, air dried, and purified by chromatography on silica gel using hexane/EtOAc (4:1) as eluent to give **(31)** (2.23 g, 55%) as a colorless solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.66 (dd, *J* = 7.3, 1.1 Hz, 1H), 8.29 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.81 (dd, *J* = 8.3, 7.3 Hz, 2H) 7.21 (s, 2H, phenyl), 2.13 (s, 6H, 2×CH_3), 1.35 (s, 9H, *t*-butyl).

^{13}C NMR (75 MHz, $CDCl_3$): δ 163.58 (2C, 2 × C=O), 151.19 (1C, C_q), 134.55 (2C, C_q), 134.15 (2C), 131.80 (1C, C_q), 131.58 (2C), 131.14 (1C, C_q), 128.81 (1C, C_q), 127.00 (2C), 125.66 (2C), 122.87 (2C, C_q), 34.48 (1C, C_q, tBu), 31.40 (3C, 3×CH_3, tBu), 18.13 (2C, 2×CH_3).

HRMS-NSI (m/z): $[M+H]^+$ Calcd for $C_{24}H_{24}NO_2$, 358.1807; Found 358.1802.

***N*-(4-*tert*-Butyl-2,6-dimethylphenyl)perylene-3,4-dicarboximide (32)**



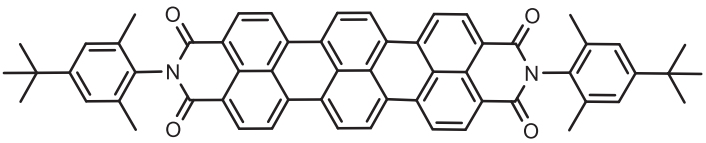
A mixture of perylene-3,4,9,10-tetracarboxylic dianhydride (**1**, 2.03 g, 5.18 mmol), 4-*t*-butyl-2,6-dimethylaniline **(30)**, 496 mg, 2.8 mmol), $Zn(OAc)_2{\cdot}2H_2O$ (733 mg, 3.33 mmol), imidazole (10.3 g) and water (4.43 ml) were stirred vigorously at 245 °C in a round bottomed flask sealed with a PTFE screw cap for 4 d. The resultant mixture was poured onto $HCl_{aq.}$ (2 M, 500 ml), filtered, dried in an oven at 100 °C overnight and chromatographed on silica gel using chloroform as eluent to give **(32)** (886 mg, 88%) as a red solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.66 (d, *J* = 8.1 Hz, 2H, perylene), 8.46-8.50 (m, 4H, perylene), 7.93 (d, *J* = 8.0 Hz, 2H, perylene), 7.66 (t, *J* = 7.8 Hz, 2H, perylene), 7.22 (s, 2H, phenyl), 2.16 (s, 6H, 2×CH_3), 1.36 (s, 9H, *t*-butyl).

^{13}C NMR (75 MHz, $CDCl_3$): δ 163.36 (2C, 2 × C=O), 151.10 (1C, C_q), 137.44 (2C, C_q), 134.57 (2C, C_q), 134.24 (1C, C_q), 131.82 (2C), 131.31(1C, C_q), 130.91 (2C), 130.48 (1C, C_q), 129.13 (2C, C_q), 127.90 (1C, C_q), 127.00 (2C), 125.69 (2C), 123.76 (2C), 121.04 (2C, C_q), 120.12 (2C), 34.49 (1C, C_q, tBu), 31.43 (3C, 3×CH_3, tBu) , 18.23 (2C, 2×CH_3).

HRMS-NSI (m/z): $[M]^+$ Calcd for $C_{34}H_{27}NO_2$, 481.2042; Found 481.2044.

***N,N'*-Bis(4-*tert*-Butyl-2,6-dimethylphenyl)-3,4,11,12-terrylenetetracarboxylic diimide (tb-DXT):**



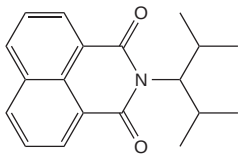
Compound **(31)** (350 mg, 0.98 mmol) and **(32)** (117 mg, 0.24 mmol) were dissolved in DBN/diglyme (1:1, 10 ml) in a flame-dried Schlenk. Then *t*-BuONa (468 mg, 4.88 mmol) was added and the mixture was heated to 130 °C for 3 h under argon. TLC ($CHCl_3$) analysis showed unreacted **(32)**, so more *t*-BuONa (100 mg, 1.04 mmol) was added and the mixture was heated to 150 °C for 3 h, after which **(31)** (175 mg, 0.49 mmol) was added and the mixture was heated to 160 °C overnight. The resultant mixture was poured onto $HCl_{aq.}$ (2 M, 200 ml), filtered, washed with water (100 ml), dried under high vacuum and chromatographed on silica gel using chloroform as eluent to give **tb-DXT** (40 mg, 20%) as a blue solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.77-8.72 (m, 8H, H-2, 5, 7, 8, 10, 13, 15, 16), 8.64 (d, *J* = 8.2 Hz, 4H, H-1, 6, 9, 14), 7.24 (s, 4H, phenyl), 2.18 (s, 12H, 4×CH_3), 1.37 (s, 18H, 2×*t*-butyl).

^{13}C NMR (75 MHz, $CDCl_3$): δ 162.82, 151.47, 135.04, 134.51, 131.94, 130.81, 125.77, 123.54, 123.30, 34.52, 31.40, 18.18.

HRMS-NSI (m/z): $[M+H]^+$ Calcd for $C_{58}H_{46}N_2O_4$, 834.3458; Found 834.3429.

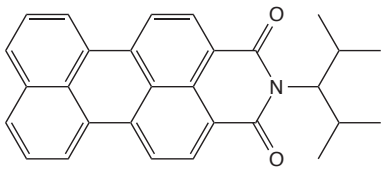
2-(2,4-Dimethylpentan-3-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (36):



A mixture containing 1,8-naphthalic anhydride **(35)** (0.3 g, 1.5 mmol) and 2,4-dimethyl-3-pentanone **(26)**, 0.2 g, (1.74 mmol) in 4 g of imidazole (58 mmol) was heated to 150 °C for 4.5 h under argon. The resultant mixture was poured on ice and 100 ml 2M HCl was added. The product was extracted with DCM and the product isolated by evaporation of DCM.The solid was dried and purified by chromatography on silica gel using DCM/MeOH(99:1) as eluent to give **(36)** (0.26 g, 58.8%) as a colorless solid.

^{1}H NMR (360 MHz, $CDCl_3$): δ 8.51 (dxd, 2H, aromatic proton), 8.16 (d, 2H aromatic proton), 7.68 (dxd, 2H, aromatic proton), 4.66 (dxd, 1H, NCH), 2.61 (o, 2H, isopropyl) 1.02 (d, 6H, isopropyl) 0.834 (d, 6H, isopropyl).

2-(2,4-Dimethylpentan-3-yl)-1H-benzo[10,5]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione (37):

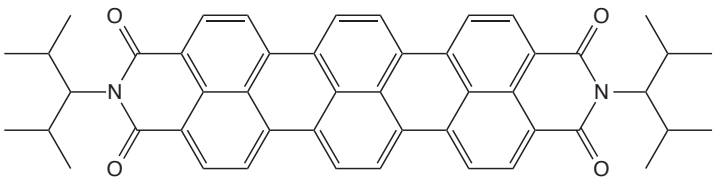


A mixture of 2.75 g (7.01 mmol) **(1)**, 0.47 g (4.10 mmol) **(27)**, 1 g (5.45 mmol) of $Zn(OAc)_2$, 6 ml of H_2O and 19 g (205.6 mmol) of imidazole was vigorously stirred under an argon atmosphere at 190 ℃ for 24 h. The reaction was quenched by slow adding of 75 ml (2 M) HCl. The solid was filtered out and dried in an oven. The raw product was purified by column chromatograph, which gave 0.12 g bright orange solid, the yield was 52%.

^{1}H NMR (360 MHz. $CDCl_3$): δ 8.47-8.52 (m, J = 7 Hz, 2H), 8.24-8.28 (t, J = 7 Hz, 4H), 7.78-7.80 (d, J = 8 Hz, 2H), 7.50-7.54 (t, J = 8 Hz, 2H), 4.74-4.79 (t, J = 8 Hz, 1H), 2.68-2.78 (m, J = 7 Hz, 2H), 1.12-1.14 (d, J = 7 Hz, 6H), 0.94-0.96 (d, J = 7 Hz, 6H).

MS (m/z): [M^+] Calcd for $C_{29}H_{25}NO_2$, 419.52; Found 419.24.

***N,N'*-Bis(2-(2,4-dimethylpentan-3-yl)-3,4,11,12-terrylenetetracarboxylic diimide (dmpa-XT):**



Compound **(36)** (0.1 g, 0.34 mmol) and compound **(37)** (0.17 g, 0.41 mmol) were dissolved in toluene (1.2 mL), t-BuONa (0.17 g, 1.52 mmol) and DBN (0.25 g, 2.03 mmol) were dissolved in toluene (1 mL), heated to 130 ^{0}C for 15 min. The mixture of reactants were added to the mixture of catalyst drop wise then heated to 130 ^{0}C for 30 min. Then another 0.1 g **(36)**, dissolved in toluene (1 mL) was again added drop wise. All the treatments were carried out under an argon atmosphere. The mixture was stirred vigorously for 3 hours. The reaction was quenched by adding HCl (24 ml, 2 M). The product was extracted with chloroform, and purified by column chromatography, then crystallized in a mixture of DCM and hexane. The final product was a blue solid. The yield was 8%.

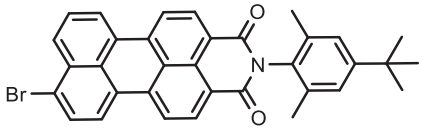
^{1}H NMR (500 MHz. $CDCl_3$): δ 8.57-8.62 (m, J = 3 Hz, 4H), 8.36-8.39 (m, J = 3 Hz, 8H), 4.78-4.81 (t, J = 8 Hz, 2H), 2.72-2.79 (m, J = 5 Hz, 4H), 1.15-1.16 (d, J = 7 Hz, 12H), 0.97-0.99 (d, J = 7 Hz, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): 165.37, 164.29, 135.36, 135.31, 131.89, 131.17, 130.80, 129.68, 128.48, 125.81, 123.99, 123.96, 122.34, 121.71, 121.29, 65.05, 29.21, 21.90, 20.73.

HRMS (m/z): $[M]^-$ Calcd for $C_{48}H_{42}N_2O_4$, 710.30; Found 710.3137.

SI1.2.2.4 Synthesis of QDI

***N*-(4-*tert*-Butyl-2,6-dimethylphenyl)-9-bromoperylene-3,4-dicarboximide (33):**



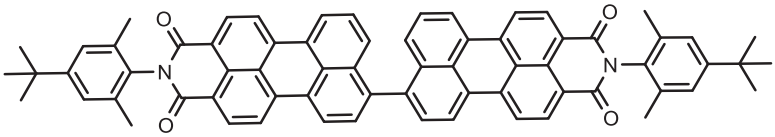
Compound **(32)** (800 mg, 1.66 mmol) was partially dissolved in chlorobenzene (100 ml), and bromine (1.2 g, 7.5 mmol) dissolved in chlorobenzene (50 ml) was added dropwise. Upon completion of addition the reaction mixture was heated to 50° C for 4 h. The solvent was removed in vacuum giving **(33)** as a dark red solid (940 mg, quantitative). The compound was

used directly in the next step. A small fraction was further purified for analysis by dissolving in a minimum amount of $CHCl_3$, adding an excess of MeOH, filtering and drying the dark red precipitate **(33)** in vacuum.

^{1}H NMR- and ^{13}C NMR-spectrum was not measured.

HRMS-NSI (m/z): $[M+H]^+$ Calcd for $C_{34}H_{27}NO_2$, 560.1220; Found 560.1233.

***N,N'*-Bis(4-*tert*-Butyl-2,6-dimethylphenyl)-9,9'-biperylene-3,4,3',4'-bis(dicarboximide) (34):**



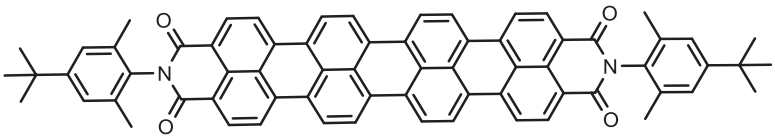
A flame-dried Schlenk was charged with 2,2'-bipyridyl (83.5 mg, 0.53 mmol), $Ni(cod)_2$ (147 mg, 0.53 mmol), cod (70.0 mg, 0.64 mmol), dry DMF (25 ml) and the mixture was degassed with 5 vacuum-argon backfill cycles. Compound **(33)** (300 mg, 0.53 mmol) was added and the mixture was heated to 70 °C for 48 h under argon. The mixture was cooled, poured onto $HCl_{aq.}$ (1 M, 400 ml). The precipitate was filtered, dried in air and chromatographed on silica gel using DCM as eluent to give **(34)** (137 mg, 53%) as a bright red solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.75-8.54 (m, 12H, biperylene), 7.76 (d, *J* = 7.6 Hz, 2H), 7.64 – 7.52 (m, 4H, biperylene), 7.24 (s, 4H, phenyl), 2.18 (s, 12H, 4×CH_3), 1.38 (s, 18H, 2×*t*-butyl).

^{13}C NMR (75 MHz, $CDCl_3$): δ 163.35, 151.19, 140.57, 137.46, 137.26, 134.60, 133.73, 132.04, 131.25, 130.58, 129.67, 129.61, 129.26, 128.34, 127.48, 127.00, 125.71, 124.09, 123.41, 121.45, 121.39, 120.63, 120.48, 34.51, 31.44, 18.23.

HRMS-NSI (m/z): $[M]^+$ Calcd for $C_{68}H_{52}N_2O_4$, 960.3927; Found 960.3913.

***N,N'*-Bis(4-*tert*-Butyl-2,6-dimethylphenyl)-3,4,13,14-quaterrylenetetracarboxylic diimide (tb-DXQ):**

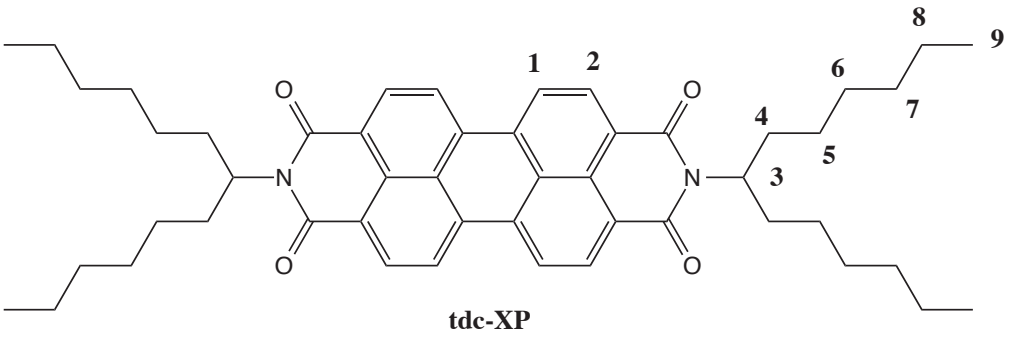


A mixture of compound **(34)** (130 mg, 0.13 mmol), KOH (≥85% pellets, 14 g), D-glucose (1 g) in absolute EtOH (20 ml) was heated to 120 °C under argon for 3 h. The dark purple mixture was then poured onto ice/$HCl_{aq.}$ (1 M, 100 ml) and 2 M $HCl_{aq.}$ was added until the pH was slightly acidic (universal indicator paper). The precipitate was filtered, dried in an oven at 80 °C overnight, and chromatographed on silica gel using DCM/MeOH (1:0→95:5, stepwise gradient) as eluent to give **tb-DXQ** (110 mg, 85%) as a dark green solid. Due to low solubility of the compound a ^{13}C-NMR spectrum could not be recorded.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.70 (d, *J* = 8.1 Hz, 4H, H-2, 5, 12, 15), 8.60-8.49 (m, 12H, quaterrylene), 7.26 (s, 4H, phenyl + $CHCl_3$), 2.20 (s, 12H, 4×CH_3), 1.38 (s, 18H, 2×*t*-butyl).

HRMS-NSI (m/z): $[M+H]^+$ Calcd for $C_{58}H_{46}N_2O_4$, 834.3458; Found 834.3429.

SI1.2.3 NMR and HRMS



tdc-XP

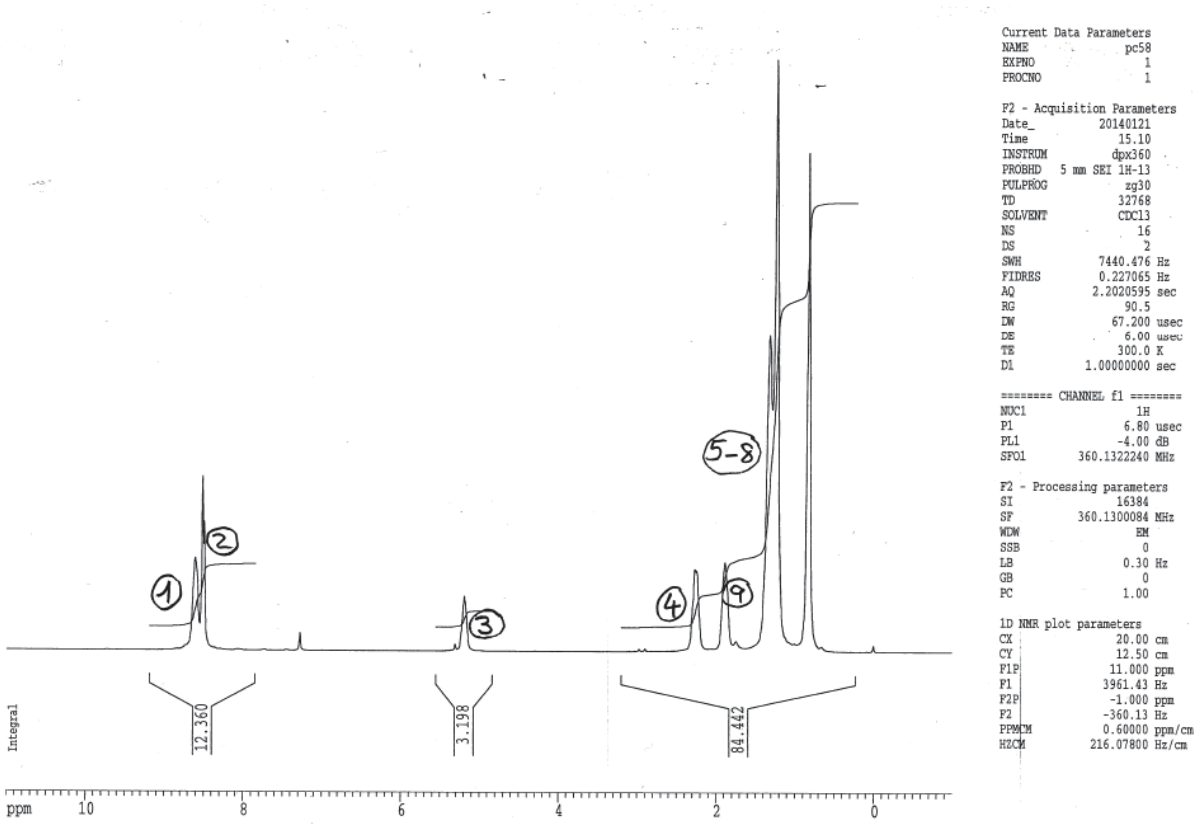


Figure SI1a. ^{1}H NMR spectrum of **tdc-XP** in $CDCl_3$.

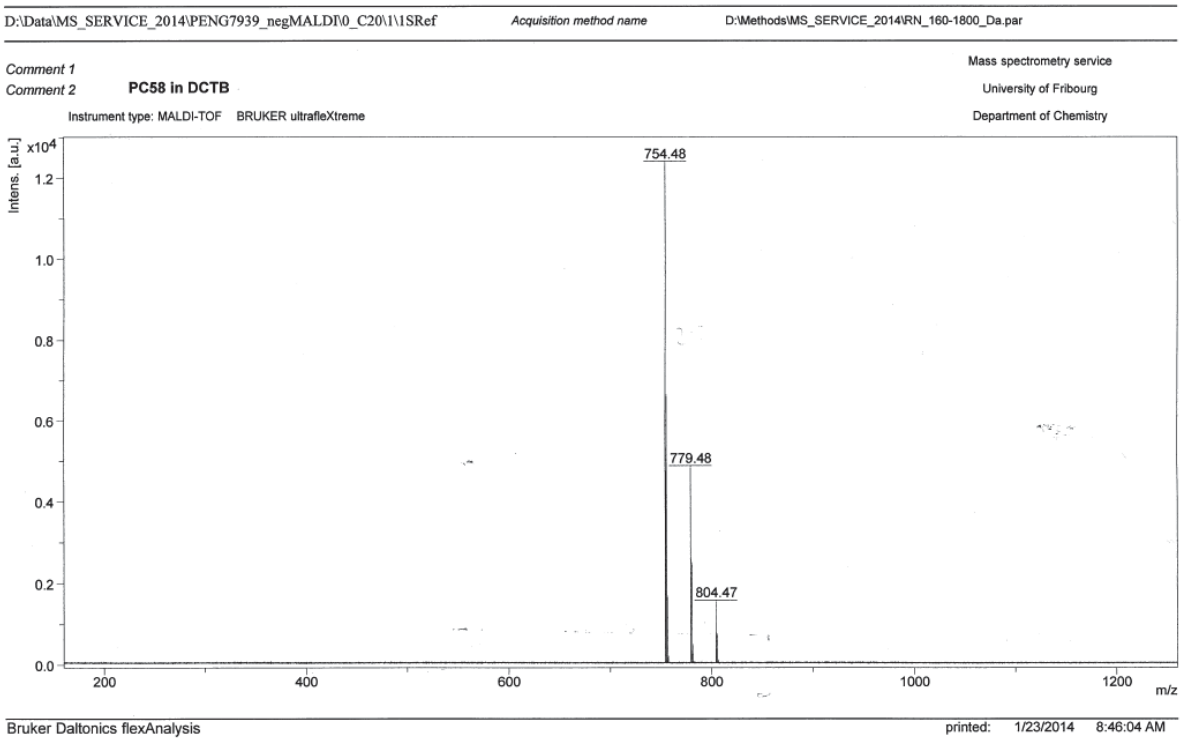


Figure SI1b. MS spectrum of **tdc-XP**.

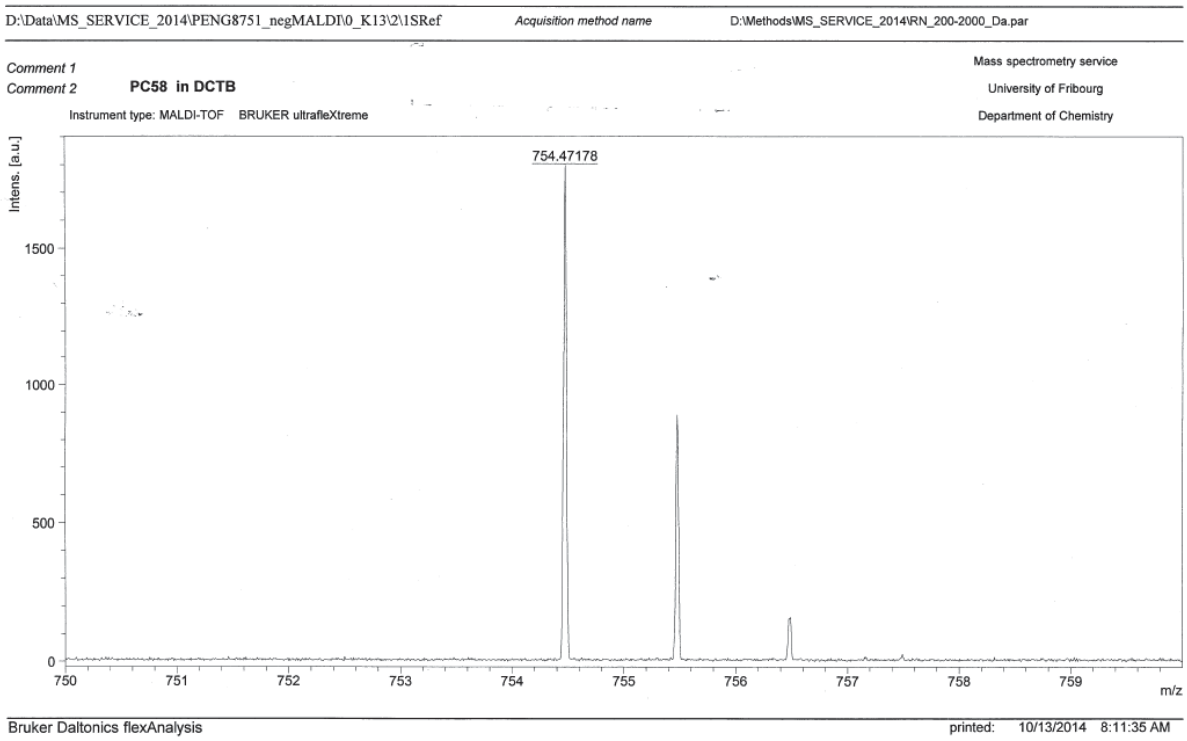
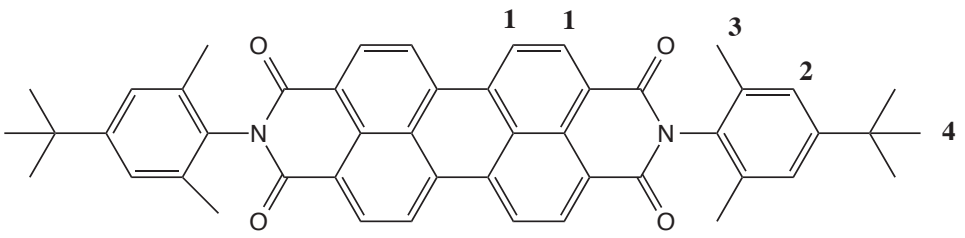


Figure SI1c. HRMS spectrum of **tdc-XP**.



tb-DXP

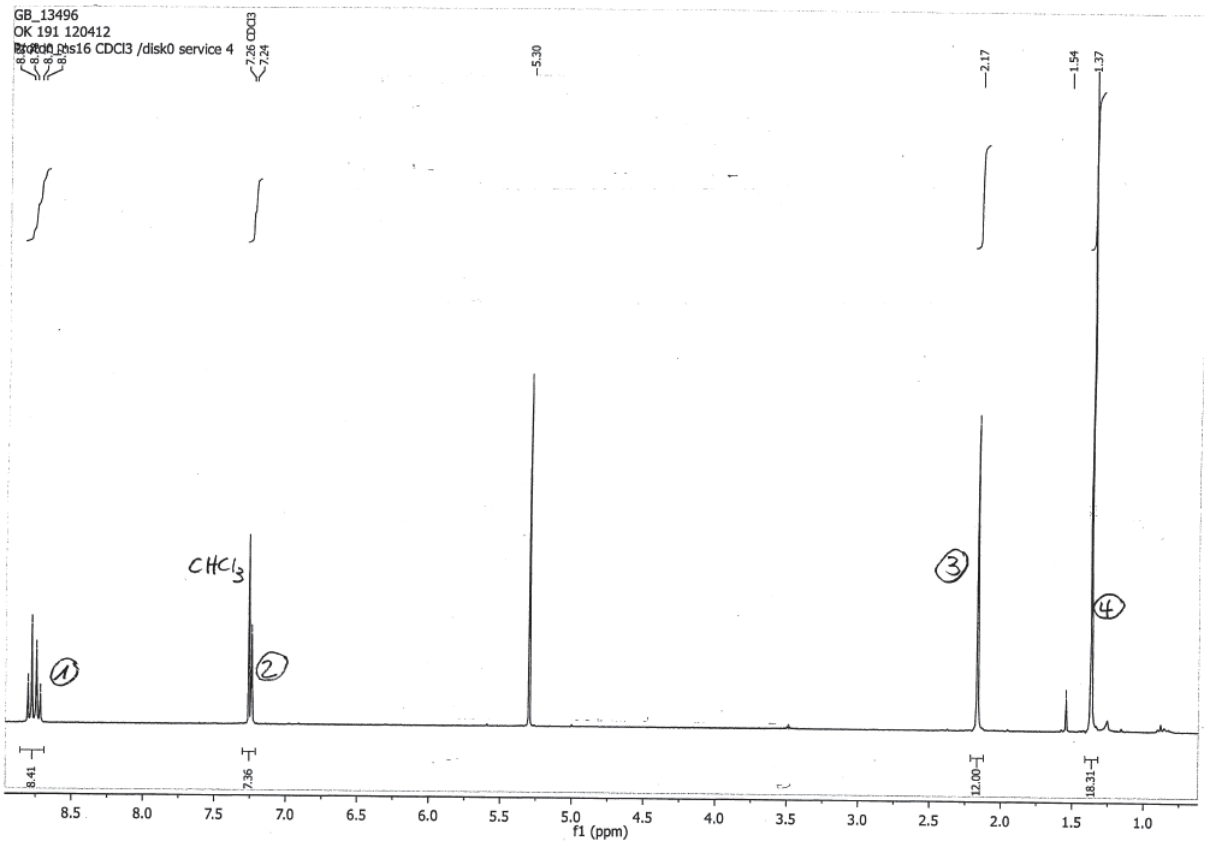


Figure SI2a. ^{1}H NMR spectrum of **tb-DXP** in $CDCl_3$.

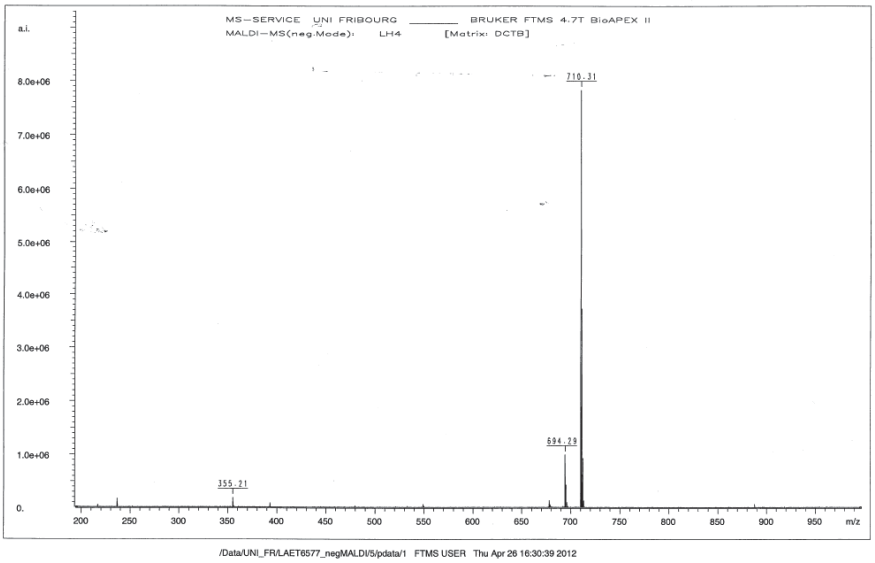


Figure SI2b. MS spectrum of **tb-DXP**.

Ion mass = 710.3152780

Charge = -1

#	C	H	N	O	mass	DBE	error
*** Mass Analysis for mass 710.3152780							
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2	46	40	5	3	710.3136638	29.5	1.614e-03
3	45	44	1	7	710.3123264	24.5	2.952e-03
4	39	44	5	8	710.3195370	20.5	4.259e-03
5	43	42	4	6	710.3109837	25.0	4.294e-03
6	41	46	2	9	710.3208797	20.0	5.602e-03
7	40	44	3	9	710.3083036	20.5	6.974e-03
8	44	44	3	6	710.3235597	24.5	8.282e-03
9	50	38	4	1	710.3051104	34.0	1.017e-02
10	47	42	4	3	710.3262398	29.0	1.096e-02

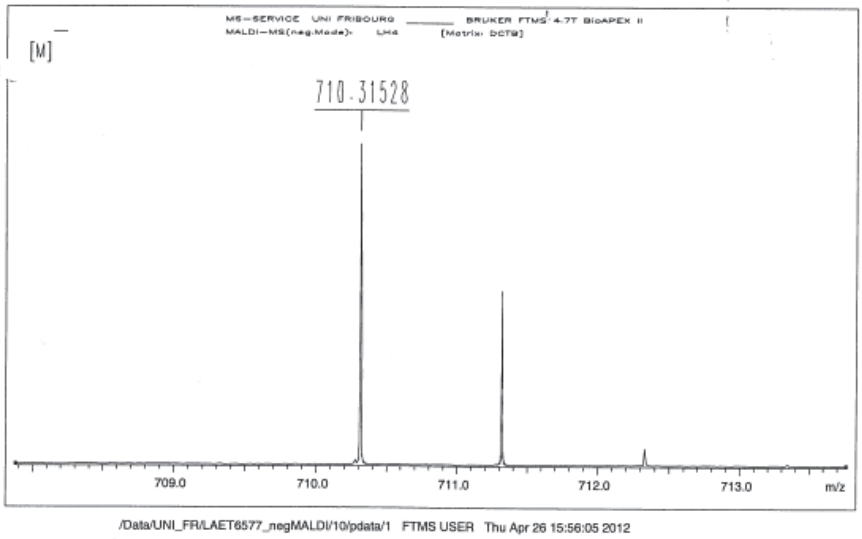
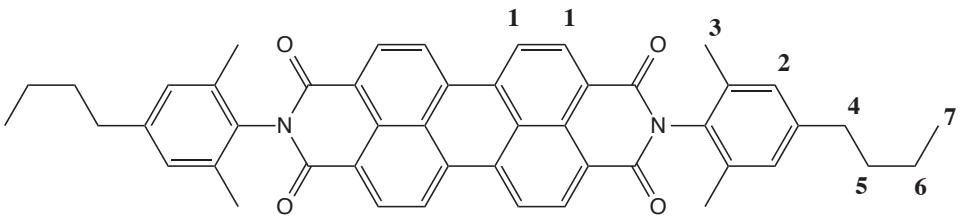


Figure SI2c. HRMS spectrum of **tb-DXP**.



b-DXP

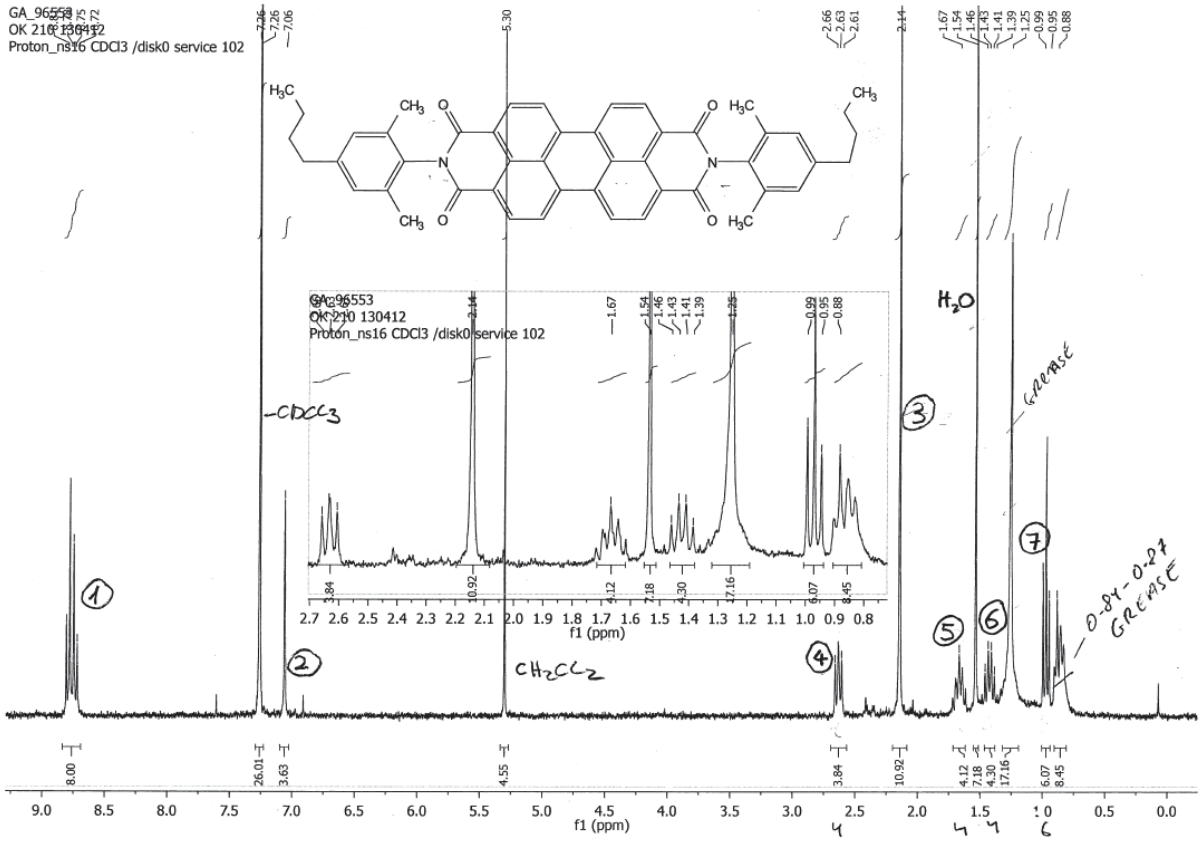


Figure SI3a. ^{1}H NMR spectrum of **b-DXP** in $CDCl_3$.

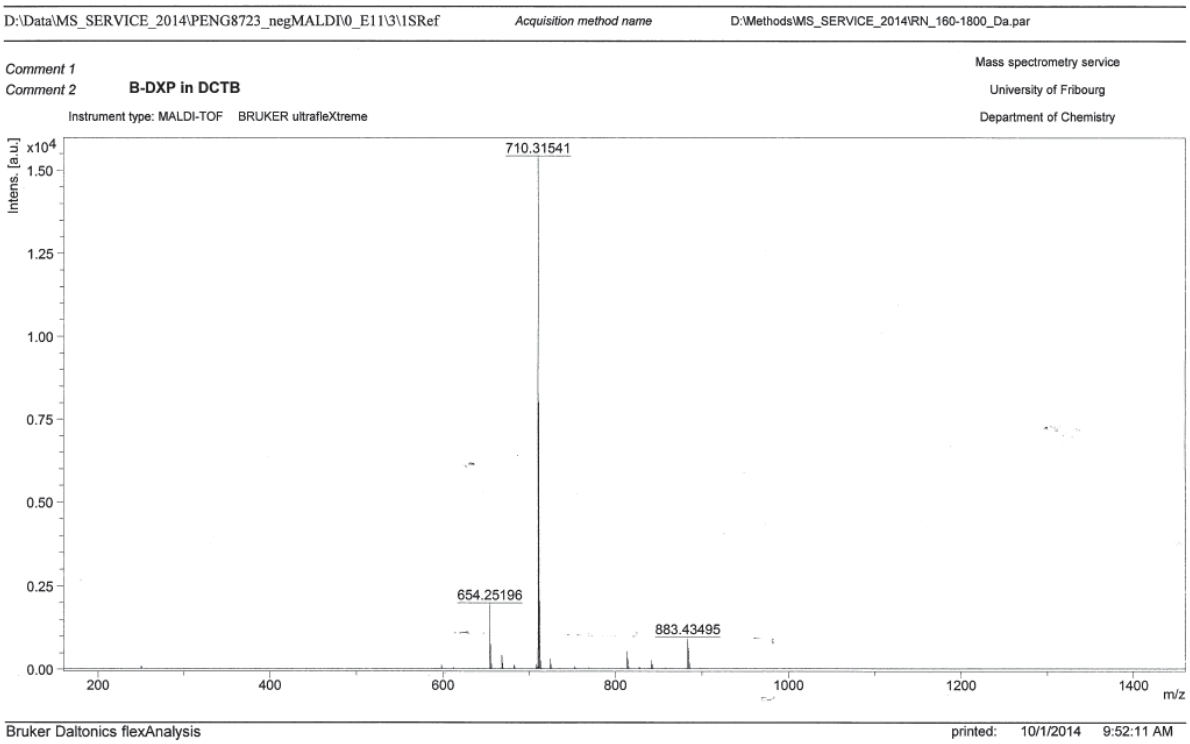


Figure SI3b. MS spectrum of **b-DXP**.

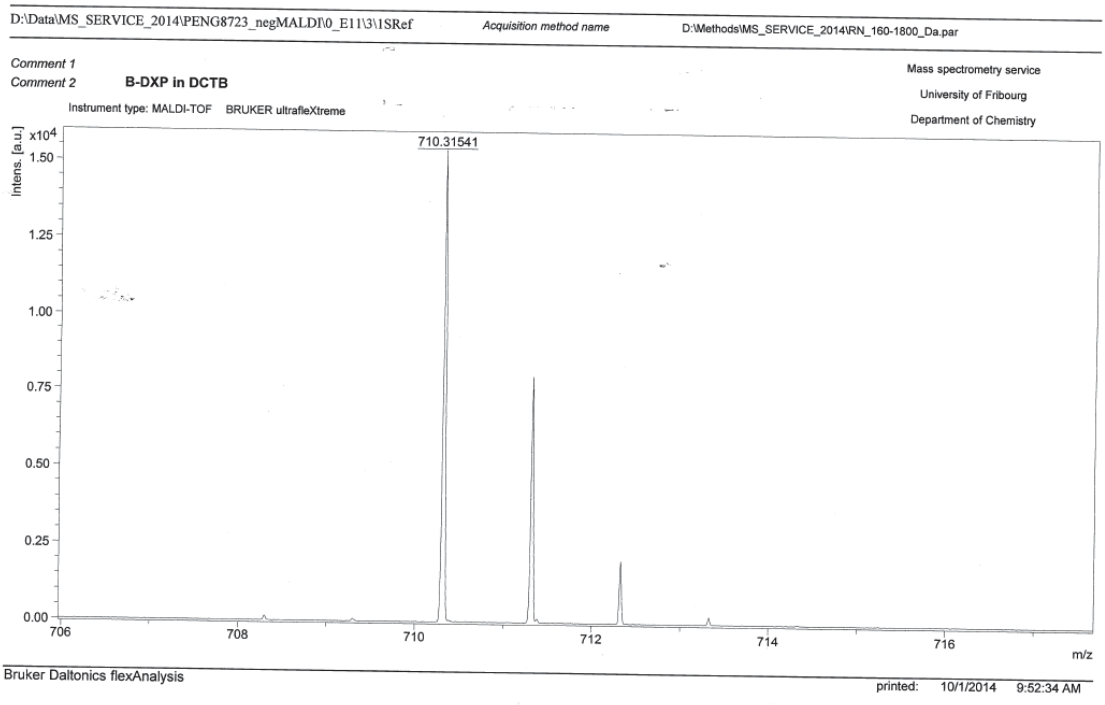
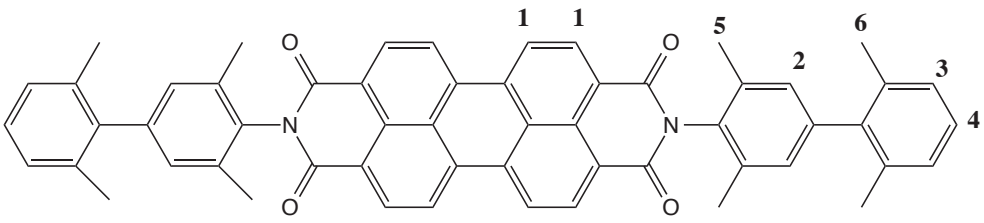


Figure SI3c. HRMS spectrum of **b-DXP**.



dmp-DXP

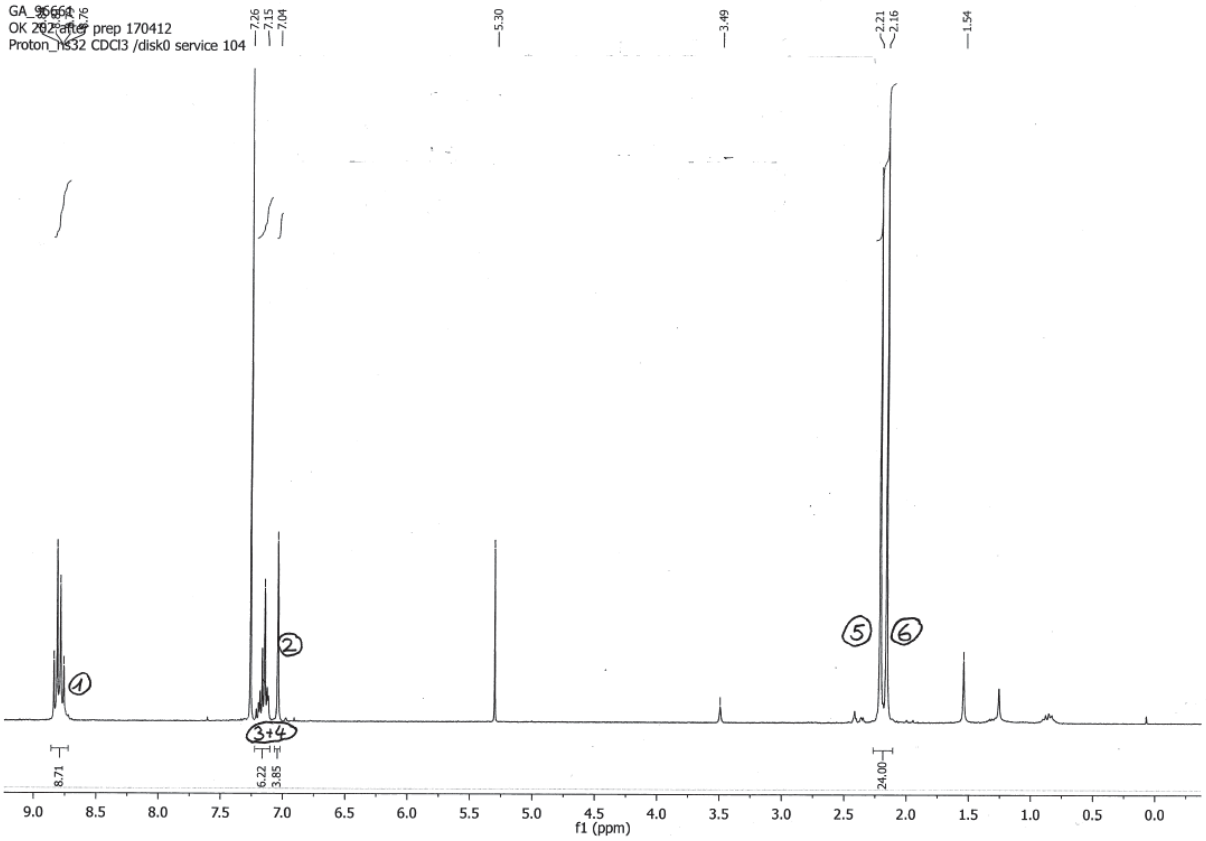


Figure SI4a. ^{1}H NMR spectrum of **dmp-DXP** in $CDCl_3$.

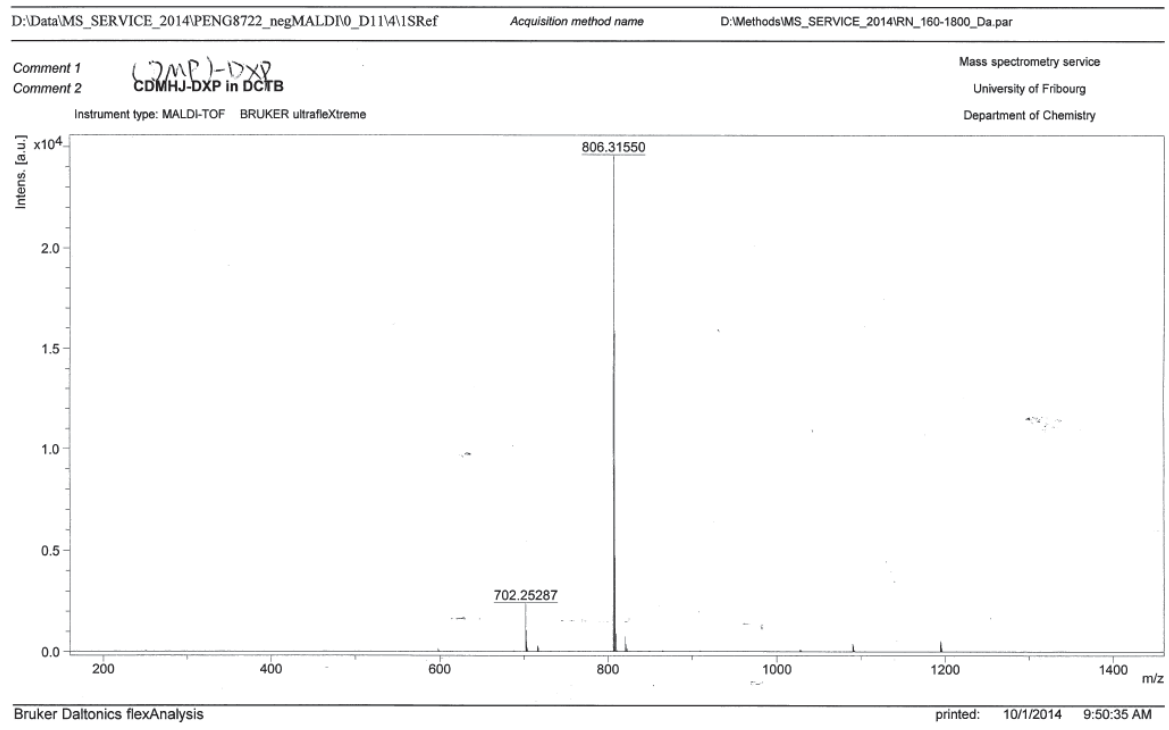


Figure SI4b. MS spectrum of **dmp-DXP**.

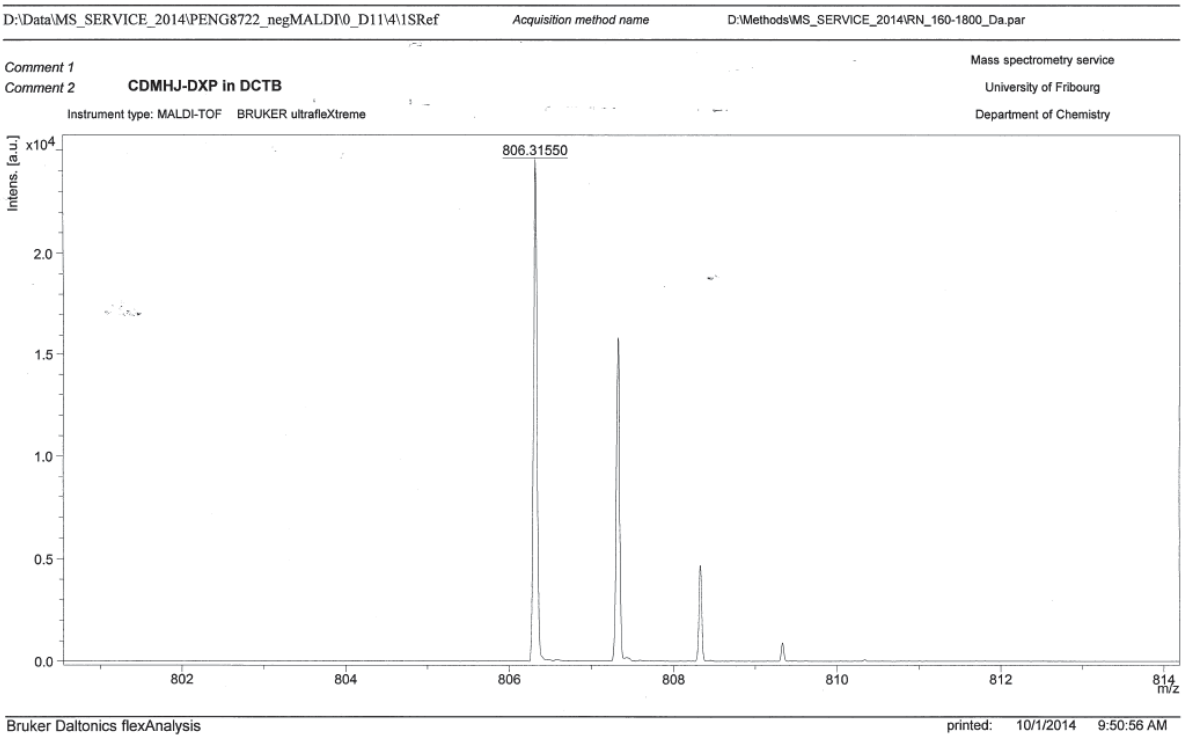
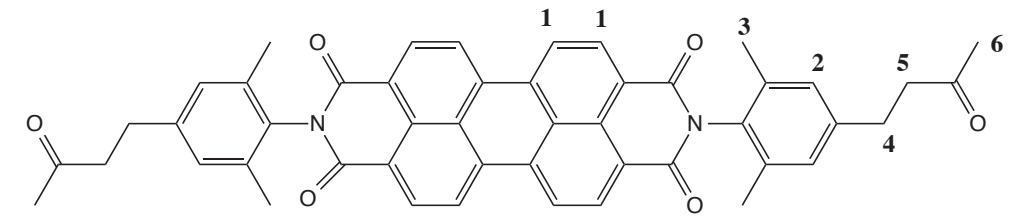


Figure SI4c. HRMS spectrum of **dmp-DXP**.



bone-DXP

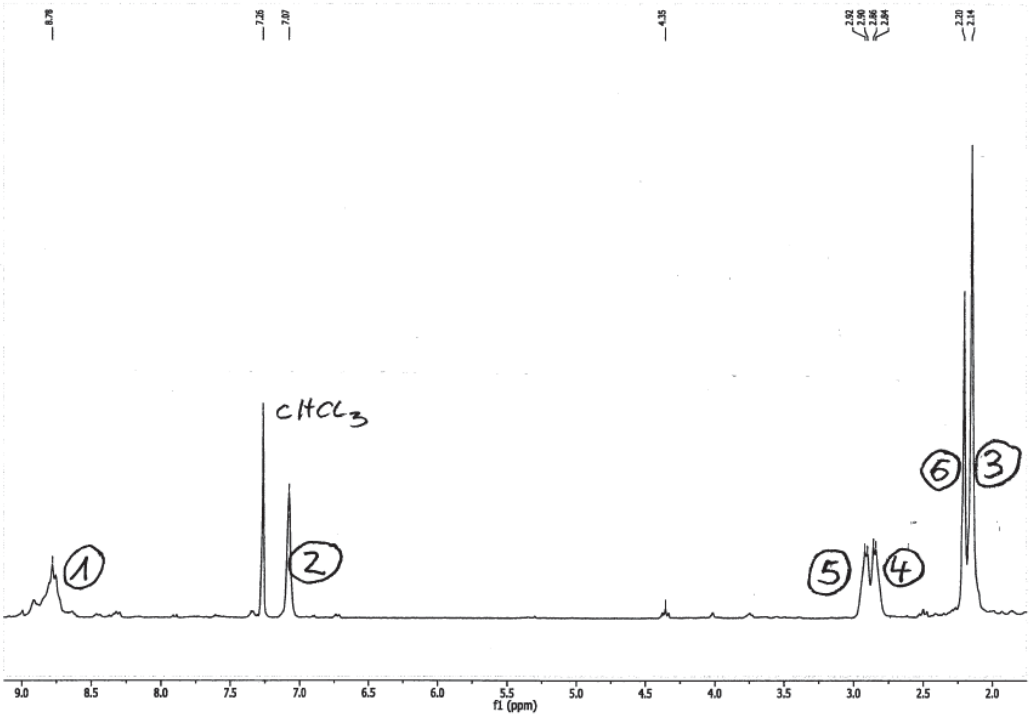


Figure SI5a. ^{1}H NMR spectrum of **bone-DXP** in $CDCl_3$.

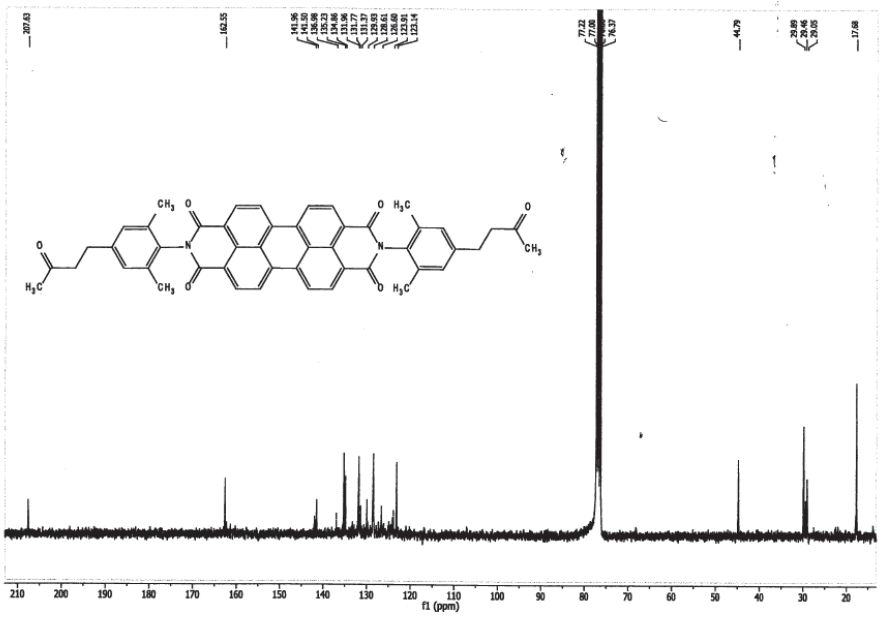
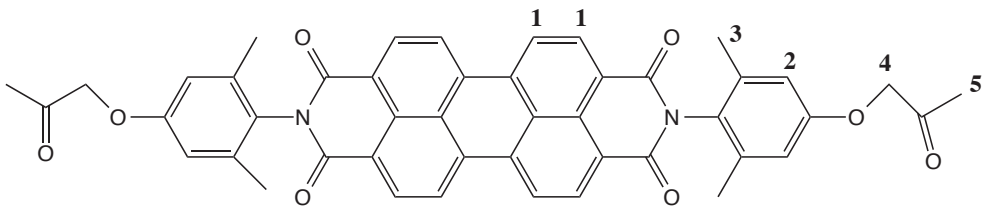


Figure SI5b. ^{13}C NMR spectrum of **bone-DXP** in $CDCl_3$.



o-bone-DXP

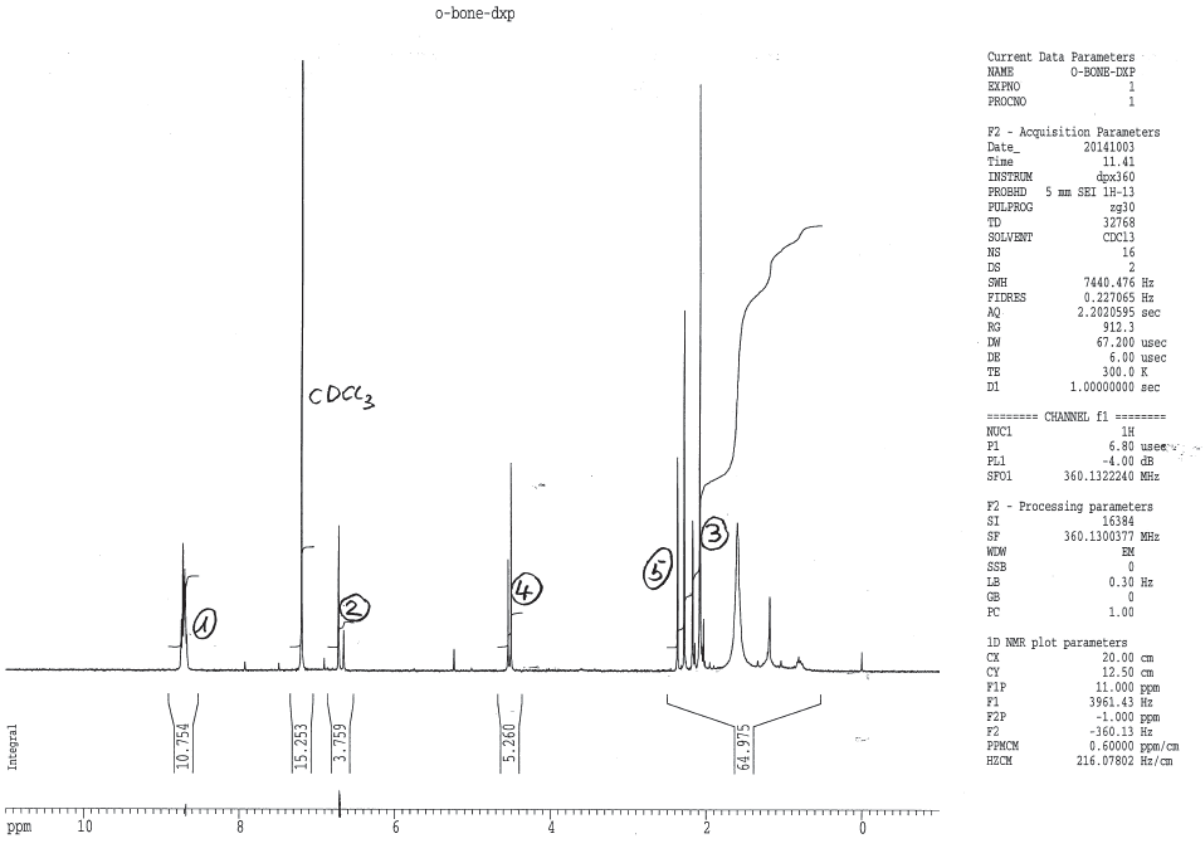


Figure SI6a. ^{1}H NMR spectrum of **o-bone-DXP** in $CDCl_3$.

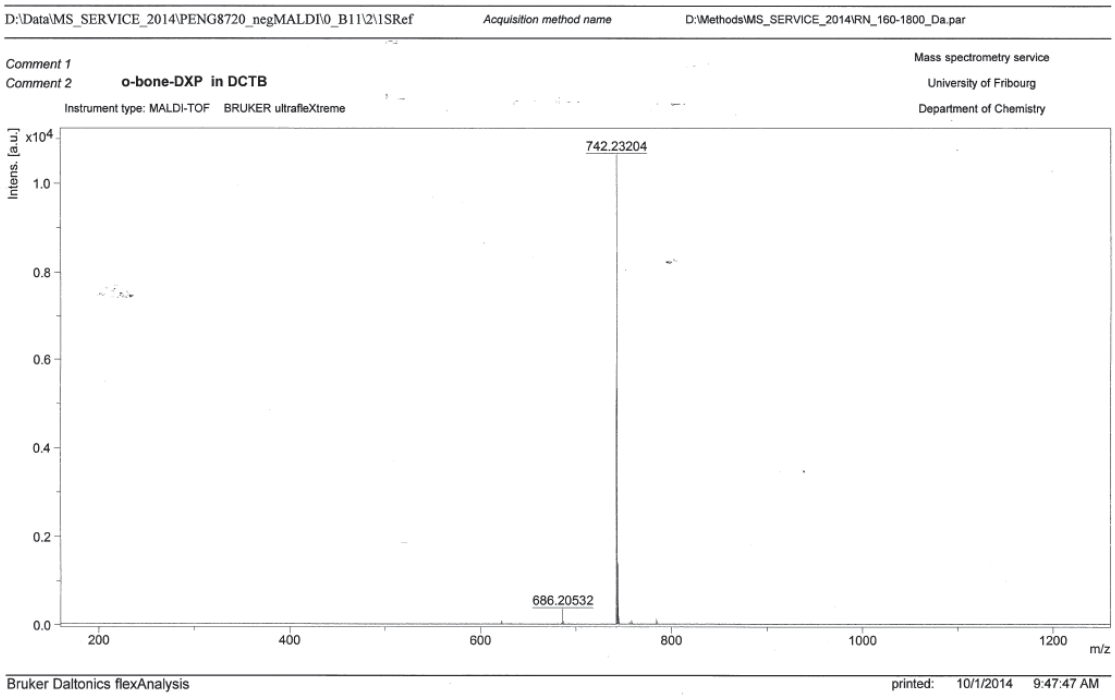


Figure SI6b. MS spectrum of **o-bone-DXP**.

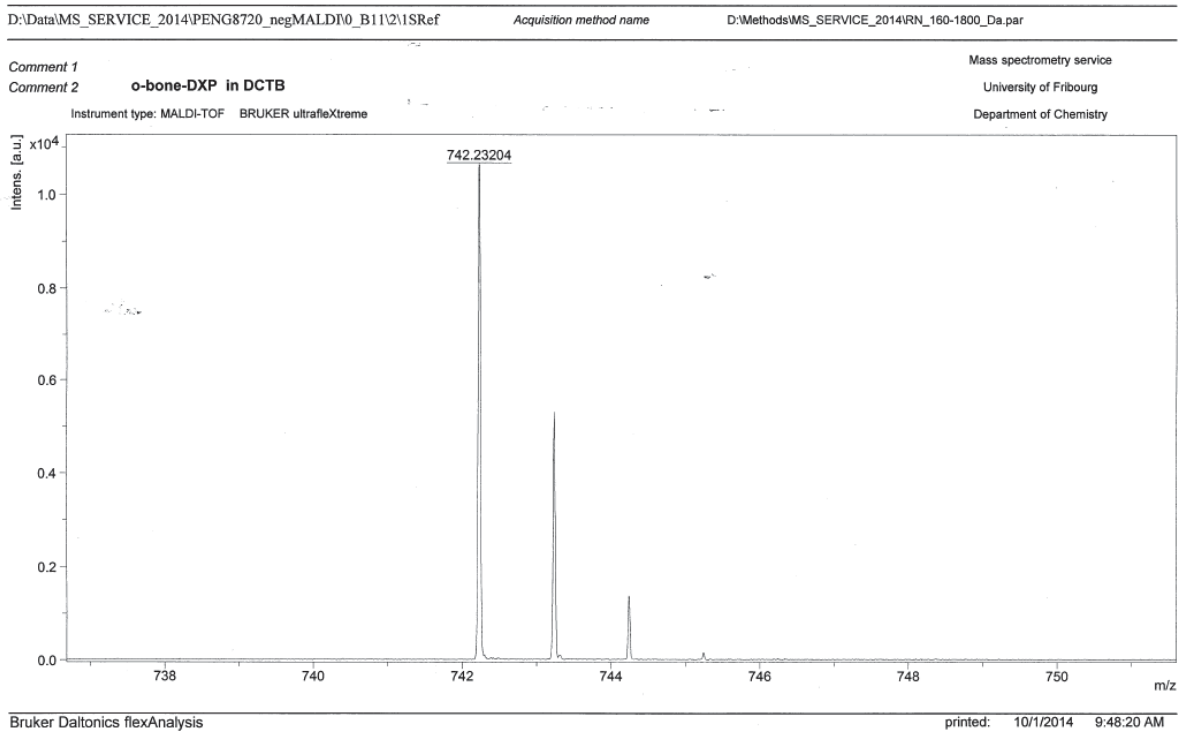
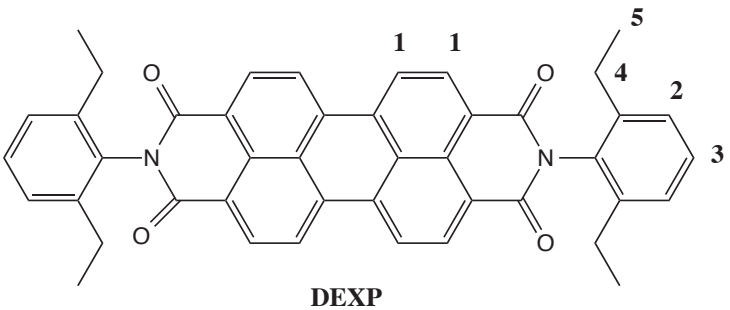


Figure SI6c. HRMS spectrum of **o-bone-DXP**.



DEXP

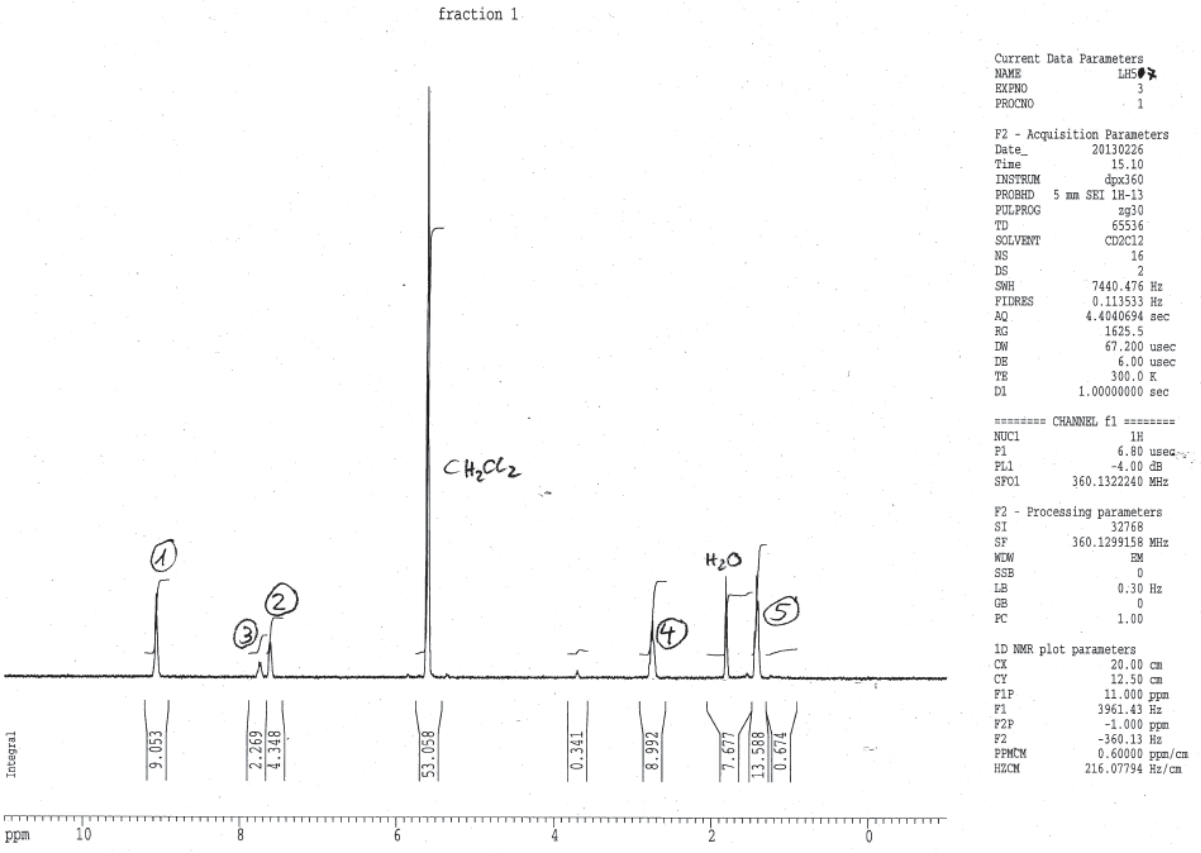


Figure SI7a. ^{1}H NMR spectrum of **DEXP** in $CDCl_3$.

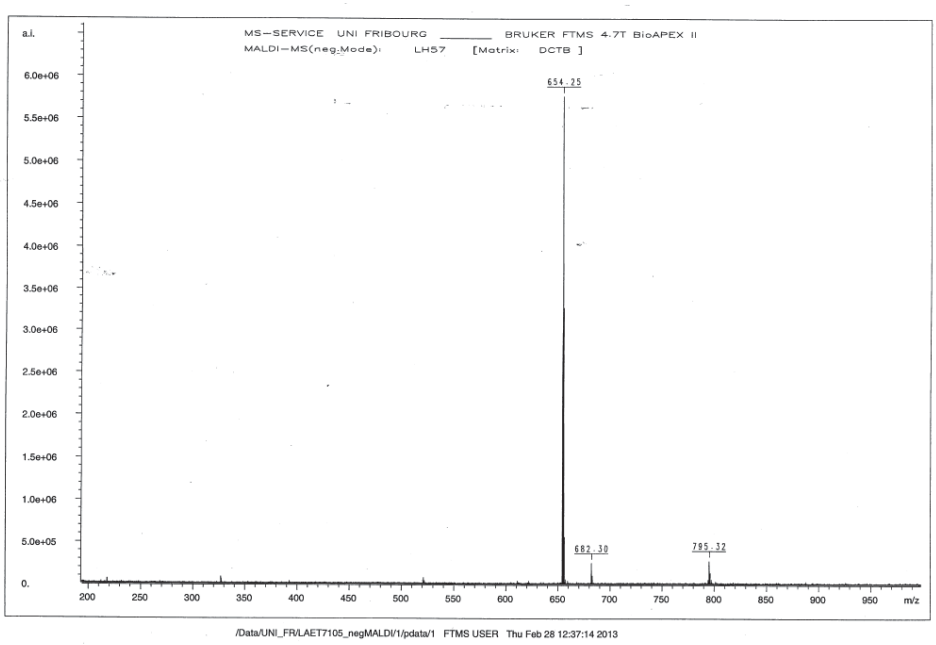


Figure SI7b. MS spectrum of **DEXP**.

	C	H	N	O	mass	DBE	error
*** Mass Analysis for mass 654.2520780							
1	44	34	2	4	654.2524062	29.0	3.282e-04
2	42	32	5	3	654.2510635	29.5	1.015e-03
3	41	36	1	7	654.2497261	24.5	2.352e-03
4	47	32	3	1	654.2550862	33.5	3.008e-03
5	39	34	4	6	654.2483834	25.0	3.695e-03
6	35	36	5	8	654.2569367	20.5	4.859e-03
7	37	38	2	9	654.2582794	20.0	6.201e-03
8	36	36	3	9	654.2457034	20.5	6.375e-03
9	48	32	1	2	654.2438529	33.5	8.225e-03
10	40	36	3	6	654.2609595	24.5	8.881e-03

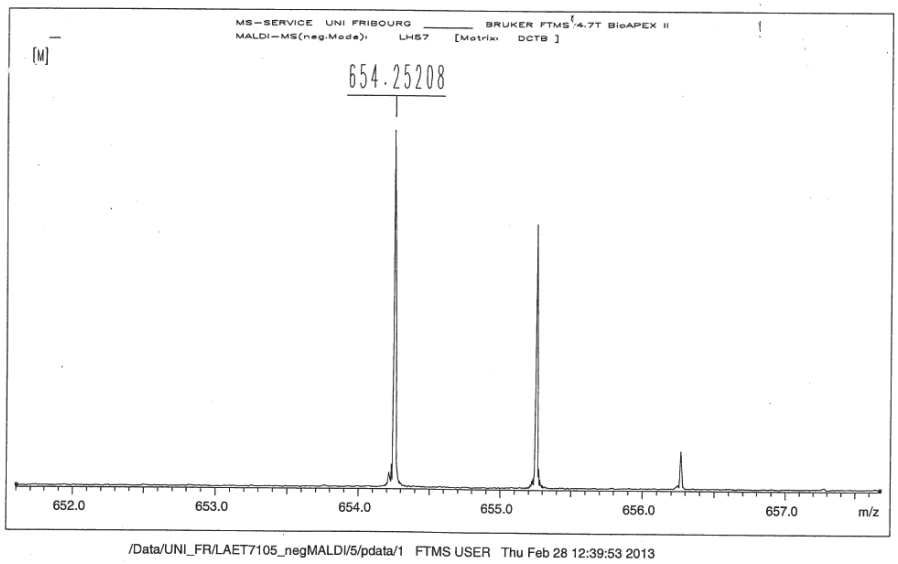
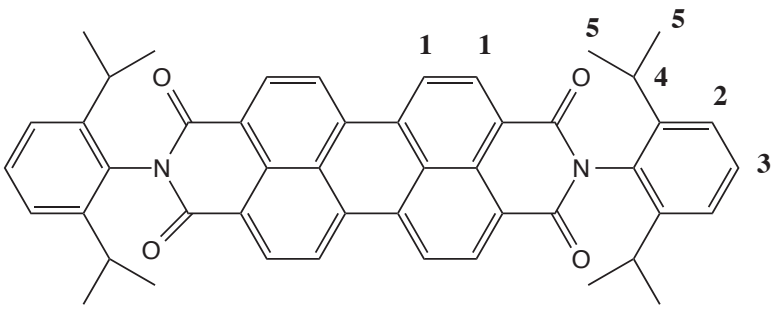


Figure SI7c. HRMS spectrum of **DEXP**.



DIXP

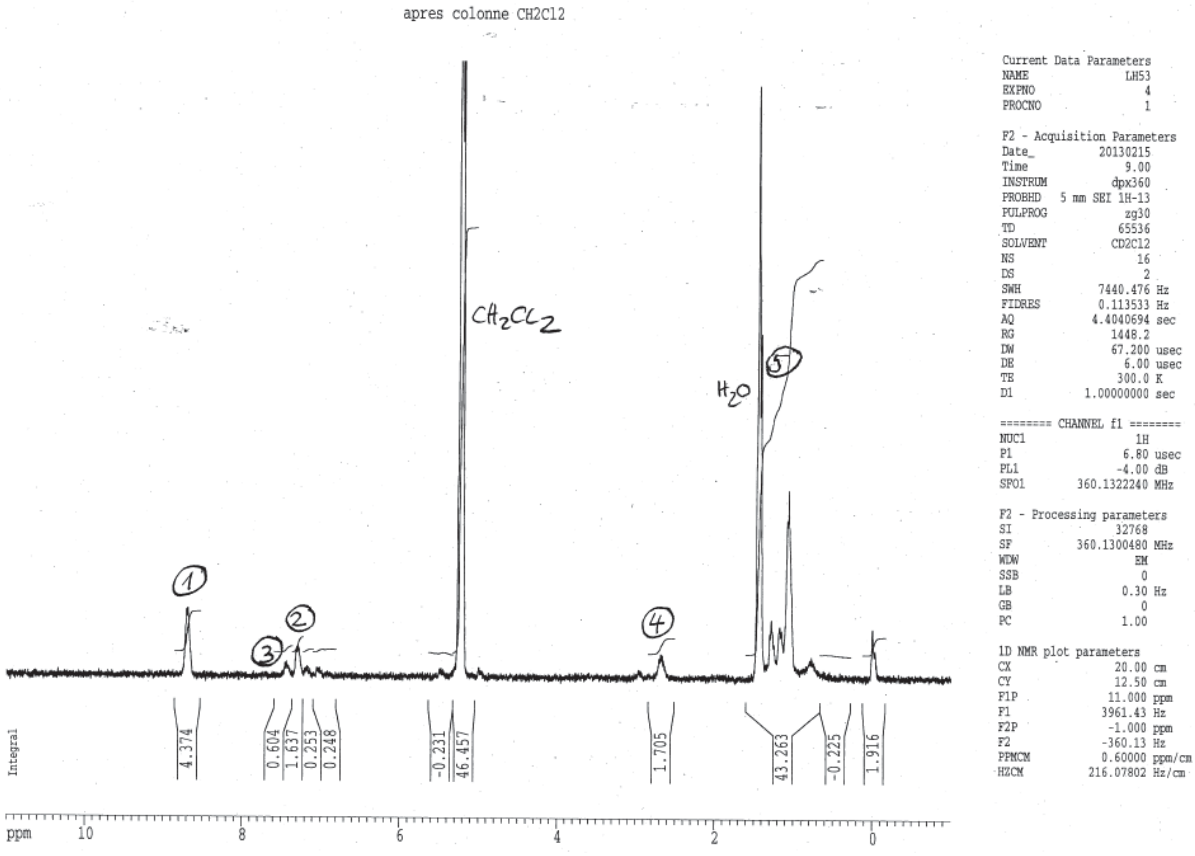


Figure SI8a. ^{1}H NMR spectrum of **DIXP** in CD_2Cl_2.

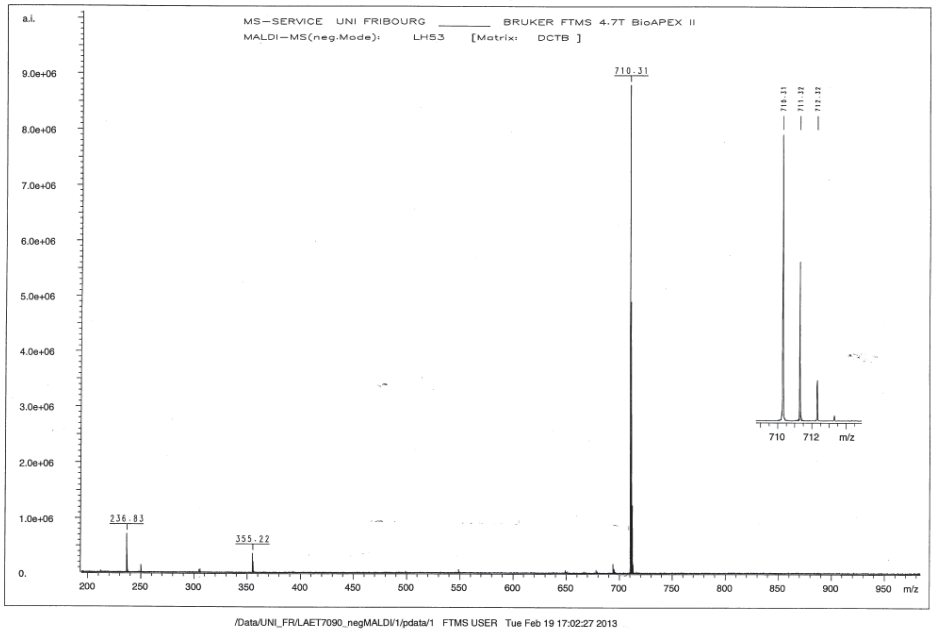


Figure SI8b. MS spectrum of **DIXP**.

#	C	H	N	O	mass	DBE	error
*** Mass Analysis for mass 710.3152290							
1	48	42	2	4	710.3150064	29.0	2.226e-04
2	46	40	5	3	710.3136638	29.5	1.565e-03
3	50	38	4	1	710.3051104	34.0	1.012e-02
4	47	42	4	3	710.3262398	29.0	1.101e-02
5	49	44	1	4	710.3275825	28.5	1.235e-02
6	47	40	3	4	710.3024304	29.5	1.280e-02
7	43	44	5	5	710.3347931	24.5	1.956e-02
8	49	36	5	1	710.2925344	34.5	2.269e-02
9	48	44	3	3	710.3388159	28.5	2.359e-02
10	48	40	1	5	710.2911970	29.5	2.403e-02

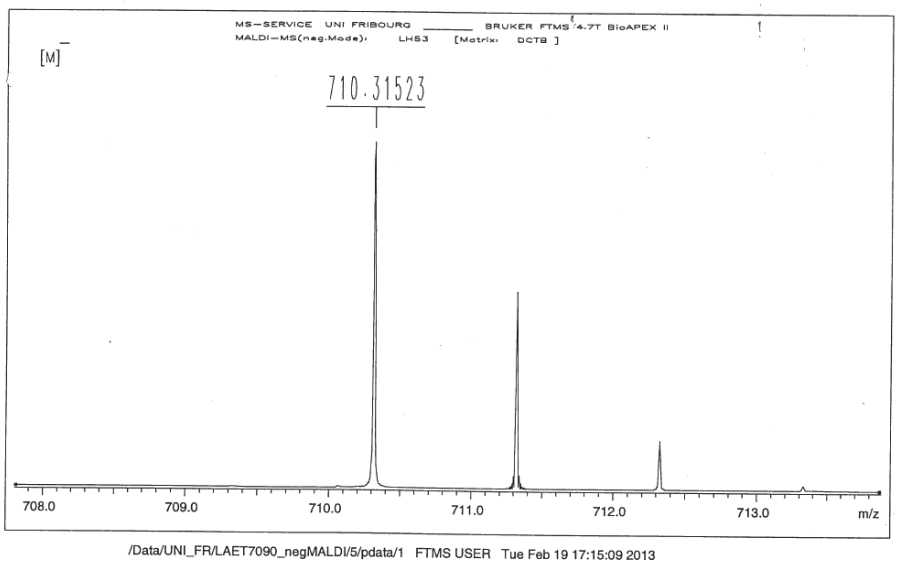
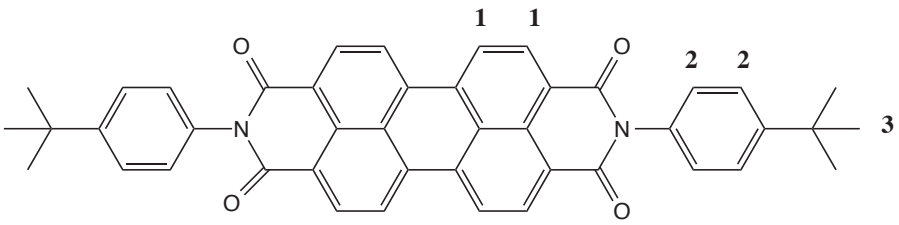


Figure SI8c. HRMS spectrum of **DIXP**.



tb-XP

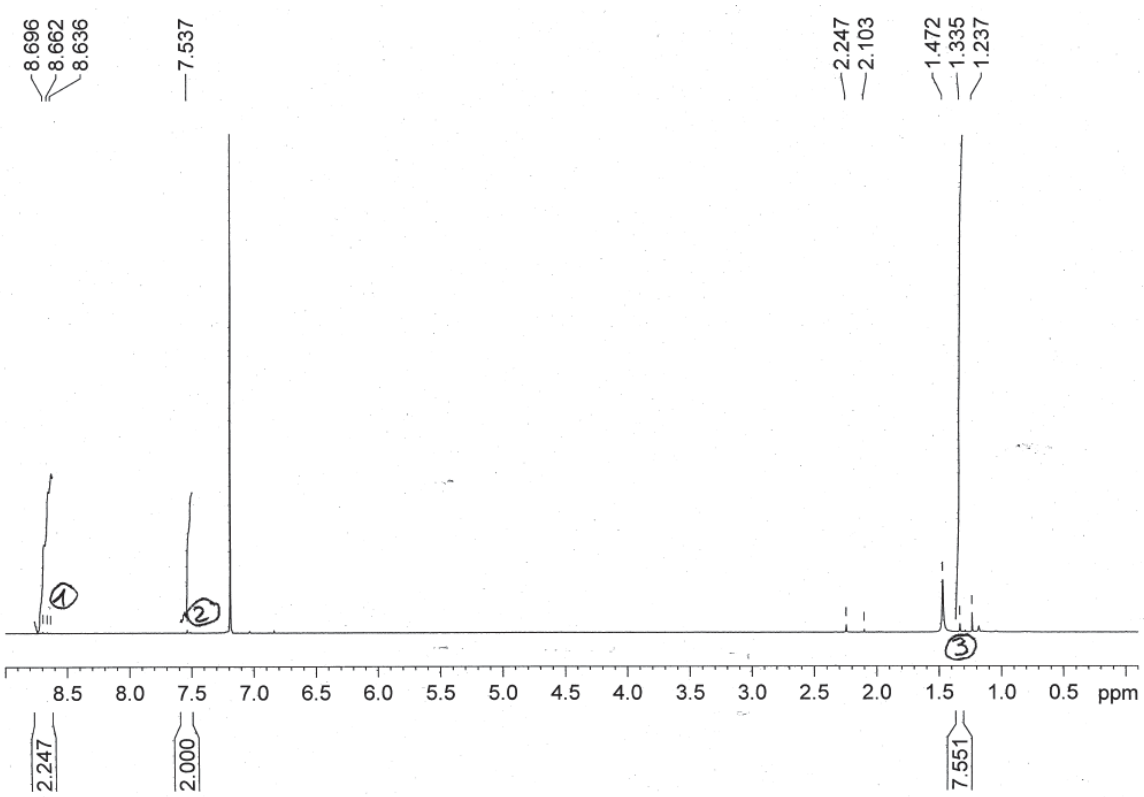


Figure SI9a. ^{1}H NMR spectrum of **tb-XP** in $CDCl_3$.

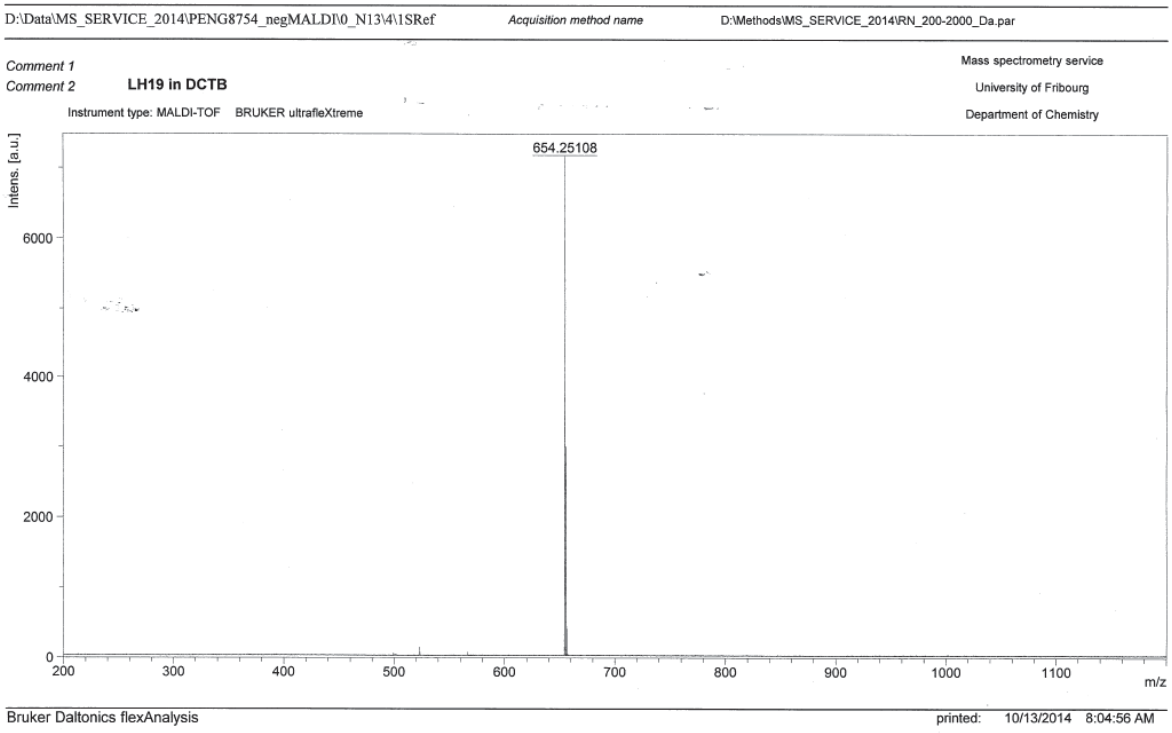


Figure SI9b. MS spectrum of **tb-XP**.

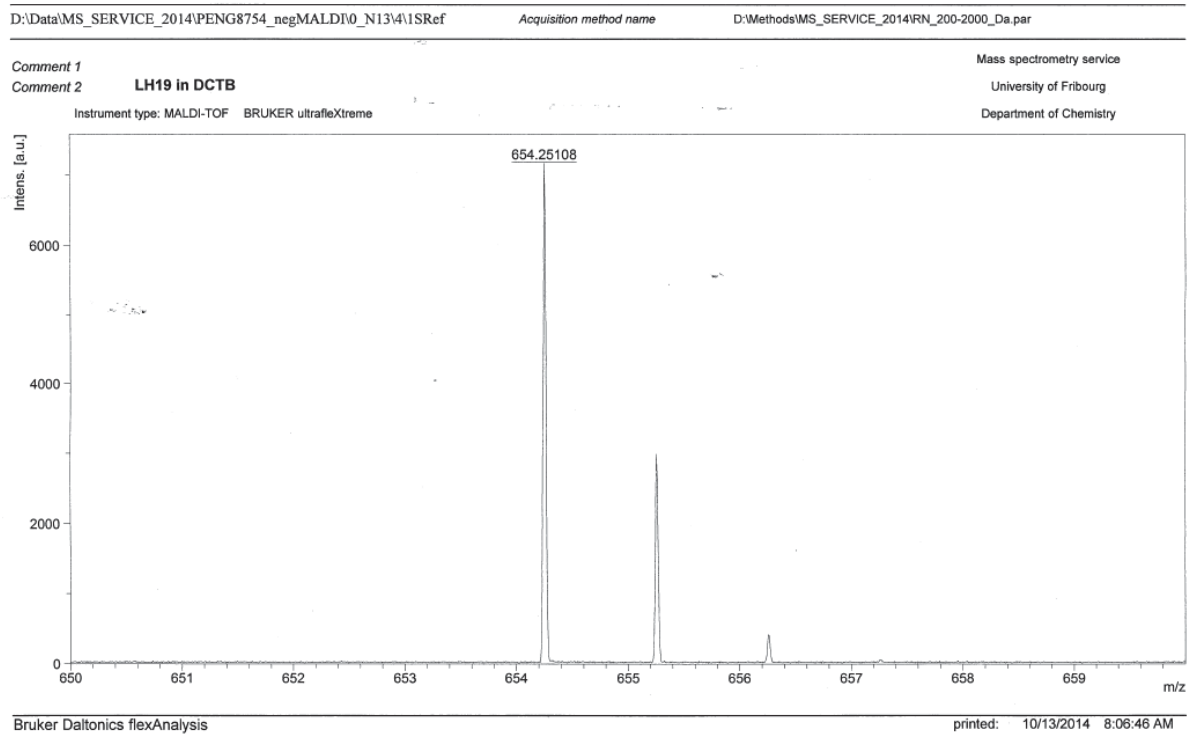
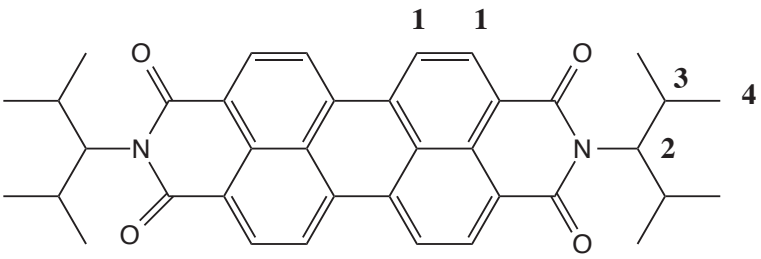


Figure SI9c. HRMS spectrum of **tb-XP**.



dmpa-XP

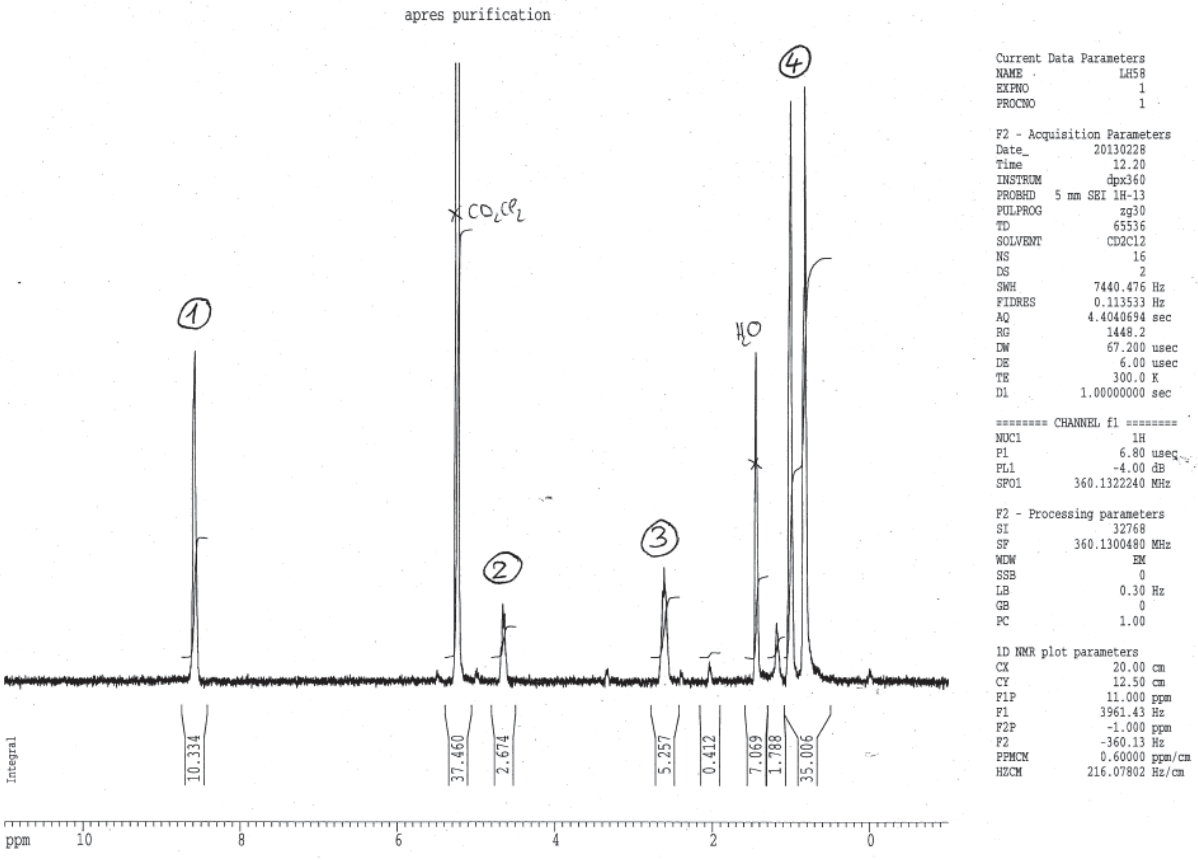


Figure SI10a. ^{1}H NMR spectrum of **dmpa-XP** in CD_2Cl_2.

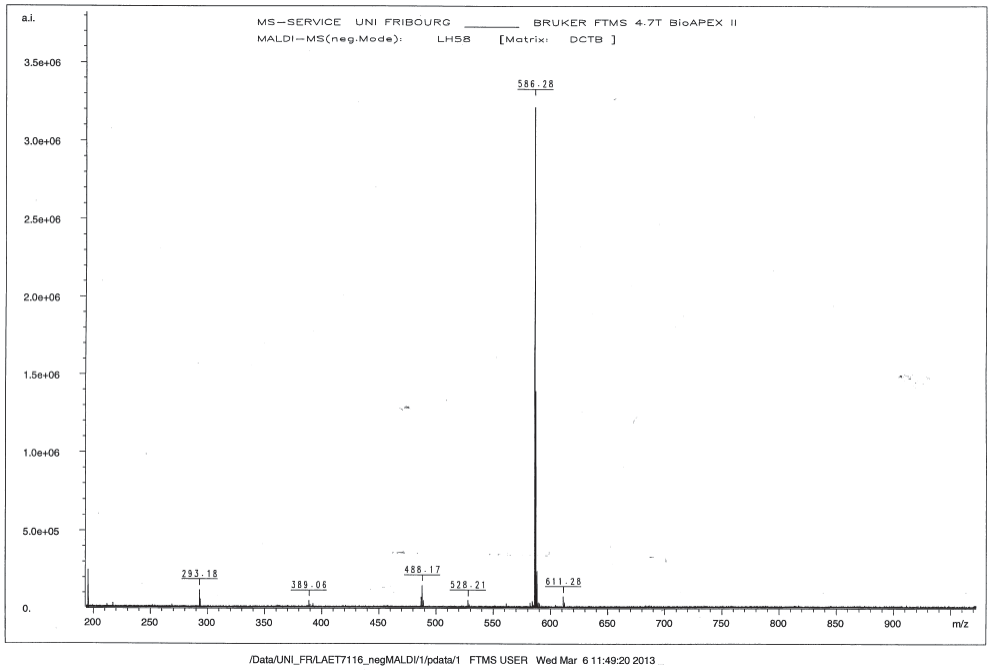


Figure SI10b. MS spectrum of **dmpa-XP**.

#	C	H	N	O	mass	DBE	error
*** Mass Analysis for mass 586.2838510							
1	38	38	2	4	586.2837063	21.0	1.447e-04
2	36	36	5	3	586.2823636	21.5	1.487e-03
3	41	36	3	1	586.2863864	25.5	2.535e-03
4	35	40	1	7	586.2810262	16.5	2.825e-03
5	33	38	4	6	586.2796836	17.0	4.167e-03
6	29	40	5	8	586.2882369	12.5	4.386e-03
7	31	42	2	9	586.2895795	12.0	5.729e-03
8	30	40	3	9	586.2770035	12.5	6.848e-03
9	34	40	3	6	586.2922596	16.5	8.409e-03
10	42	36	1	2	586.2751530	25.5	8.698e-03

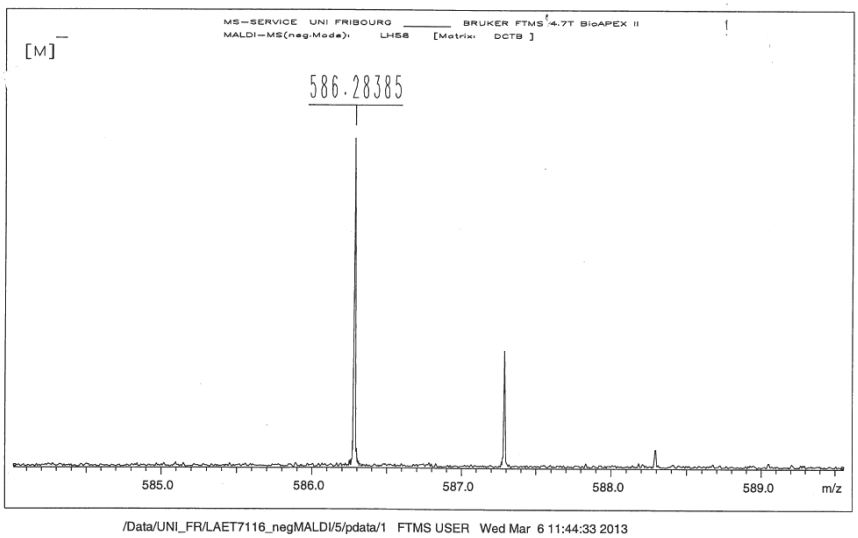
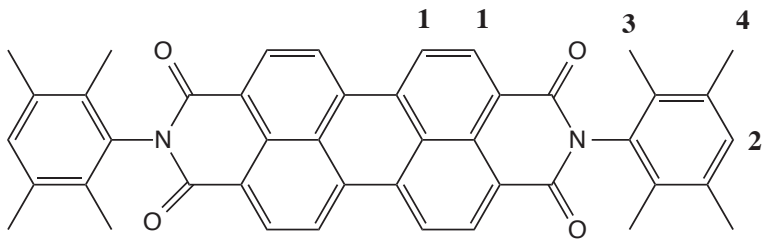


Figure SI10c. HRMS spectrum of **dmpa-XP**.



dm-DXP

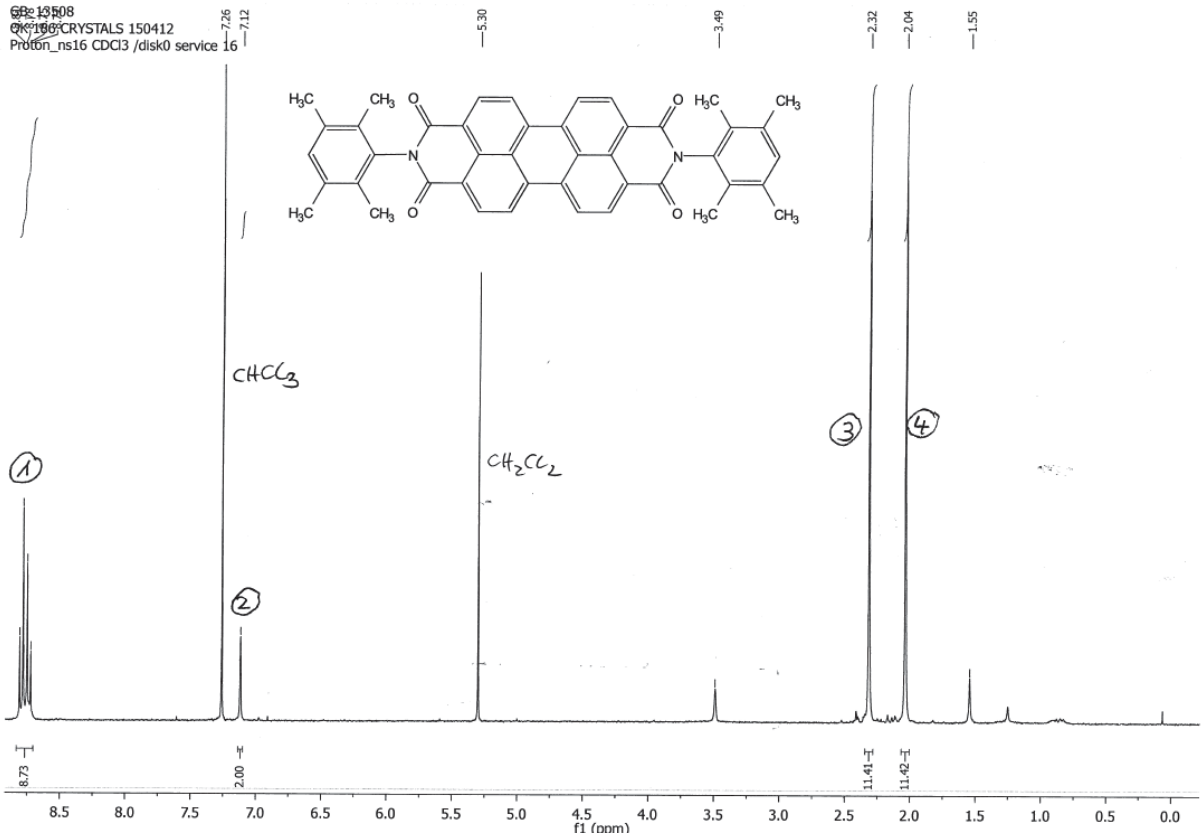


Figure SI11a. ^{1}H NMR spectrum of **dm-DXP** in $CDCl_3$.

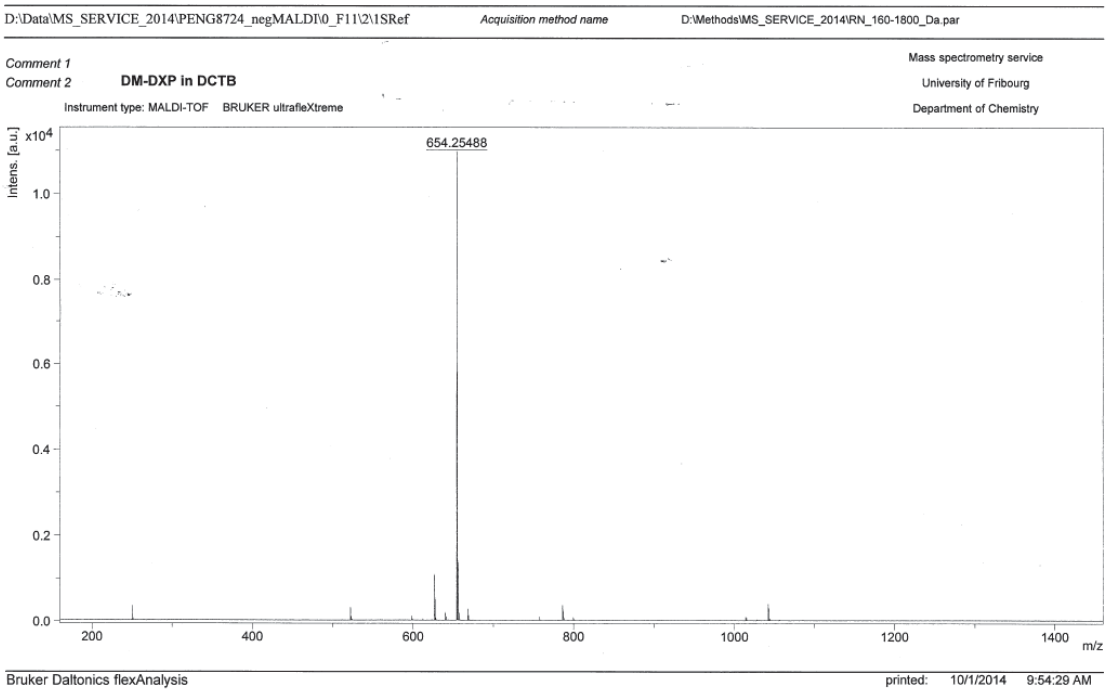


Figure SI11b. MS spectrum of **dm-DXP**.

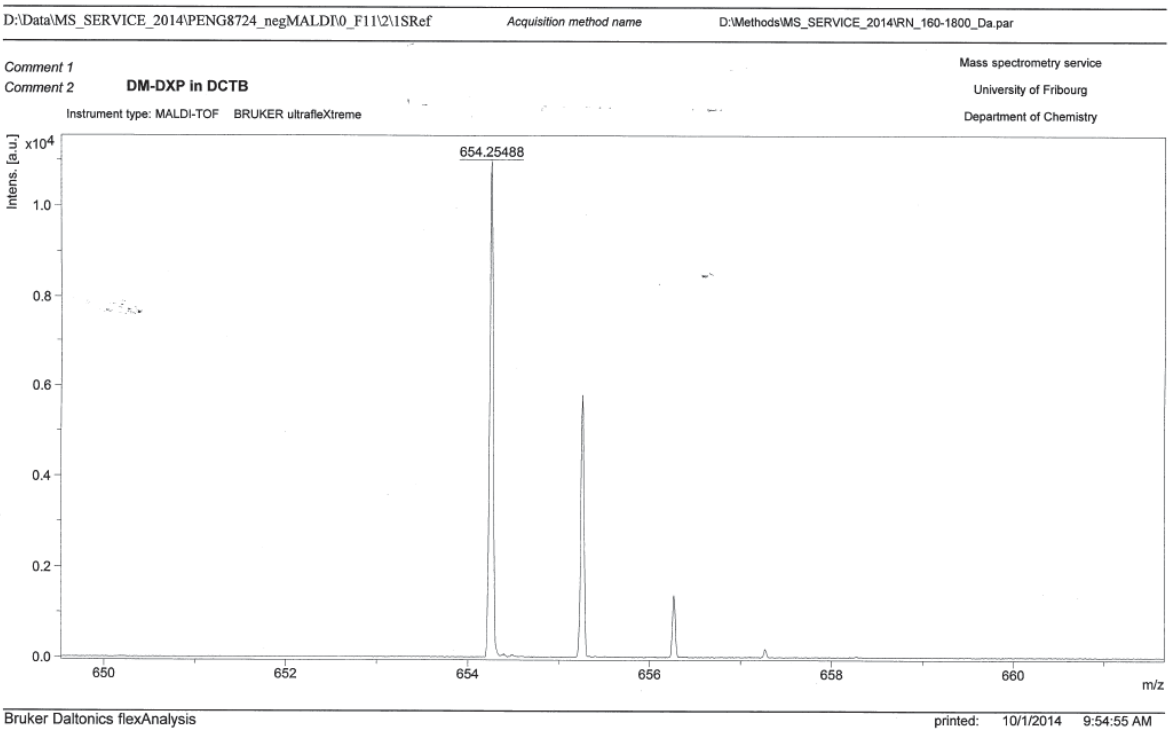
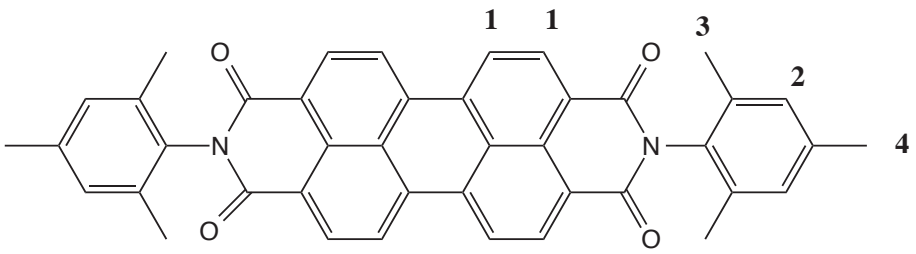


Figure SI11c. HRMS spectrum of **dm-DXP**.



m-DXP

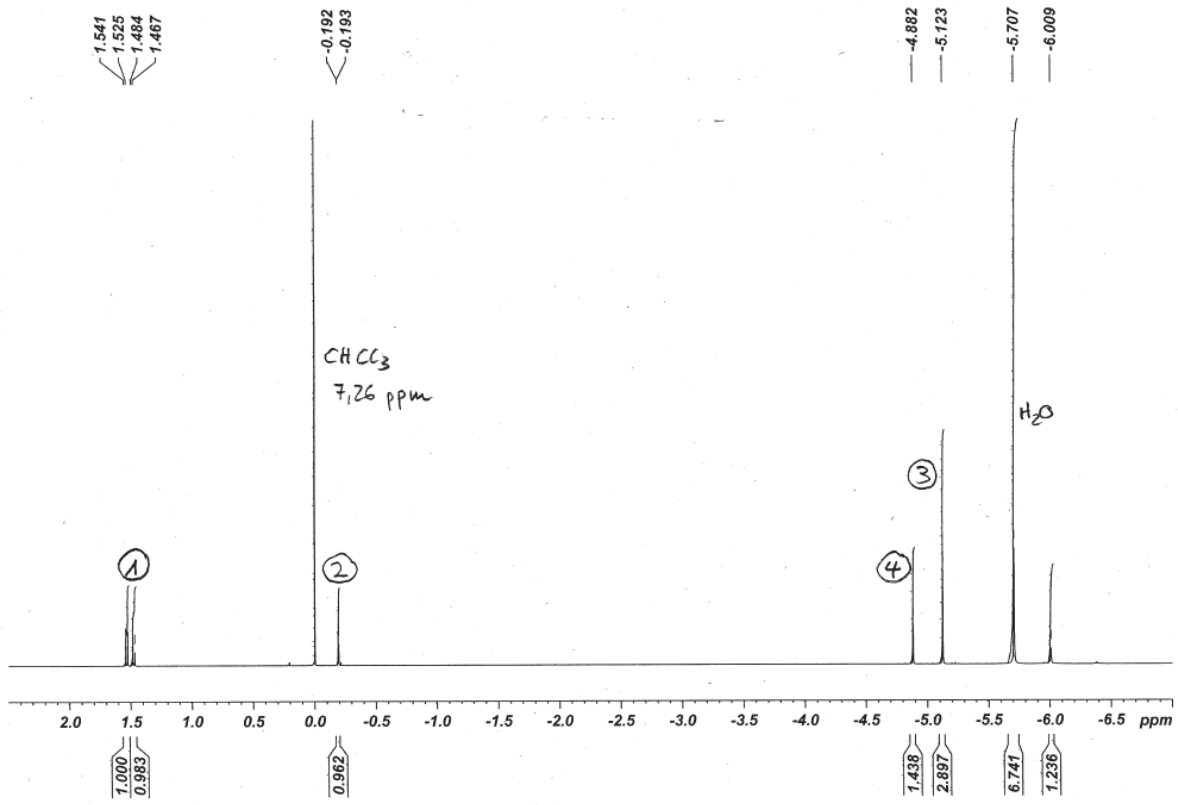


Figure SI12a. ^{1}H NMR spectrum of **m-DXP** in $CDCl_3$.

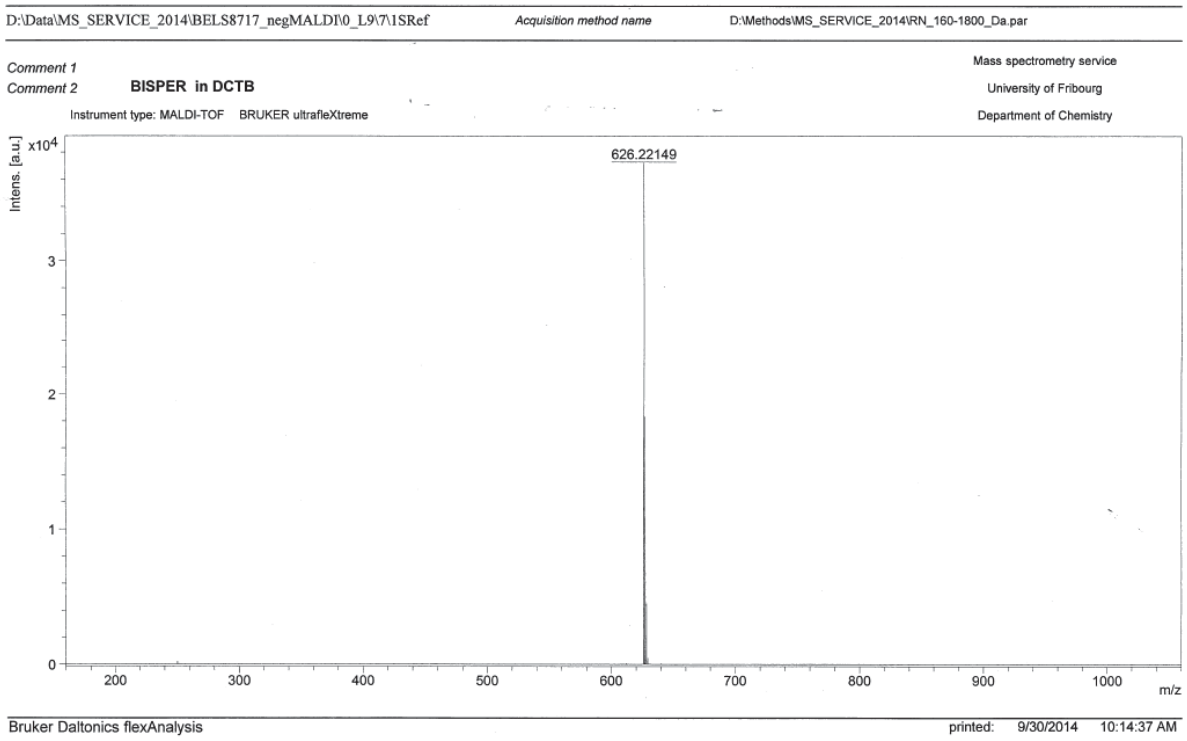


Figure SI12b. MS spectrum of **m-DXP**.

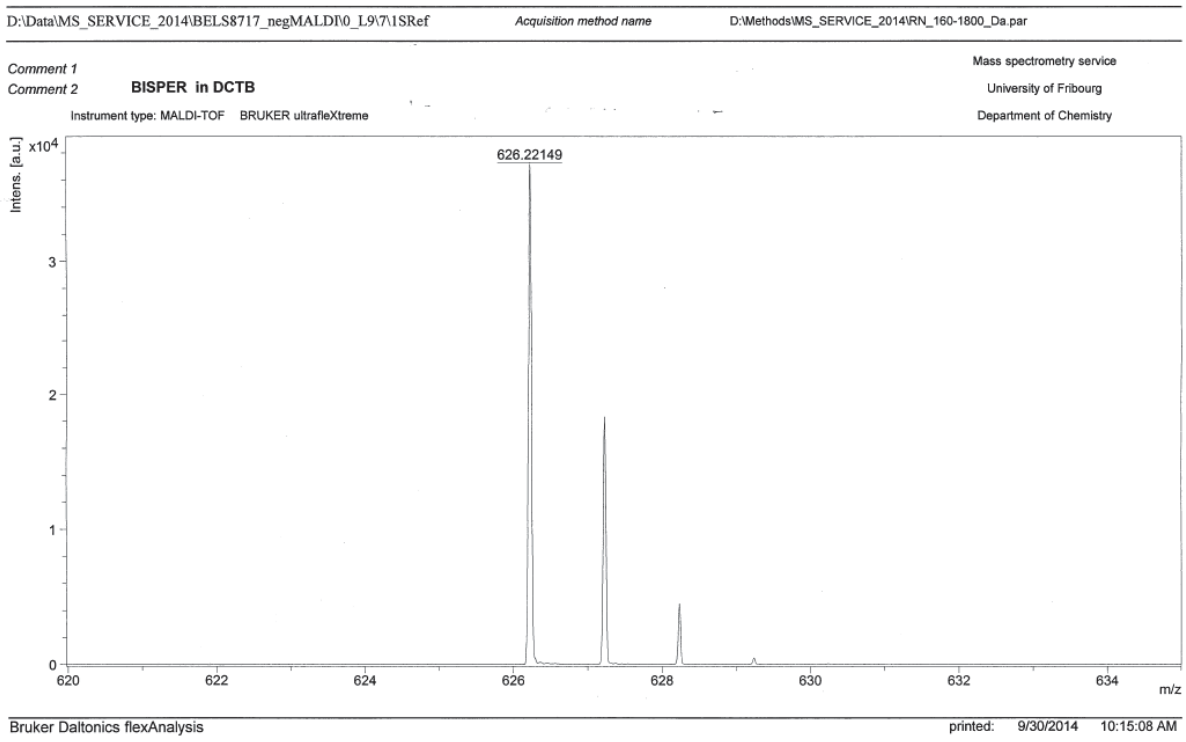
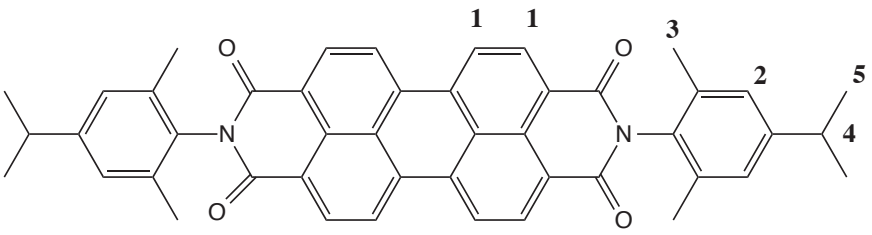


Figure SI12c. HRMS spectrum of **m-DXP**.



ip-DXP and isomer

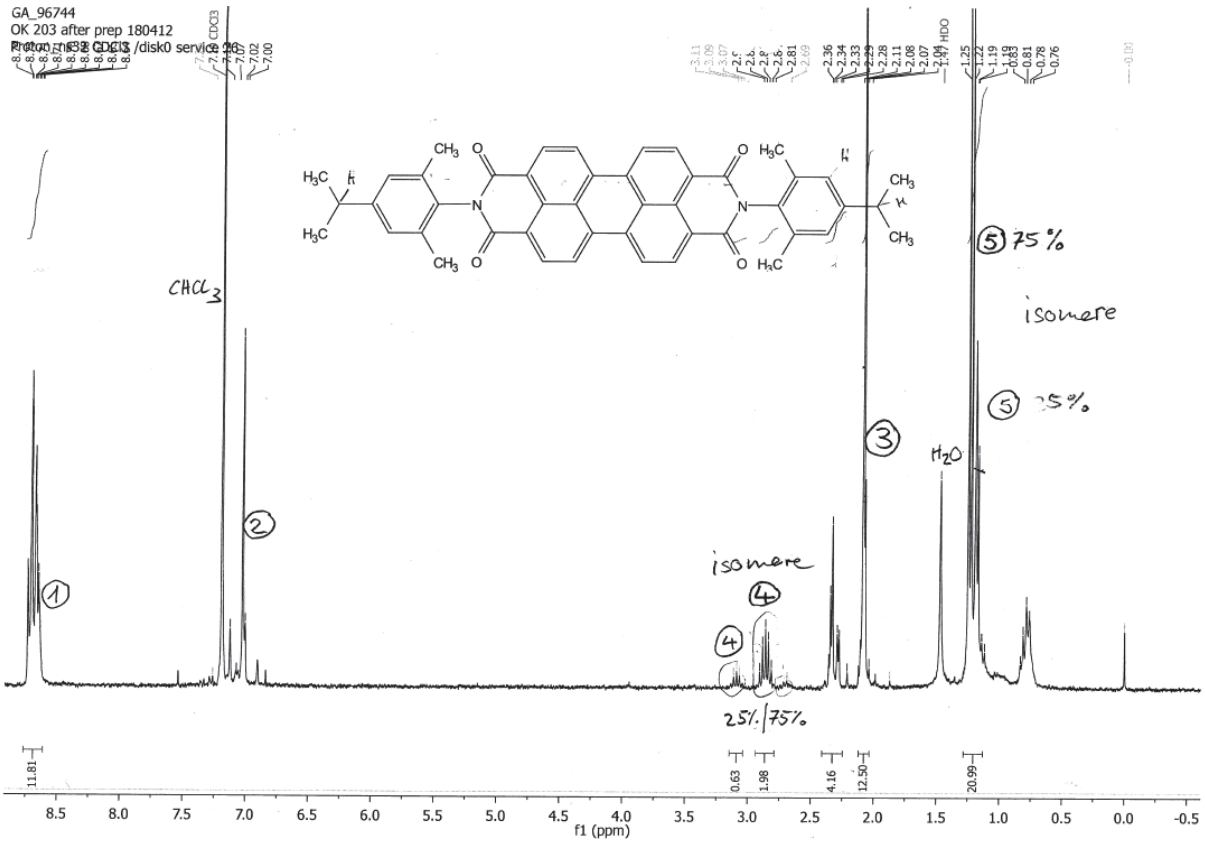


Figure SI13a. ^{1}H NMR spectrum of **ip-DXP and isomers** in $CDCl_3$.

m/z= 678.2906-688.2906

m/z	Theo. Mass	Delta (ppm)	Composition
683.2906	683.2904	0.21	$C_{46}H_{39}O_4N_2$
	683.2880	3.73	$C_{44}H_{40}O_4N_2Na$
	683.3006	-14.67	$C_{45}H_{42}O_4NNa$

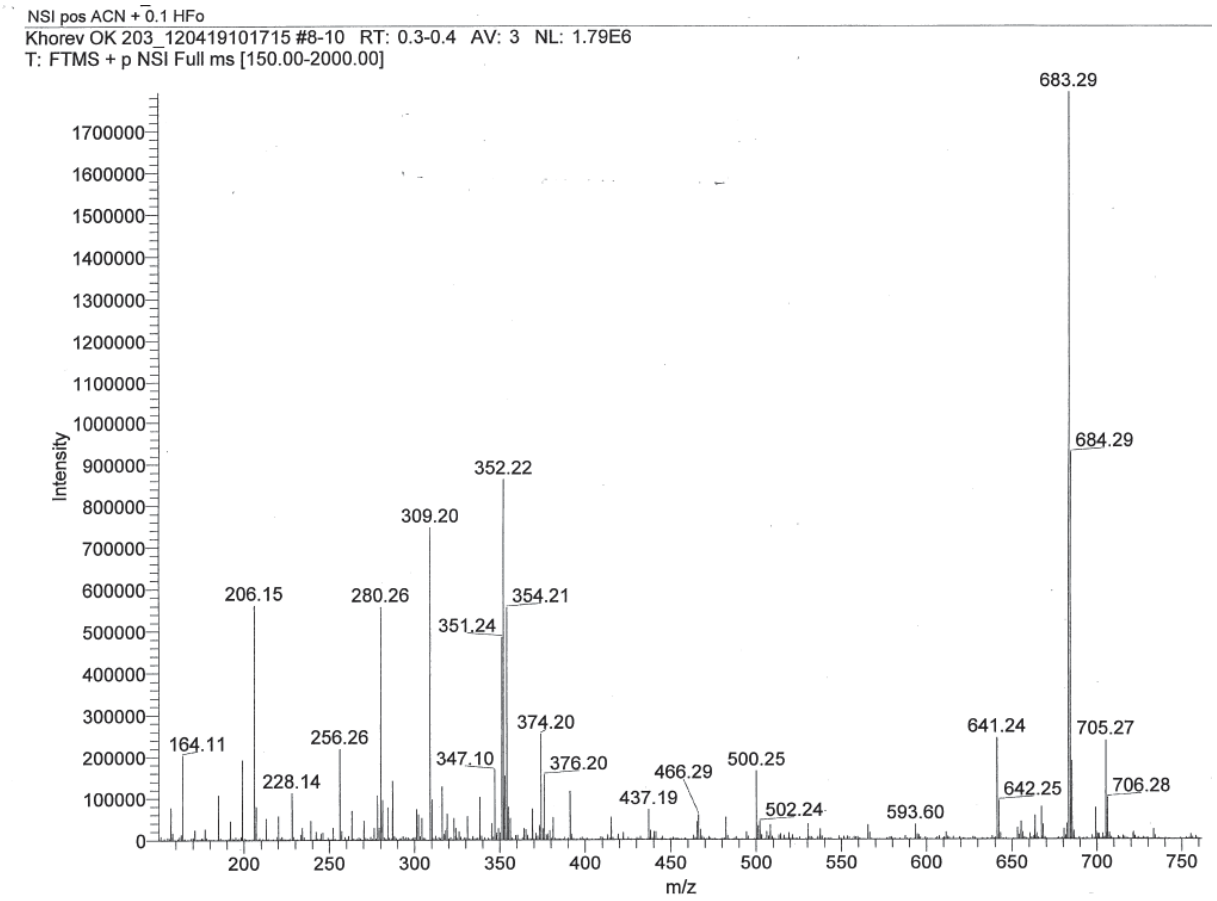


Figure SI13b. MS spectrum of **ip-DXP and isomers**.

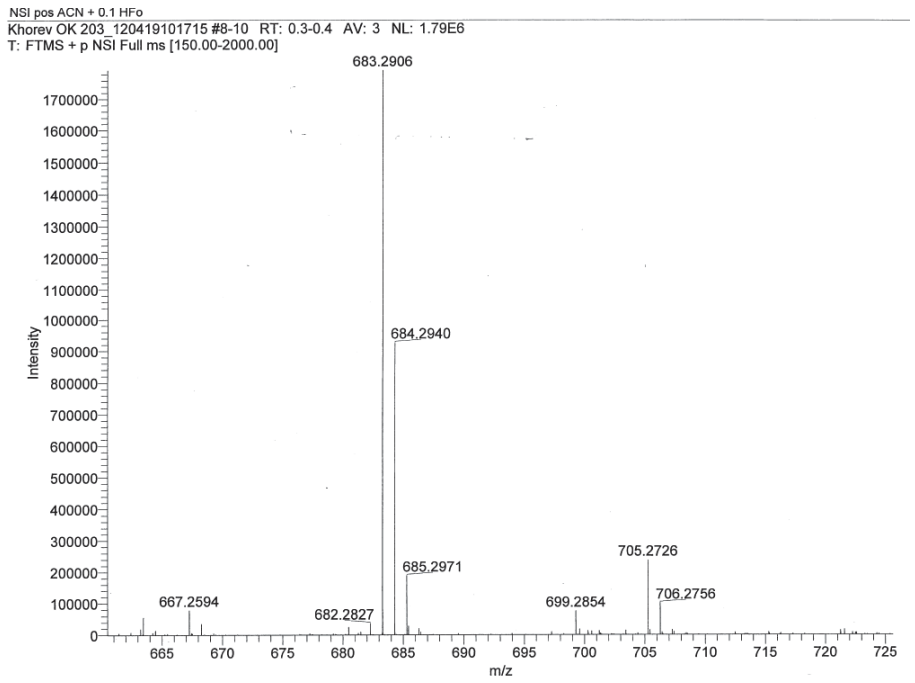
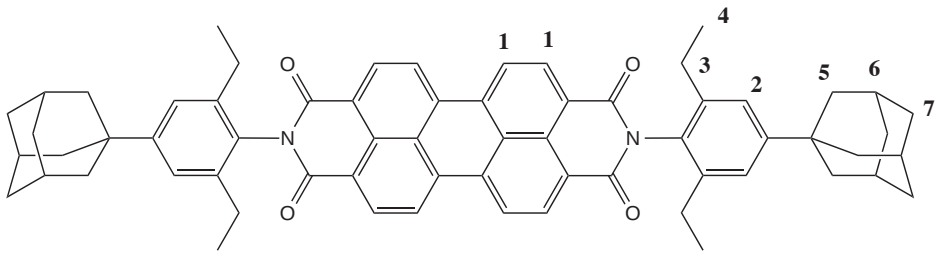


Figure SI13c. HRMS spectrum of **ip-DXP and isomers**.



ADE-XP

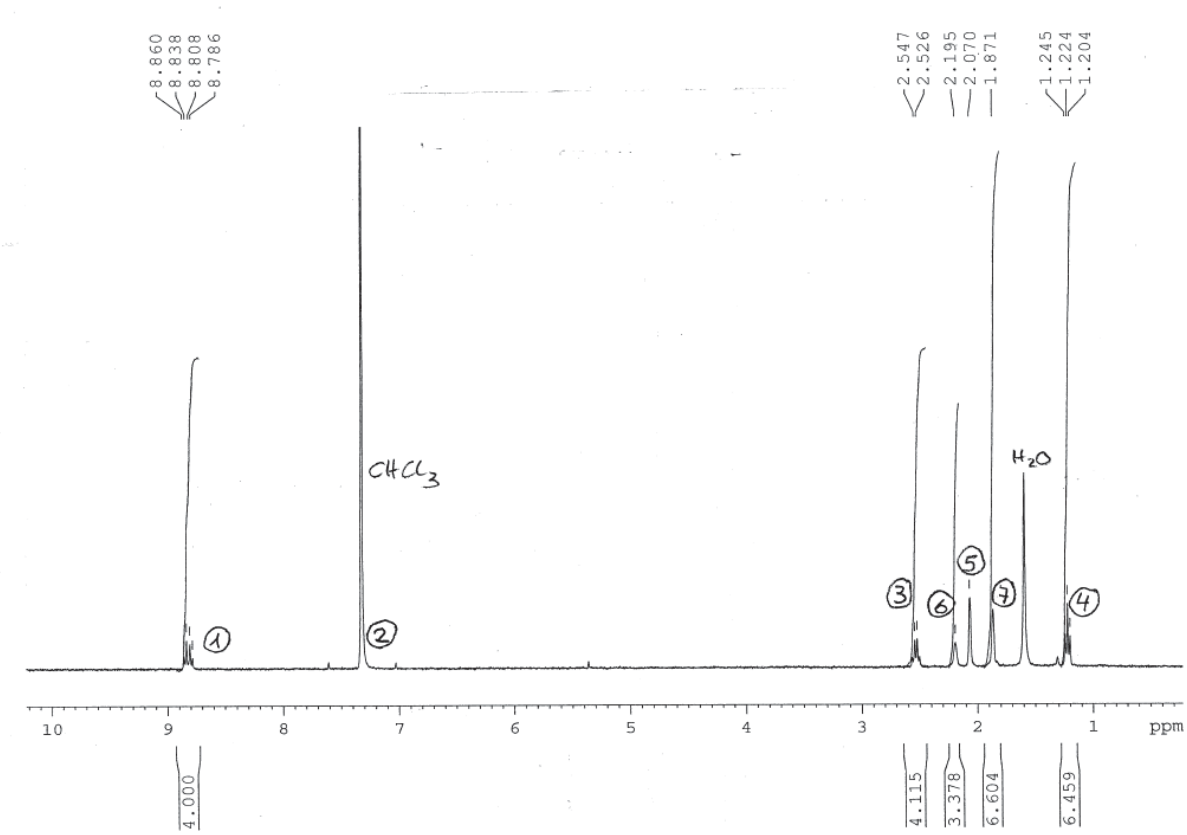


Figure SI14a. ^{1}H NMR spectrum of **ADE-XP** in $CDCl_3$.

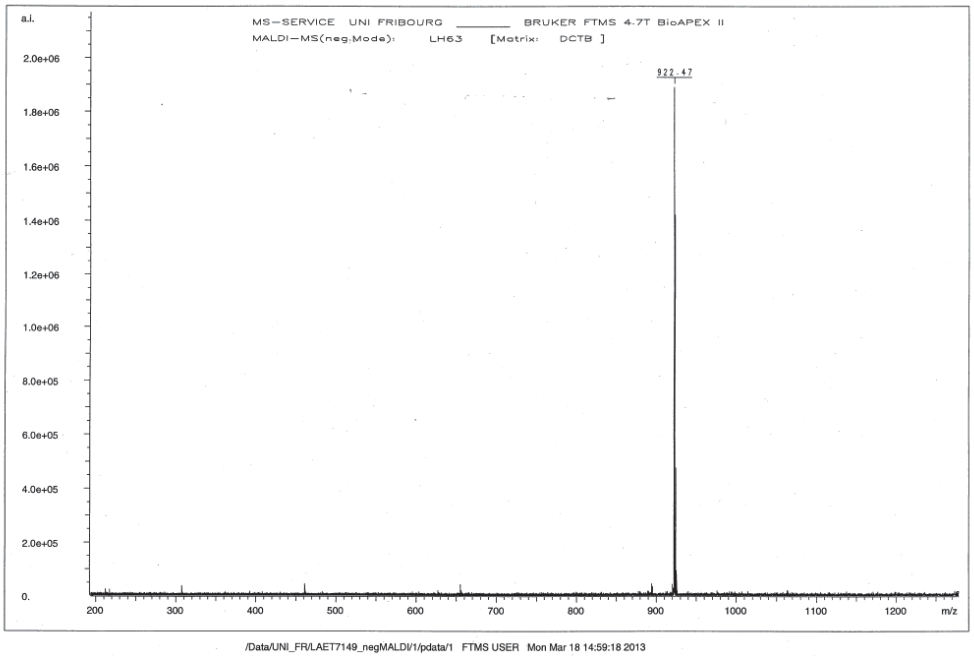


Figure SI14b. MS spectrum of **ADE-XP**.

#	C	H	N	O	mass	DBE	error
*** Mass Analysis for mass 922.4711130							
1	64	62	2	4	922.4715071	35.0	3.941e-04
2	48	62	10	9	922.4706722	23.0	4.408e-04
3	50	64	7	10	922.4720149	22.5	9.019e-04
4	62	60	5	3	922.4701644	35.5	9.486e-04
5	61	64	1	7	922.4688270	30.5	2.286e-03
6	60	58	8	2	922.4688217	36.0	2.291e-03
7	67	60	3	1	922.4741871	39.5	3.074e-03
8	53	62	8	7	922.4746950	27.0	3.582e-03
9	59	62	4	6	922.4674843	31.0	3.629e-03
10	55	64	5	8	922.4760376	26.5	4.925e-03

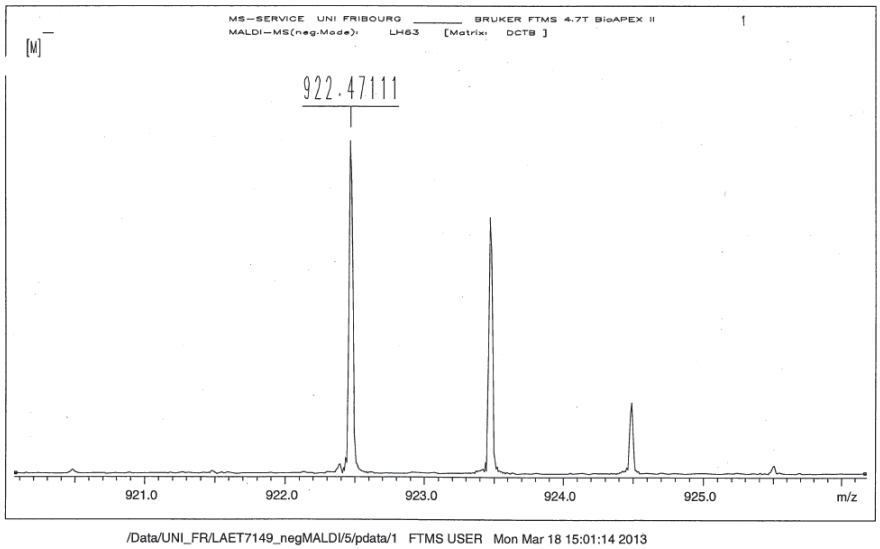
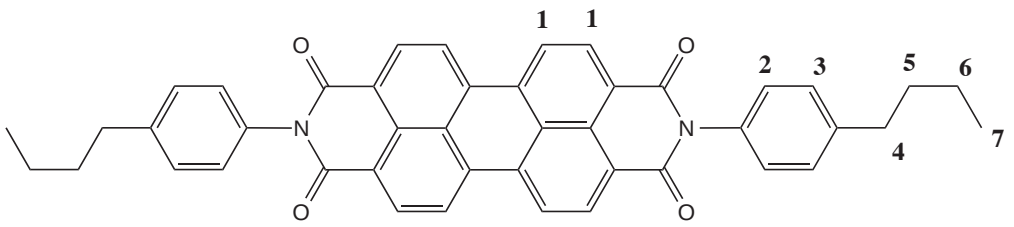


Figure SI14c. HRMS spectrum of **ADE-XP**.



b-XP

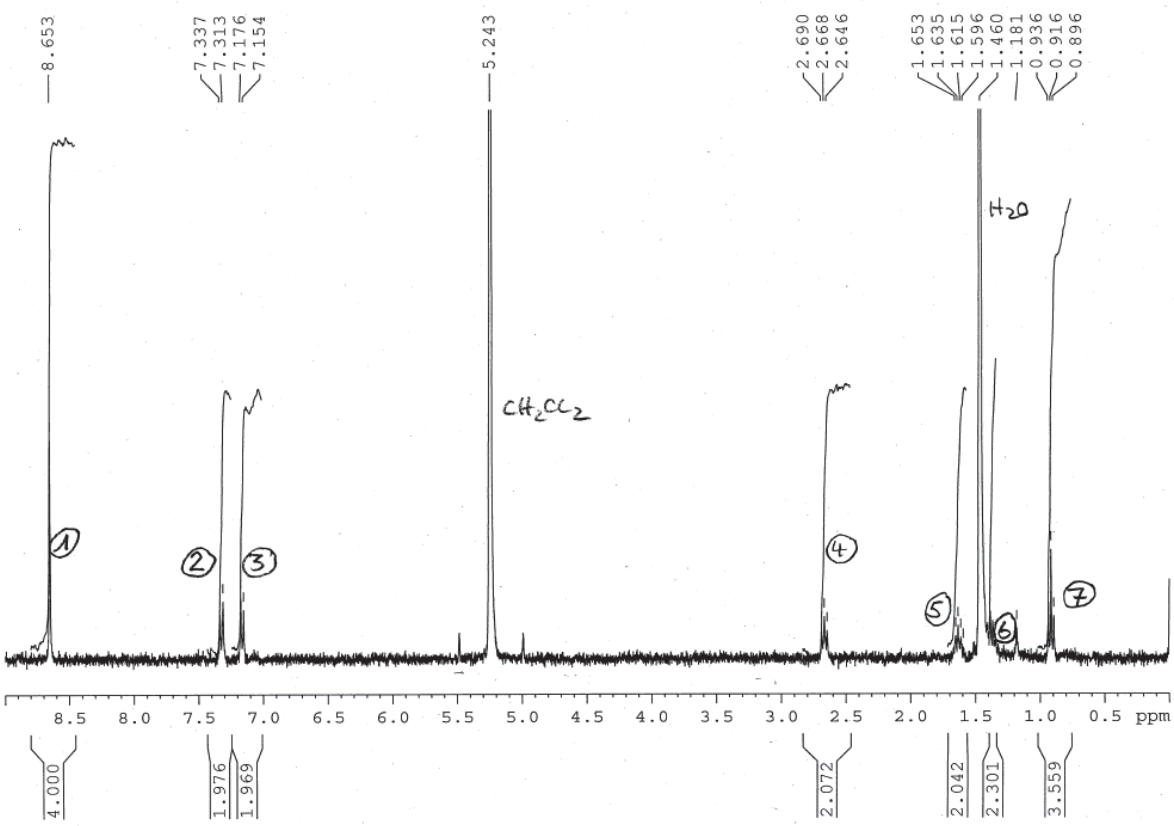


Figure SI15a. ^{1}H NMR spectrum of **b-XP** in CD_2Cl_2.

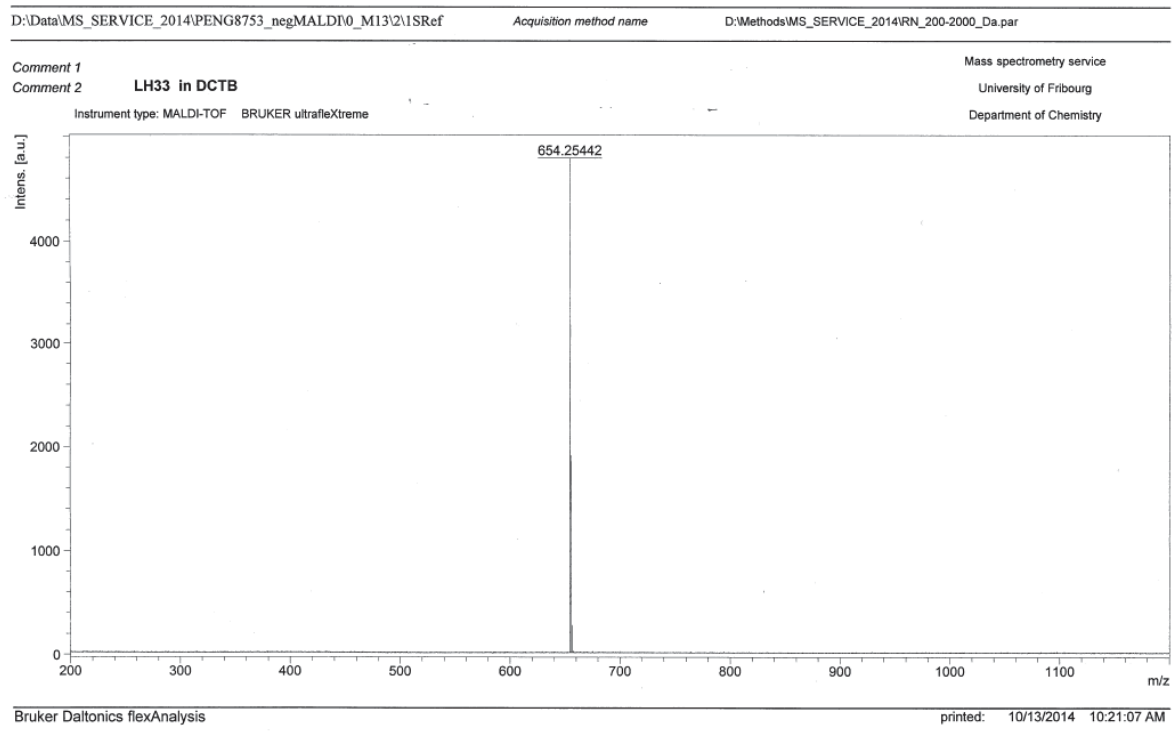


Figure SI15b. MS spectrum of **b-XP**.

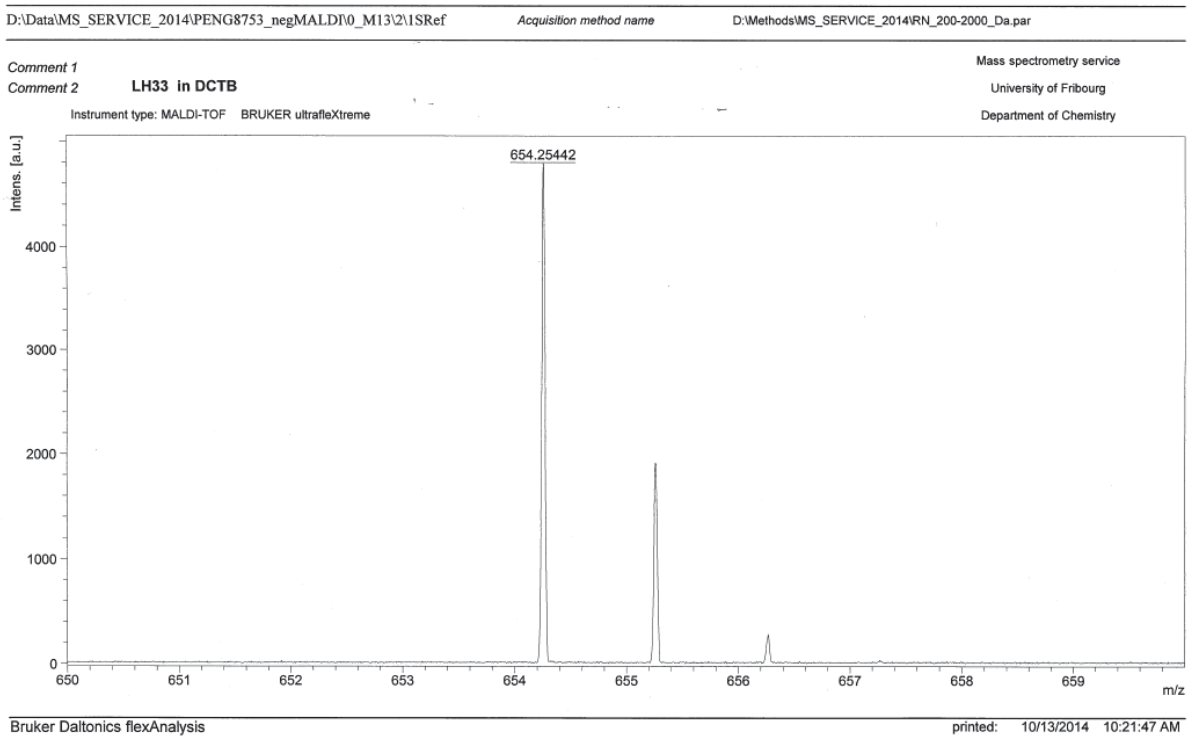
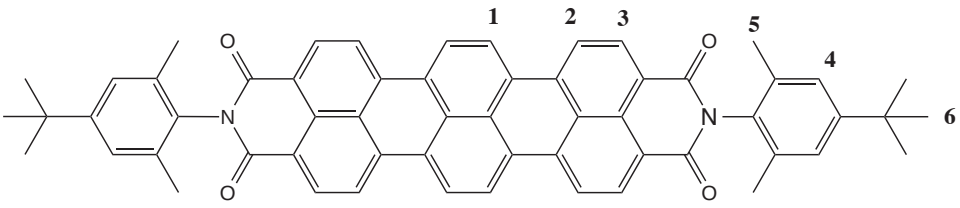


Figure SI15c. HRMS spectrum of **b-XP**.



tb-DXT

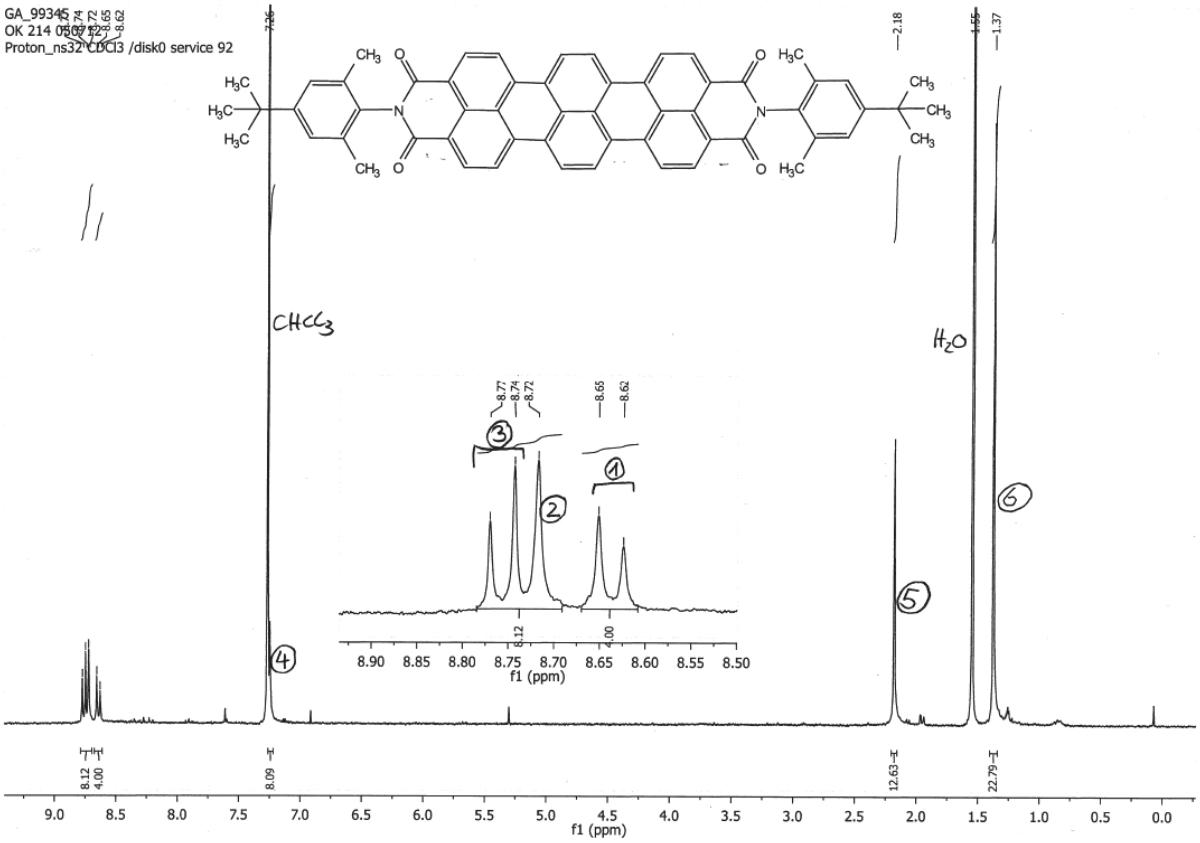


Figure SI16a. ^{1}H NMR spectrum of **tb-DXT** in $CDCl_3$.

m/z= 829.3429-839.3429

m/z	Theo. Mass	Delta (ppm)	Composition
834.3429	834.3425	0.44	$C_{55}H_{48}O_7N$
	834.3439	-1.16	$C_{56}H_{44}O_3N_5$
	834.3412	2.05	$C_{53}H_{46}O_6N_4$
	834.3452	-2.77	$C_{58}H_{46}O_4N_2$
	834.3398	3.66	$C_{52}H_{50}O_{10}$
	834.3471	-4.99	$C_{46}H_{50}O_{11}N_4$
	834.3385	5.27	$C_{50}H_{48}O_9N_3$
	834.3484	-6.59	$C_{48}H_{52}O_{12}N$
	834.3497	-8.20	$C_{49}H_{48}O_8N_5$
	834.3358	8.48	$C_{47}H_{50}O_{12}N_2$

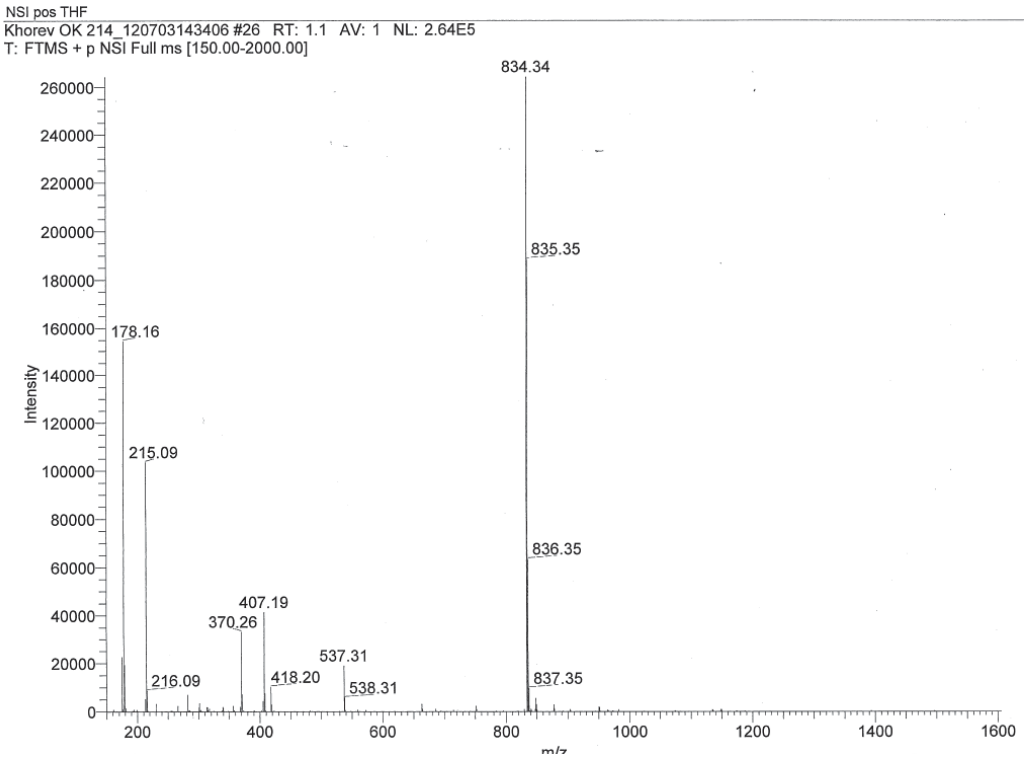


Figure SI16b. MS spectrum of **tb-DXT**.

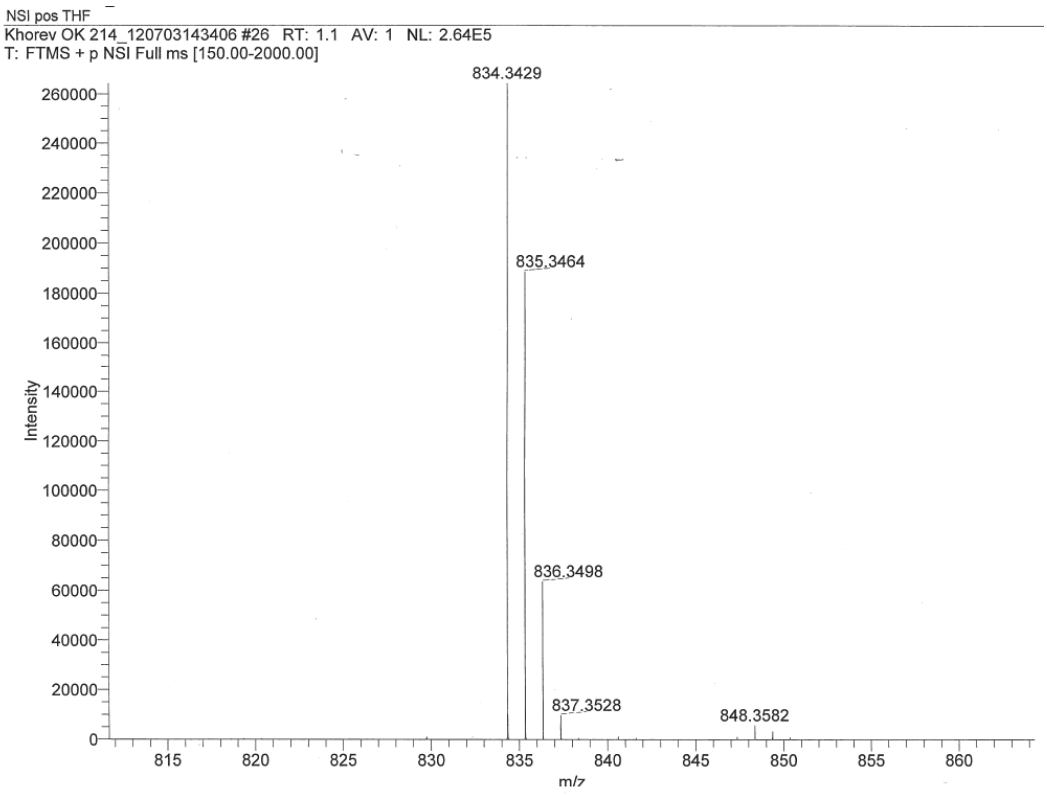
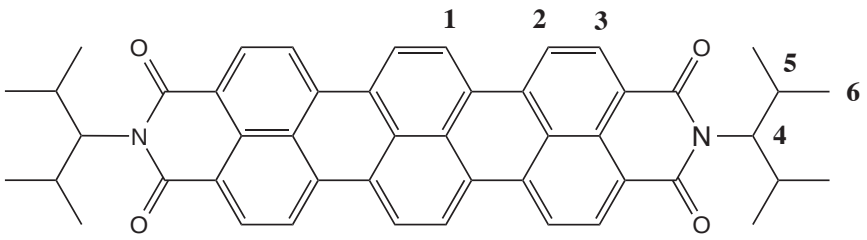


Figure SI16c. HRMS spectrum of **tb-DXT**.



dmpa-XT

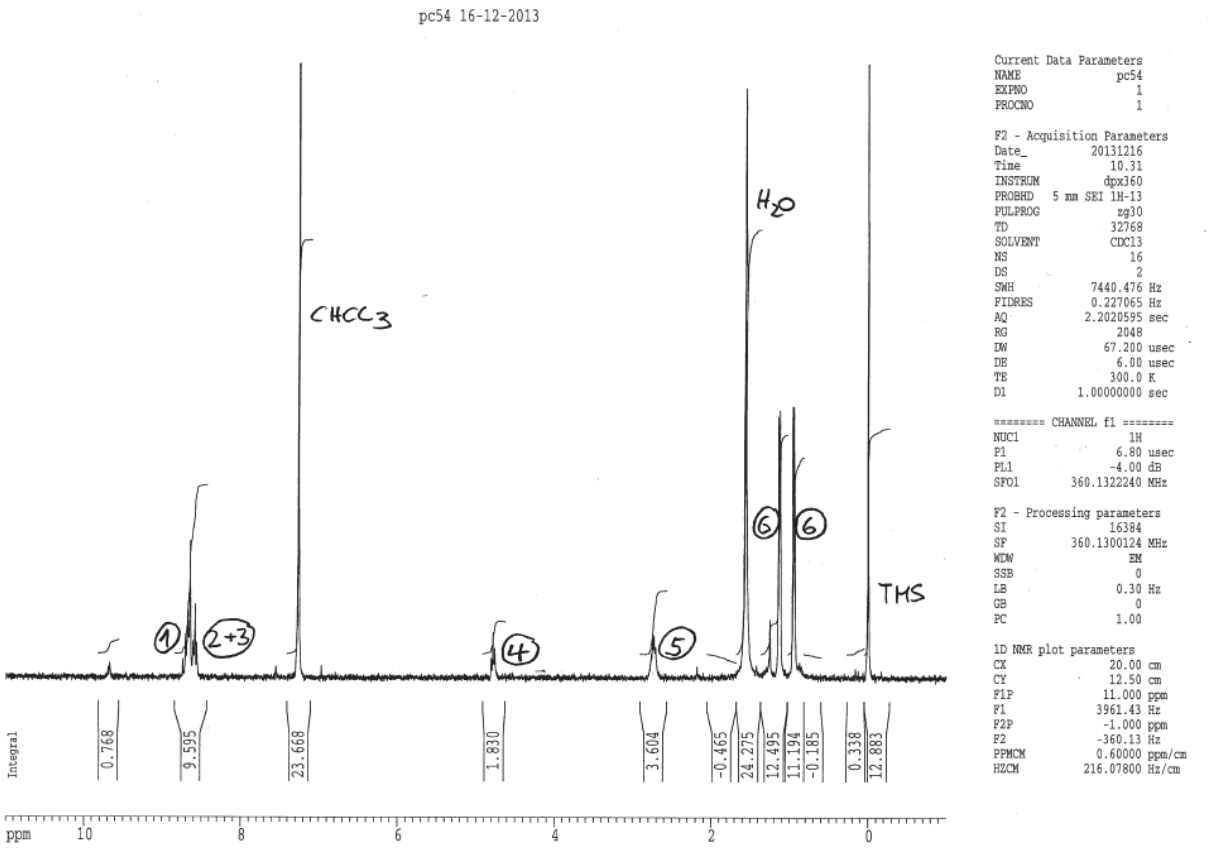


Figure SI17a. ^{1}H NMR spectrum of **dmpa-XT** in $CDCl_3$.

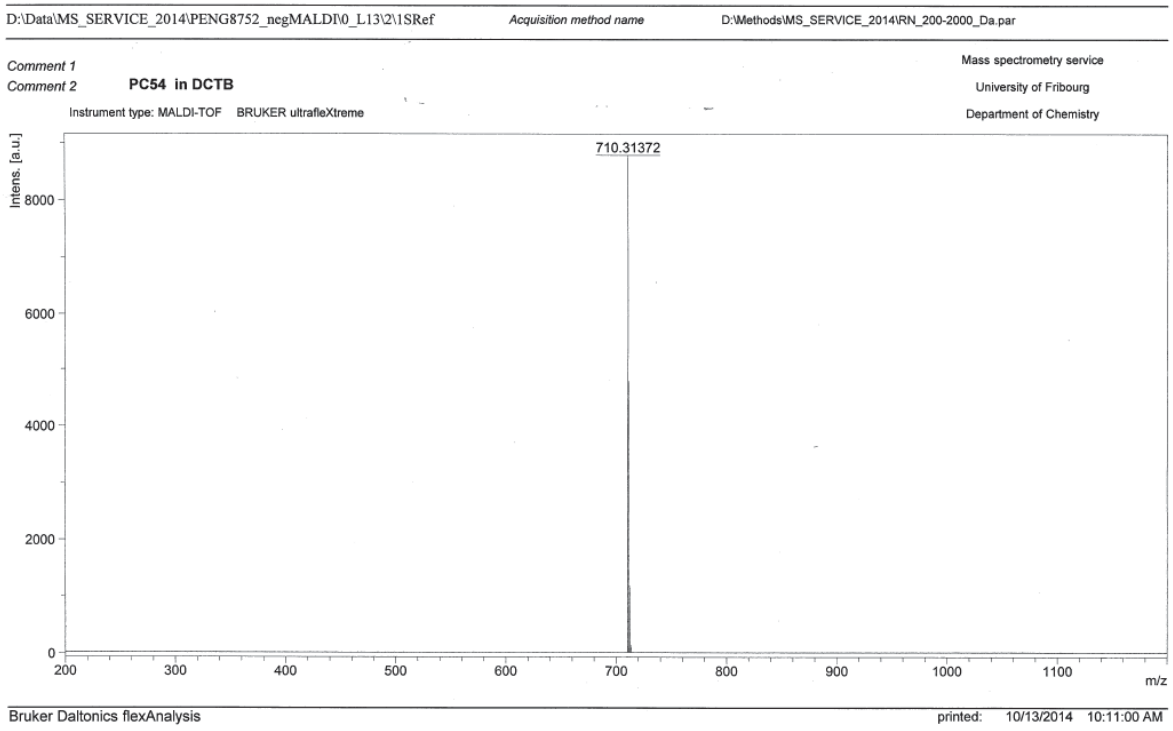


Figure SI17b. MS spectrum of **dmpa-XT**.

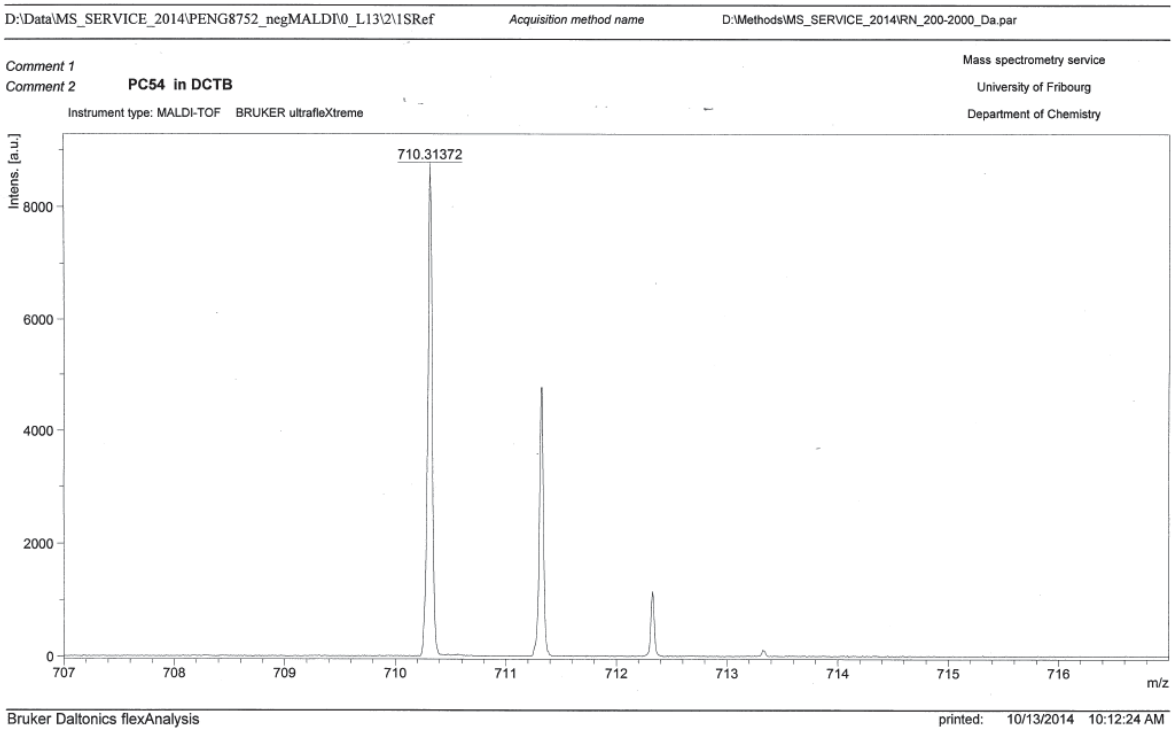
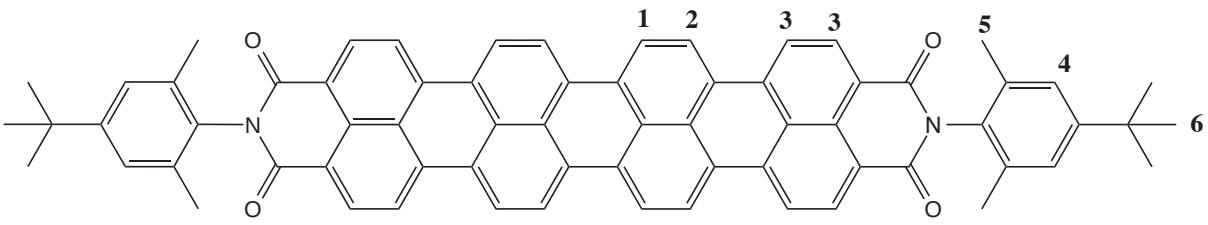


Figure SI17c. HRMS spectrum of **dmpa-XT**.



tb-DXQ

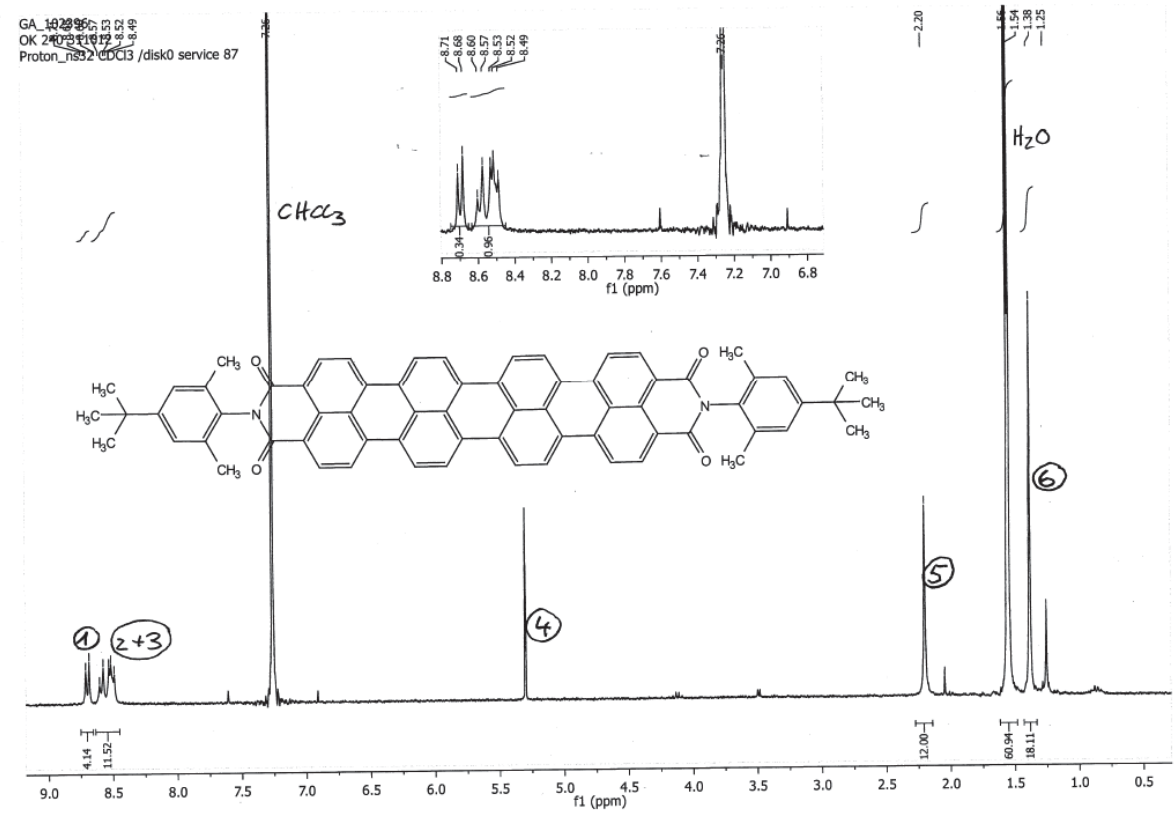


Figure SI18a. ^{1}H NMR spectrum of **tb-DXQ** in $CDCl_3$.

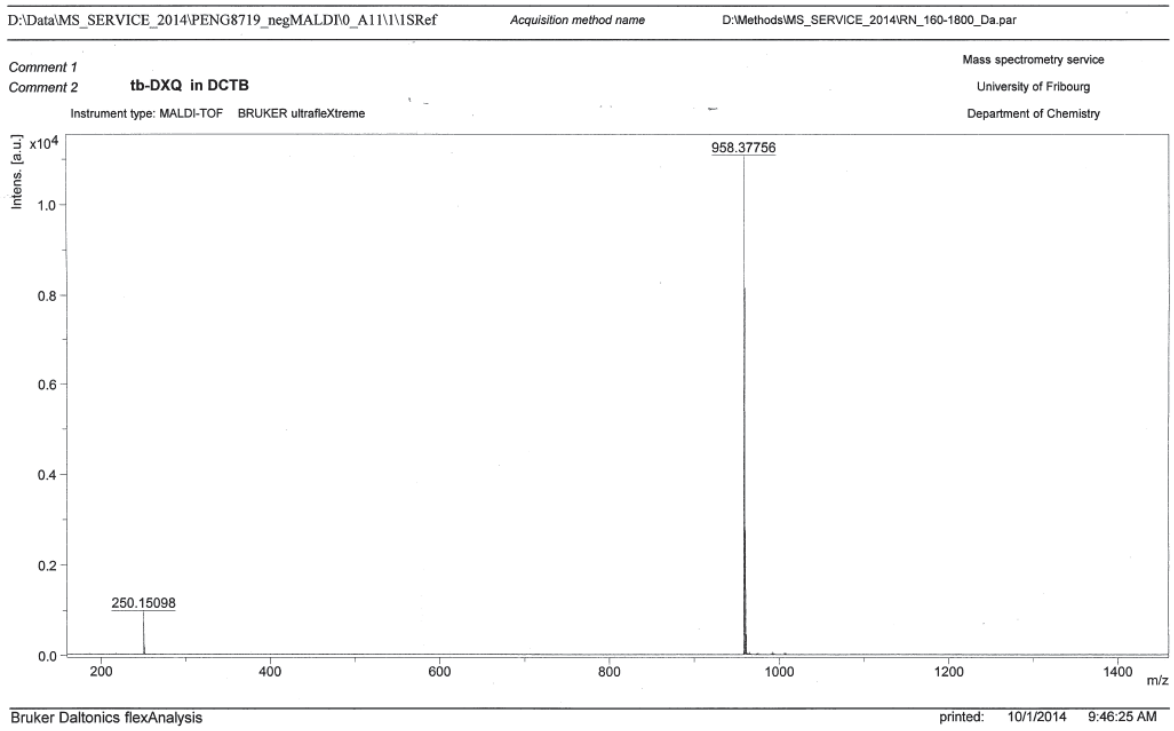


Figure SI18b. MS spectrum of **tb-DXQ**.

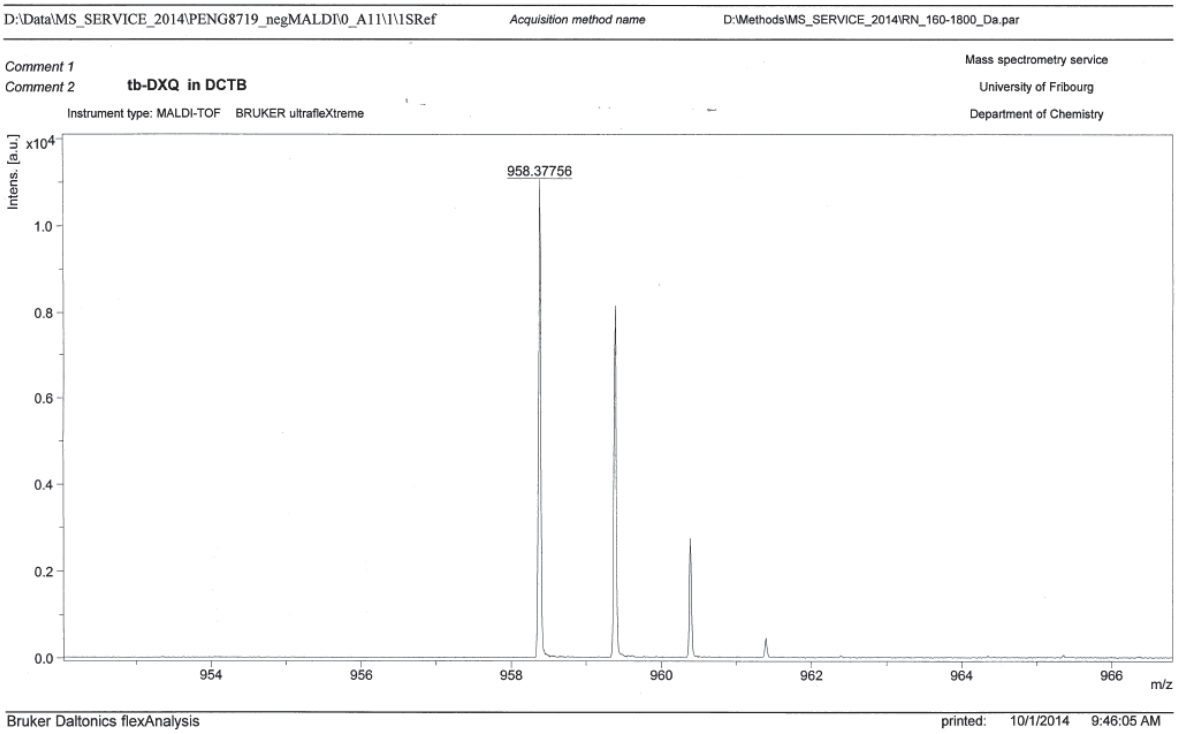


Figure SI18c. HRMS spectrum of **tb-DXQ**.

SI1.3 Synthesis of barrel-shaped ZL

Barrel-shaped ZL crystals with an average length and diameter of 500 nm were prepared according to the procedure reported in ref. [4]. The synthesis gel had an oxide ratio of 2.83 K_2O : 1.00 Al_2O_3 : 9.83 SiO_2 : 165.6 H_2O. The reactant amounts were chosen so that two 40 ml PTFE pressure vessels could be filled to an operating level corresponding to ca. ¾ of the total volume. - An aluminate solution (solution A) was prepared by first dissolving 8.1 g of potassium hydroxide in 25.4 g of doubly distilled water. Once the KOH was fully dissolved, 3.5 g of aluminum hydroxide was added and the solution refluxed for 16 h. The slightly turbid solution was then cooled to r.t. and water loss was compensated. The silica solution (solution B) was prepared by adding 30.2 g of doubly distilled water to 12.9 g of Aerosil OX-50. The mixture was dispersed with an Ultra Turrax T18 basic (IKA) for 15 min at 16000 rpm. The dispersion was left standing at r. t. for 1 h before dispersing it again for 8 min at 16000 rpm. After this second dispersion step, solution A was quickly poured into solution B under vigorous stirring. The resulting viscous white gel was aged for 3 min at r. t. under strong stirring before being evenly split on the two pressure vessels. Crystallization took place in a rotating oven at 160 °C for 42 h with a rotation speed of 20 rpm. Once the reaction was finished, the vessels were cooled in an ice bath for 1 h before opening them. The milky white suspension was centrifuged for 15 min at 3100 rpm. The white residue was then washed with boiling doubly distilled water until the pH of the supernatant was 7.

SI1.4 Synthesis and Post-Synthetic Treatment of ZL (Zeolite L, LTL Type)

The ZL crystals were synthesized following the reported procedure.[5] However, we have also tested to what extent commercial ZL materials such as the HSZ-500 from TOSOH Corporation (type HSZ-500KOA, length about 400 nm, width about 500 nm) can be used. Commercial materials do not feature well-defined morphology and may contain larger amounts of amorphous contributions and cations other that K^+. In both cases it is necessary to perform a post-synthesis cation exchange with KNO_3 in order to ensure that the composition of the charge compensating ions of the ZL is well defined. Suspending the ZL crystals in a highly concentrated aqueous KNO_3 solution and letting it exchange at r.t. for about 3 h is the usual treatment. The exchanged ZL is washed two times with deionized water to remove excess KNO_3 adsorbed to the ZL surface. The ion exchange and washing steps not only ensure that the ZL is present in the pure K^+ state, i.e. ZL(3.6 K^+), but also helps in eliminating small amorphous impurities. The latter stay in the supernatant of the washing solutions after the ion exchange. The commercial ZL material contained about 15%wt of such impurities, while no significant amounts were present in the self-synthesized material. Removal of this amorphous phase is very important, as it will otherwise cause issues with the insertion of dyes. The amorphous particles can adsorb dye molecules on their outer surface and these dyes will not experience the same environment or protection as those inside the ZL channels. This can complicate the analysis of the spectral properties and stability of the dye-ZL composite. Another issue related to the presence of this amorphous phase arises during the determination of the composites dye loading: the amorphous material has a different

molecular weight and does not have the same dye adsorption capacity as the ZL. This will cause a large uncertainty in dye content determination by an HF test.[5] Therefore it is essential to remove any such impurities – mostly present in commercial materials – from the ZL sample before loading dyes through the gas phase.

SI1.5 Synthesis Procedures of dye-ZL composites

Depending on their nature, organic dyes were inserted into the channels of ZL either by ion exchange or through an adsorption process. Cationic species were incorporated into ZL by first dispersing the host material in an appropriate solvent such as deionized water. The required amount of dye was then added to the ZL suspension as a stock solution, usually dissolved in the same solvent. The ion exchange was carried out either at room temperature or under gentle heating in order to increase the reaction rate. However, one has to be careful when heating the dye-containing ZL dispersion, because the organic molecules can decompose if the exchange conditions are too harsh. The critical temperature regime depends very much on the kind of dyes used and on the applied conditions. An example of this behavior is the cationic dye oxazine1 ($Ox1^+$). If the ion exchange process was carried out at a temperature above 70 °C, most of the dye decomposed, and only very small loadings could be achieved. Performing the same procedure at room temperature or 40 °C led to higher $Ox1^+$ loadings as the dye did not decompose under these conditions.[6] Neutral dyes were inserted into the ZL channels through adsorption in an evacuated and heated ampoule. In this process the appropriate amount of dye was first adsorbed to the outer surface of the ZL by dispersing the host material in a dye solution. A rotatory evaporator was then used to remove the solvent, and after grinding it to a fine powder in an agate mortar, the solid residue was transferred into a glass ampoule. The ampoule was evacuated and kept under dynamic vacuum conditions for 16 h in order to remove most of the oxygen and water. This step is crucial, since the presence of larger amounts of water or oxygen in conjunction with high temperatures (above 200 °C) lead to the decomposition of the organic dyes. Melting the glass tube once the evacuation process was completed sealed the ampoule. Dye insertion took place at temperatures between 180 °C and 260 °C with time periods ranging from 24 h to 72 h, depending on the dye molecules and desired loading. The ampoules were heated either in a tube oven or in a salt bath. Insertion time and temperature regime are the two central conditions influencing the amount of dye loading that can be achieved. A higher temperature leads to faster diffusion of the dyes along the surfaces and channels of ZL, while longer insertion times allow the dyes to travel further. It is important, however, to stress that each organic dye has an upper temperature limit above which it may decompose. For example, most of the PDIs described in this study survived loading processes with temperatures of up to 280 °C. The dye tdc-XP, however, is much more sensitive to thermal decomposition and was best inserted at 180 °C. This upper limit for the loading temperature has to be assessed for each individual dye. The shape and size of a dye molecule have a great influence on the loading behavior. If the end groups of a rylene dye are much larger than the ZL pore opening then it will not be possible to insert it into the channels

(see e.g. the perylene derivative ADE-XP). In order to explore this substituent-loading relationship, a series of experiments were carried out where all loading conditions were kept constant and only the dye type was varied. The loading temperature was set to 260 °C with an insertion time of 72 h and a target loading of p(dye) = 0.5. After completing the loading process, the samples were washed three times with DCM to remove dyes adsorbed onto the outer surfaces of the ZL. The effective dye loading of each material was determined by dissolving the dye-ZL composites with HF and by measuring the dye concentration of the resulting solution.[3] The strategy of the synthesis procedure for obtaining organized composites is outlined in Scheme 1A. The final, red-emitting acceptor dye Hostasol Red (HR) was inserted first into ZL with a loading p(HR). Once this step was completed, a green emitting donor dye (tb-DXP) was incorporated into the channels via gas phase adsorption and a loading of p(tb-DXP). A second neutral donor dye, DMP, was then inserted into the two dye-ZL composite in the same way and with a loading of p(DMP). Finally, the channel entrances were sealed with APTES (Table 3) to prevent any dye losses from the ZL, resulting in the final composite DMP,tb-DXP,HR-ZLp(HR),p(tb-DXP),p(DMP)-APTES This inverted loading strategy has proven to be efficient for preparing such antenna materials. An argument being that the final acceptor will be located deep in the channels and protected from leaking out during post-synthesis treatments by the presence of the combined donors tb-DXP and DMP. The physico-chemical characteristics of the ZL channels, namely their high polarity and acidity, can have a strong influence on the stability and luminescence behavior of the inserted dyes. We showed in a recent study that these channel properties could be tuned by replacing some of the exchangeable metal cations with organic ones, such as IMZ^+.[3] Such a pre-treatment is especially important if HR is to be loaded into ZL. The IMZ^+ exchange was carried out as described above for cationic dyes, using an aqueous IMZ^+ solution and letting the reaction run at room temperature for 3 h. The exchanged material was then washed two times with deionized water and dried in an oven at 60 °C prior to dye loading.

Preparation of HR-ZL and HR-ZL(yM^+,xIMZ^+), $M^+ = K^+$ or Cs^+. Prior to the gas phase loading procedure, the barrel-shaped ZL was submitted to an ion exchange with either KNO_3 or IMZ^+. In such a procedure, 100 mg of the ZL was suspended in 10 ml of an aqueous solution of KNO_3 or IMZ^+ (c = 0.01 M in both cases). The suspension was left stirring at 70 °C for 18 h. The ZL material was then centrifuged off (15 min at 2100 rpm) and washed once with 10 ml of deionized water. The nano-sized ZL was Cs^+ exchanged in a similar fashion. The gas phase loading procedure for HR was carried out as follows: 100 mg of ion-exchanged ZL (either with K^+, Cs^+ or IMZ^+) and 2.2 mg of HR (corresponding to a target loading of p = 0.5) were weighed into a 25 ml round bottom flask. After the addition of 10 ml of dichloromethane, the mixture was sonicated for 5 seconds to dissolve the dye and disperse the ZL. The solvent was removed on a rotary evaporator at 40 °C and a pressure of 600 mbar. The HR coated ZL material was then transferred from the flask into an agate mortar and ground into a fine powder. The powdered material was filled into a glass ampoule (25 mm x 20 mm) and dried on a vacuum line at r.t. for 24 h at a pressure of 2×10^{-2} mbar. After sealing the ampoule under vacuum, the gas phase insertion process took place in a rotating oven or a salt bath at 270 °C (K^+, Cs^+) or 150 °C (IMZ^+) for 3 d.

The ampoule was then removed from the heating source and cooled down to r. t. After opening the ampoule, the dye-loaded ZL was washed 3 times with 20 ml portions of dichloromethane. The supernatant of the third washing showed no traces of HR. The HR-ZL(3.6IMZ^+) composite kept its pinkish-red coloring and strong luminescence after longer exposure to humidity, while the Cs^+ and K^+ type quickly changed to a very weakly luminescent violet color; see Fig. 3B and Fig. 3C in literature [6]. Furthermore, a sample of the HR-ZL(3.6IMZ^+) was stored in water for 2 weeks and did not show any color changes or reduction in luminescence intensity, Fig. 3D; literature [4]. Effective p of HR was determined by HF analysis (see below).

Preparation of tb-DXP,HR-ZL(yK^+,xIMZ^+). This composite was synthesized by first loading barrel-shaped ZL with IMZ^+. For this, 1 g of the ZL was suspended in a mixture of 13.2 ml of deionized water and 1.8 ml of an aqueous stock solution of IMZ^+ (c = 0.1 M), and letting it stir for 18 h at 70 °C. The amount of IMZ^+ used here corresponds to a target loading of 0.5 IMZ^+ per ZL unit cells. The ZL(IMZ^+) was collected by centrifugation (15 min; 2100 rpm) and washed once with 10 ml of deionized water. HR was loaded into the ZL(3.1K^+,0.5IMZ^+) by means of gas phase adsorption with a target loading level of p = 0.04. For this, 200 mg of the ZL was mixed with 33.3 ml of an HR stock solution in dichloromethane (c = 4 x 10^{-5} M) in a 50 ml round bottom flask. The mixture was dispersed in an ultrasonic bath for 5 s. After removal of the solvent on a rotary evaporator (40 °C, 700 mbar), the residue was ground to a fine powder in an agate mortar. The powder was dried on a vacuum line at r. t. at a pressure of 2x10^{-2} mbar for 24 h after being filled into a small glass ampoule. Once the ampoule was sealed, the insertion took place at 185 °C for 3 d. The HR-ZL(3.1K^+,0.5IMZ^+) composite was then removed from the ampoule. Insertion of the donor dye tb-DXP was performed in a similar way: 200 mg of the HR-ZL(3.1K^+,0.5IMZ^+) was mixed with 4.9 mg of tb-DXP (corresponding to a target loading of p = 0.3) in a 25 ml round bottom flask. After addition of 20 ml of dichloromethane, the mixture was dispersed for 5 s in an ultrasonic bath. The solvent was then evaporated on a rotary evaporator (40 °C, 700 mbar). The residue was removed from the flask and ground to a fine powder in an agate mortar. The powder, after being transferred into a small glass ampoule, was dried for 24 h at r. t. on a vacuum line. The sealed ampoule was put into a salt bath at 210 °C for 3 d in order to load the tb-DXP. Once the process was complete, the tb-DXP,HR-ZL(3.1K^+,0.5IMZ^+) composite was removed from the ampoule and washed three times with 20 ml portions of dichloromethane. The effective p of the two dyes was determined by HF analysis.

Preparation of DMPOPOP,tb-DXP,HR-ZL(yK^+,xIMZ^+). In order to prepare this three dye composite, 100 mg of the tb-DXP,HR(3.1K^+,0.5IMZ^+) obtained above was mixed with 1.6 mg of DMPOPOP in a 50 ml round bottom flask (corresponding to a target loading of p = 0.3). After addition of 10 ml of dichloromethane, the mixture was treated for 5 s in an ultrasonic bath. The solvent was removed on a rotary evaporator (40 °C, 700 mbar), the solid residue collected and ground to a fine powder in an agate mortar. After transferring this powder into a small glass ampoule, it was dried on a vacuum line for 24 h at r.t. The ampoule was then sealed under vacuum and put into a salt bath at 180 °C for 3 days. Once the loading process was completed, the composite DMPOPOP,tb-DXP,HR(3.1K^+,0.5IMZ^+) was removed from the ampoule and

washed three times with 20 ml portions of dichloromethane. The effective p(DMPOPOP) was determined by HF analysis.

Dye-ZL-Composite Sealing Procedure. 400 mg of dye-loaded ZL composite was weighted into a silanized 100 ml round bottom flask and 70 ml of toluene was added. After a 10 s pre-treatment in an ultrasonic bath, the mixture was dispersed for 20 min with a rotor/stator dispersion unit (IKA Ultra Turrax T18 basic with S18N-10G tool) at 16'000 rpm. 50 µl of APTES were then added and dispersed at 16'000 rpm for 3 h more. Once the reaction was completed, the dispersion was transferred into a glass centrifuge tube and centrifuged for 15 min at 2'300 rpm (1'200 RCF/g). The supernatant was discarded and the residue washed once with 40 ml of toluene. The sealed material was then dried in a vacuum oven at 65 °C for 8 h.

Surface Modification of Sealed ZL Materials. The crystal surface of sealed ZL composites obtained in the previous step can be further modified with other alkoxysilanes. 170 mg of the sealed, dye-loaded ZL composite was weighted into a silanized 100 ml round bottom flask. After addition of 70 ml of toluene and a 10 s treatment in an ultrasonic bath, the material was dispersed for 20 min with a rotor/stator dispersion unit at 16'000 rpm. 800 µl of C18-TES was then added and the mixture was dispersed for an additional 3 h at 16'000 rpm. Once the reaction was completed, the dispersion was transferred into a glass centrifuge tube and the residue collected after centrifugation at 2'300 rpm (1'200 RCF/g) for 15 min. The residue was washed once with 20 ml of toluene and dried in a vacuum oven at 65 °C for 8 h.

SI1.6 Analysis Methods

Absorption spectra were recorded with a Lambda 25 spectrophotometer (PerkinElmer) with a slit width of 1 nm and a scan speed of 120 nm/min. Luminescence spectra were obtained from an LS50B (PerkinElmer) by using a slit width of 7.5 nm for oil-glass-sandwiches (OGS) and of 2.5 nm for liquid samples with a scan speed was of 120 nm / min. Both spectrometers were equipped with a custom-built sample holder for the OG samples as described in ref. [3]; Fig. 3. Fluorescence microscopy images were recorded with an Olympus BX 60 microscope equipped with a SiS CC-12 high-sensitivity CCD camera and a 100X magnification objective. Scanning electron microscopy images were recorded with a Philips XL30 with an acceleration voltage of 2 kV. - The photostability of both dye-ZL composites and pure dyes in PMMA was investigated by using thin films applied on PMMA waveguides (50 x 20 x 1.5 mm, optical grade) in an Atlas Suntest XLS+ (by Ametek Measurements and Calibration Technologies) for accelerated light stability tests. The unit was equipped with a climate control unit (SunCool) and a 1700 W xenon arc lamp. Samples were cooled so that their temperature remained at about 35 °C. The thin PMMA films were prepared by typically dispersing 10 mg to 20 mg of a dye-ZL composite in 0.5 ml of chloroform in an ultrasonic bath for 30 s. 2 ml of a PMMA solution in chloroform (33%wt) was then added to the dye-ZL suspension and the mixture was stirred for 3 h at room temperature. The mixture was degassed for 30 s in an ultrasonic bath before the film was applied

on the PMMA waveguide by means of a film applicator (Elcometer K3505) over the whole waveguide length. The wet film thickness was set to 250 µm and had an effective thickness of about 100 µm after drying. Similar films were prepared with the pure dyes dissolved in PMMA. In these cases, about 2 mg of the dye was dissolved in 5 ml of chloroform and then mixed with 2.5 g of PMMA. The mixture was stirred for 3 h at r.t. until the PMMA was dissolved completely. The rest of the procedure was carried out as described above. Absorption spectra were recorded before and after light exposure.

Leaking Tests of Sealed Dye-ZL Composites. In order to monitor the effectiveness of the sealing procedure, 15 mg of the ZL composites (both coated and uncoated) were dispersed in 5 ml of a 1:1 mixture of acetonitrile and 1-butanol. To ensure a good dispersion, the composite was submitted to an ultrasonic treatment for 5 min. The dispersion was then left stirring at r. t. for 3 h. Afterwards, the composite was centrifuged off and the supernatant was filtered over a 0.22 µm PTFE syringe filter (Membrane Solutions, MS PTFE Syringe Filter 0.22) to remove any residual small ZL particles. The amount of leaked dye was then determined by measuring the UV-Vis spectrum of the filtered supernatant. The PEI sealed dye-ZL composites usually showed no traces of dyes present in the supernatants, while dye leaking was quite significant in the unsealed case.

Determination of Loading Levels by HF Analysis. Dissolving the ZL host and measuring the UV-Vis absorption of the dyes in the resulting solution allowed determining the effective loading levels of dye-ZL composites. In a first step, 2 mg of the loaded material was dispersed in 3 ml of ethanol (Honeywell, p.a.) in a PS cuvette. 300 µl of a 4% aqueous HF solution was then added to the suspension. The ZL host was fully dissolved after 30 min, leaving a clear solution. The loading degree was then calculated from the dye concentrations obtained from the UV-Vis absorption spectrum.

Preparation of Oil-Glass-Sandwiches (OGS) for Spectroscopy. All absorption and luminescence spectra of dye-loaded ZL composites were recorded from OGS prepared as reported in ref. [3]. The samples were prepared by suspending 1 mg of dye-loaded material in 1 ml of 1-butanol. A 200 µl droplet was then deposited on a glass microscopy cover slip (Marienfeld, 24x32mm, No. 1). A steel ring with an inner diameter of 8 mm, an outer diameter of 20 mm, and equipped with an o-ring was used to confine the droplet's spread. Once the solvent was fully evaporated, the steel ring was removed and 300 µl of immersion oil was deposited on the thin ZL layer. Placing a second cover slip on top of the immersion oil and sealing the sides with base-coat nail varnish completed the sandwich.

Preparation of ZL doped PMMA films.[3] As an alternative to OGS, thin poly(methyl methacrylate) films containing dye-loaded ZL were prepared as follows. The dye-ZL composite (1.1 mg) was suspended in 1 mL of chloroform. The homogeneous suspension was then poured into a glass Petri dish (35 mm diameter) containing 1 mL of a poly(methyl methacrylate) (Aldrich, MW ca. 120'000) solution in chloroform (c = 100 mg/mL). The dish was then covered with a cardboard plate featuring a 6 mm hole, and the solvent was evaporated at rt. The solid transparent film was removed from the glass surface by soaking it in water for ca. 10 min.

Relative Quantum Yield Measurements Using OGS. In order to measure absorption or luminescence spectra, a custom-built sample holder was used. The sample holder was designed to ensure that the incident light beam hits the OGS at the same angle of 45° in both the absorption and luminescence spectrometer. This ensures a similar geometry in both measurement types, which is crucial for relative quantum yield determinations. The OGS is placed between two black anodized aluminum plates with the dye-ZL spot centered in the 6 mm hole. The whole assembly is then inserted into the sample holder slit and fixed by tightening two Teflon screws. The anodized black aluminum plates serve as beam limiters and help in avoiding reflection effects from the glass plates. For details of these measurements we refer to ref. [3].

SI1.7 Interaction of the PDIs with the inner surface of the zeolite L nanochannels

The characteristic vibronic structure of the perylene dyes, which is also present in terrylene and quaterrylene dyes, has been used to analyze their interaction with the inner surface of the ZL nanochannels. The spectra reported in Figure SI19 have been investigated in more detail by comparing the positions of the 0-0', 0-1', 0-2' and 0-3' transitions, which can be identified in diluted solutions of these dyes. We show results of this comparison in Figure SI19 and in Table SI2. The broadening of the spectra in the dye-ZL composites with respect to the solution spectra is smaller than one might expect. The uncertainty of the band positions is small for the 0-0' transition. It increases with increasing energy because the bands are not fully resolved. It also increases from tb-DXP to tb-DXT to tb-DYQ and is not much larger in the dye-ZL composites. Their energy can be sufficiently well determined to take the conclusions presented below. We should add that the same is seen for all eleven PDI's, which could be inserted into the channels of ZL.

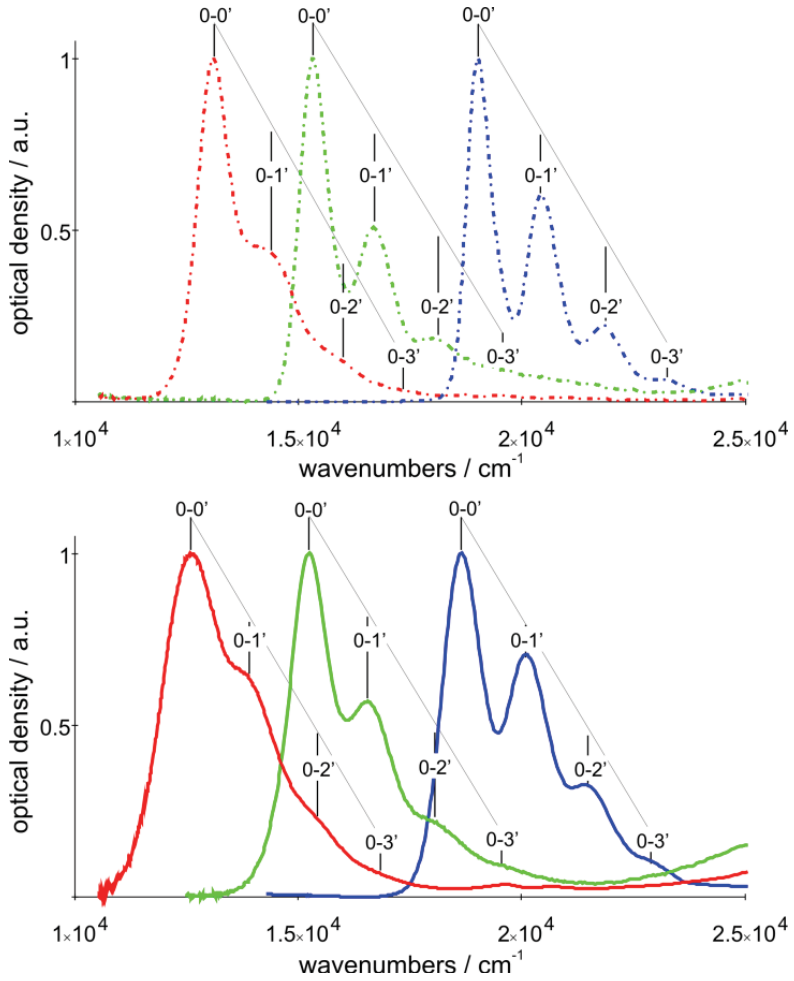


Figure SI19. Comparison of the vibronic structure of tb-DXP (blue), tb-DXT (green) and tb-DXQ (red). Upper: DCM $5x10^{-6}$ M solutions (dash-dot). Lower: dye-ZL composites (solid). Spectra were measured at room temperature.

Table SI2. Vibronic bands of tb-DXP, tb-DXT, and tb-DXQ in DCM solutions and in ZL. ΔE[ν'-(ν'+1)] is the energy difference between the 0-ν' and the 0-(ν'+1) transitions. Energies are in [cm^{-1}].

Transition	tb-DXP (DCM)	ΔE[ν'-(ν'+1)]	tb-DXT (DCM)	ΔE[ν'-(ν'+1)]	tb-DXQ (DCM)	ΔE[ν'-(ν'+1)]
0-0'	19010	---	15290	---	13020	---
0-1'	20410	1400	16670	1380	14290	1270
0-2'	21830	1420	17990	1320	15870	1580
0-3'	23150	1320	19460	1470	17240	1415

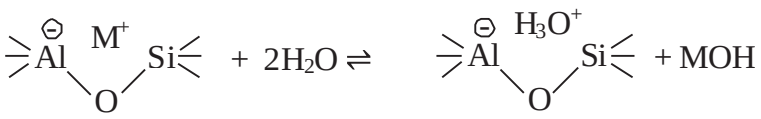
Transition	tb-DXP -ZL	ΔE[ν'-(ν'+1)]	tb-DXT -ZL	ΔE[ν'-(ν'+1)]	tb-DXQ (DCM)	ΔE[ν'-(ν'+1)]
0-0'	18660	---	15240	---	12580	---
0-1'	20080	1420	16560	1320	13790	1210
0-2'	21370	1290	17990	1430	15630	1590
0-3'	22780	1410	19460	1470	16810	1430

The comparison of the spectra of the dyes in solution and in ZL (Figure SI19) reveals that the broadening is small, that the shift of the 0-0' transition is small, and that the vibronic pattern seen in solution is preserved for the three dyes after intercalation into the nanochannels of ZL. This is remarkable. The data collected in Table SI2 allow the conclusion that the energy difference ΔE[ν'-(ν'+1)] between the 0-ν' and the 0-(ν'+1) transitions is the same in solution and in ZL, within the experimental uncertainty. These observations can be interpreted in terms of a weak interaction of the chromophore of these dyes with the inner surface of the ZL nanochannels.

It is reasonable to assume that the carbonyl groups of these dyes bind to the zeolite extra framework potassium cations, similar as was found for fluorenone (see ref. [6], which explains why the PDI based composites are easier to handle than dyes without this stabilizing interaction. This interaction does obviously not affect the photophysical properties of the chromophore.

Exchanging potassium by other monovalent alkali or divalent earth alkali cations renders the interior of the nanochannels more acidic, with the exception of Na^+, which differs little from K^+ and with the exception of Cs^+. The latter leads to less acidic conditions but it increases intersystem crossing (heavy atom effect) which is not desirable if large fluorescence quantum yield is required.

A factor which can considerably influence the fluorescence properties and also the stability of dyes inside of the ZL channels is the proton strength. This has especially been observed for HR; see ref. [7]. The acidic condition inside the nanochannels is caused by the hydrolysis reaction shown in equation SI1. It takes place at the inner surface of the ZL nanochannels. A monovalent cation M^+ binds to the ZL as charge compensating counter ion.



(1)

This reaction can be written as follows.

$ZLO^-M^+ + 2H_2O \rightleftharpoons ZLO^-H_3O^+ + M^+OH^-$ (2)

with the equilibrium constant *K*

$$K = \frac{a(ZLO^-H_3O^+)a(M^+OH^-)}{a(ZLO^-M^+)a(H_2O)^2} \quad (3)$$

We make use of the abbreviation C_0 for the total concentration of M^+ and the fact that $a(ZLO^-H_3O^+) = a(M^+OH^-)$holds, which is abbreviated as $a(H_3O^+)$. Note that the concentration of water cannot be set constant, as usually done in the description of acid-base reactions, because of the nanosized volume of the cavity, which is in the order of 0.7 nm^3. Evaluation of this information leads to the following result.

$$a(H_3O^+) = \frac{1}{2}Ka(H_2O)^2\left[\sqrt{1+4\frac{C_0}{Ka(H_2O)^2}}-1\right] \quad (4)$$

Experimentally a pH of about 3.4 is found inside of the channels for hydrated potassium exchanged ZL and 3.7 if potassium is exchanged by Cs^+ (see ref. [8]) and for additional information: *Proton activity inside the channels of zeolite L,* Albuquerque and Calzaferri see reference [9]. With this information we can calculate the equilibrium constant K. For potassium we find a value of $5.4x10^{-12}$. The value for cesium is $1.4x10^{-12}$. This result is important because it explains why the proton activity decreases with decreasing potassium concentration and it also decreases with decreasing amount of water present in the cavities. Both factors are favorably influenced when substituting some of the 3.6 exchangeable potassium cations per u.c. with IMZ^+, because the latter not only decreases the amount of potassium present, it also reduces the space available for water molecules, and it acts by itself as a weak base. We found that exchanging 0.5 up to one potassium cation improves the fluorescence yield of HR considerably. The space occupied by up to one IMZ^+ per u.c. does not prevent the dyes used in this study from entering. We assume that IMZ^+ sticks to the inner surface of the channels in a similar way as observed for methyl viologen (*Characterization of Methylviologene in the Channels of Zeolite L,* Bärlocher, Calzaferri et al.[10]. Larger amounts of IMZ^+, however, occupy a too large amount of space and therefore prevent the dyes from entering. IMZ^+ must be added prior to the dyes because the dyes do not allow the IMZ^+ to pass. For an explanation of this blocking mechanism we refer to [11].

SI1.8 FRET efficiency

The FRET efficiency is determined by calculating the ratio of the acceptor emission $Acceptor(\bar{\nu})$ and the total emission $total(\bar{\nu})$

$$FRET_{eff} = \frac{\int Acceptor(\bar{\nu})d\bar{\nu}}{\int total\,(\bar{\nu})d\bar{\nu}}$$

The acceptor emission is determined by subtracting the donor emission, which is measured separately, from the spectrum of the composite. The procedure is illustrated in Figure SI20 using the data reported in Figure 7 (see paper) for the tb-DXP,HR-ZL.01,.23(0.5IMZ$^+$) composite. We show the spectra in wavelength; for the calculations, however, wavenumbers have been used. Fluorescence quantum yields have been determined as described in ref. [3].

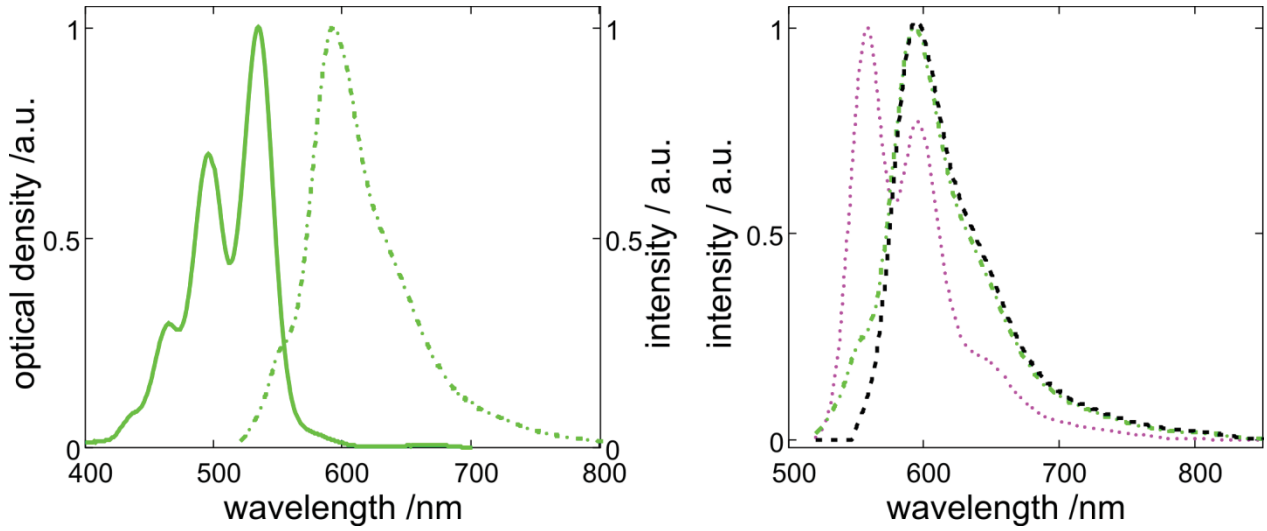


Figure SI20. Determination of FRET efficiencies. Left: Absorption (solid) and fluorescence (dash-dot) spectra of tb-DXP,HR-ZL.01,.23(0.5IMZ$^+$); see also Figure 7 (in the paper). Right: The fluorescence spectrum of the tb-DXP-ZL sample, (pink, dot) is subtracted from the spectrum of the DXP,HR-ZL.01,.23(0.5IMZ$^+$) composite (green, dash-dot) resulting in the spectrum of the acceptor (black, dash).

SI2. References

[1] J. Liu, Y. Li, Y. Li, N. Hu, *J. Appl. Polym. Sci.* **2008**, *109*, 700-707.

[2] B. L. Small, R. Rios, E. R. Fernandez, D. L. Gerlach, J. A. Halfen, M. J. Carney, *Organometallics* **2010**, *29*, 6723-631.

[3] A. Devaux, G. Calzaferri, I. Miletto, P. Cao, P. Belser, D. Brühwiler, O.Khorev, R. Häner, A. Kunzmann, *J. Phys. Chem. C* **2013**, *117*, 23034−23047.

[4] M. Pistolozzi, C. Franchini, F. Corbo, M. Muraglia, M. De Giorgi, G. Felix, C. Bertucci, *J. Pharm. Biomed. Anal*. **2010**, *53*, 179-185.

[5] A. Zabala Ruiz, D. Brühwiler, T. Ban, G. Calzaferri, *Monatshefte für Chemie* **2005**, *136*, 77-89.

[6] A. Devaux, G. Calzaferri, P. Belser, P. Cao, D. Brühwiler, A. Kunzmann, *Chem. Mater.* **2014**,

26, 6878-6885.

[7] E. Fois, G. Tabacchi, G. Calzaferri, *J. Phys. Chem. C* **2010**, *114*, 10572-10579.

[8] G. Calzaferri, S. Huber, H. Maas, C. Minkowski, *Angew. Chem. Int. Ed.* **2003**, *42*, 3732-3758.

[9] R. Q. Albuquerque, G. Calzaferri, *Chem. Eur. J.* **2007**, *13*, 8939-8952.

[10] B. Hennessy, S. Megelski, C. Marcolli, V. Shklover, C. Bärlocher, G. Calzaferri, *J. Phys. Chem. B* **1999**, *103*, 3340-3351.

[11] D. Brühwiler, N. Gfeller, G. Calzaferri, *J. Phys. Chem. B* **1998**, *102*, 2923-2929.