SUPPLEMENTARY INFORMATION

Fluorescence Quenching and Enhancement of Vitrifiable Oligofluorenes End-Capped with Tetraphenylethene (TPE)

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CONTENTS

1. EXPERIMENTAL.

All commercially available starting materials, reagents and solvents were used as supplied, unless otherwise stated, and were purchased from Aladdin, Acros Organics and Puyang Huicheng Chemical Co. Ltd. All reactions were carried out under a dry nitrogen atmosphere unless water was used as a solvent or reagent and the temperatures were measured externally. For brominations no nitrogen was used to prevent contamination of the nitrogen line. $Pd(PPh_3)_4$ was synthesised according to the literature with slight modification.[1] DMF was dried over $CaCl_2$ with stirring overnight followed by distillation under reduced pressure. Tri(isopropyl)borate was distilled over sodium wire. THF was dried using sodium wire and benzophenone indicator. DCM was dried over calcium sulfate and distilled. Reported yields are isolated yields. Purification of most intermediates and all final products was accomplished in most cases by gravity column chromatography, using silica gel. For qualitative purity tests of all intermediates and final products, a single spot (visualised using UV-light at 254 nm and 365 nm) was obtained. Elemental analysis was used for quantitative purity checks of all final products. ^{1}H NMR spectra are reported in parts per million (PPM) relative to tetramethylsilane as an internal standard. For F1-PP the residual solvent peak of CH_2Cl_2 in CD_2Cl_2 was taken as the internal standard. Tetraphenylethene was synthesised following a literature McMurry reaction[2] using benzophenone and oligo-5-fluorene was synthesised according to the previous literature[3], with ^{1}HNMR and mass spectra in good agreement. 2-Bromo-9,9-dioctylfluorene was synthesised according to the previous literature with slight modification (83.8 % yield).[4]

a) INSTRUMENTATION.

DSC: PerkinElmer Instruments (Diamond DSC)
TG/DTA: SII Exstar 6000, (TG/DTA 6300).
UV-VIS: Shimadzu UV-VIS-NIR Spectrophotometer (UV-3600)
PL: Edinburgh instruments (FLSP920 spectrometers)
^{1}HNMR: (Bruker AV400).
Mass Spectrometry: Agilent (1100 LC/MSD Trap), MALDI-TOF
Elemental Analysis: Elementar (Vario Micro-cube).
X Ray Diffraction: PANalytical B.V. (X' Pert PRO).
Atomic Force Microscopy: Bruker (Veeco Dimension^{TM} 3100 SPM).
Fluorescence Microscopy: Olympus BX61.
GC-MS: PerkinElmer ELAN DRC-e.
HPLC: Waters 1525 Binary HPLC Pump with 2489 UV-VIS Detector.

(b) SYNTHESIS.

2,7-Dibromo-9,9-dioctylfluorene (2).

A solution of 2,7-dibromofluorene (**1**, 20.0 g, 0.0617 mol), pulverised KOH (20.8 g, 0.3704 mol), KI (1.02 g, 0.0062 mol) in DMSO (200 ml) was cooled using an ice/H_2O/salt bath and stirred for 10 minutes. 1-Bromooctane (29.8 g, 0.1543 mol) was slowly added over a period of 30 minutes, allowed to warm to room temperature and stirred overnight. The reaction mixture was poured into ice-water (200 ml) and the organics extracted using hexane (2 x 200 ml). The organic extracts were combined, washed with brine (3 x 200 ml), water (1 x 100 ml), dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude product was recrystallised using ethanol and filtered to yield a white crystalline solid (28.5 g, 84.1 %).
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.57 (quint, 4H), 0.83 (t, 6H), 1.05-1.19 (m, 20H), 1.89-1.93 (m, 4H), 7.44-7.46 (m, 4H), 7.51 (d, 2H, J = 8.8 Hz).
MS m/z (ACPI): 548.4 (M^+).

9,9-Dioctylfluorene-2-boronic acid (4).

n-Butyllithium (2.5 M in hexanes, 15.4 ml, 0.0384 mol) was added slowly to a solution of 2-bromo-9,9-dioctylfluorene (**3**, 15.0 g, 0.0320 mol) in dry THF (250 ml) at approximately -78 ^{o}C. The resulting reaction mixture was stirred at the same temperature for one hour and subsequently tri(isopropyl)borate (12.0 g, 0.0640 mol) was added to quench the lithium salt. The reaction was warmed to room temperature and stirred overnight. Dilute HCl (20% v/v, 200 ml) was added and stirred for one hour. The organics were extracted into diethylether (2 x 200 ml), washed with water (1 x 200 ml), dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude boronic acid was purified by gravity column chromatography (silica gel) using gradient elution (hexane 100%, ethyl acetate:hexane; 10%:90%, 20%:80%, 100 % and finally acetone 100%) to yield a white powder (5.54 g, 39.9 %).
^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ (ppm) 0.48 (quint, 4H), 0.77 (t, 6H), 1.04-1.18 (m, 20H), 1.93-1.97 (m, 4H), 7.30-7.32 (m, 2H), 7.41-7.43 (m, 1H), 7.73-7.83 (m, 4H), 7.99 (br. s, 2H, -OH).
IR ν_{max}/cm^{-1}: 3419, 3061, 2926, 2860, 1607, 1568, 1490, 1462, 1414, 1326, 1221, 1114, 1079, 916, 837, 743, 698.

2,2'-Bis(9,9-dioctylfluorene) (5).

9,9-Dioctylfluorene-2-boronic acid (**4**, 2.70 g, 0.0062 mol), 2-bromo-9,9-dioctylfluorene (**3**, 2.65 g, 0.0056 mol), aqueous Na_2CO_3 (1.20 g, 0.0113 mol) and DME (80 ml) were all added to a 3-neck round bottomed flask and the system was evacuated, with the aid of a vacuum pump, and filled with nitrogen 3 times. Subsequently, $Pd(PPh_3)_4$ (0.33 g, 0.28 mmol) was added and the reaction mixture was refluxed overnight. Water was added and the organics extracted into

DCM (2 x 100 ml), dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude product was purified by gravity column chromatography (silica gel) using 100 % hexane to yield a white powder (3.16 g, 71.8 %).
^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.71 (quint, 8H), 0.80 (t, 12H), 1.07-1.20 (m, 40H), 1.97-2.08 (m, 8H), 7.29-7.37 (m, 6H), 7.61 (s, 2H), 7.63 (d, 2H, *J* = 7.6 Hz), 7.73 (2H, d, *J* = 8.0 Hz), 7.76 (d, 2H, J = 8.0 Hz).
MS m/z (APCI): 779.8 (M^+).

2,2’:7’,2”-Ter(9,9-dioctylfluorene) (6).

9,9-Dioctylfluorene-2-boronic acid (**4**, 2.70 g, 0.0062 mol), 2,7-dibromo-9,9-dioctylfluorene (**2**, 1.48 g, 0.0027 mol), aqueous Na_2CO_3 (0.86 g, 0.0081 mol) and DME (50 ml) were all added to a 3-neck round bottomed flask and the system was evacuated, with the aid of a vacuum pump, and filled with nitrogen 3 times. Subsequently, $Pd(PPh_3)_4$ (0.16 g, 0.13 mmol) was added and the reaction mixture was refluxed overnight. Water (100 ml) was added and the organics extracted into DCM (2 x 100 ml), dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude product was purified by gravity column chromatography (silica gel) using 100% hexane to yield a white powder (2.41 g, 76.5 %).
^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.70 (m, 12H), 0.79 (overlapping t, 18H), 1.08-1.19 (m, 60H), 2.00-2.12 (m, 12H), 7.33-7.36 (m, 6H), 7.64-7.67 (m, 8H), 7.74-7.80 (m, 6H).
MS m/z (APCI): 1168.2 (M^+).

7,7’-Dibromo-2,2'-bis(9,9-dioctylfluorene) (7).

Bromine (0.90 g, 0.0056 mol) was added slowly to a solution of 2,2'-bis(9,9-dioctylfluorene) (**5**, 2.00 g, 0.0026 mol) in dry DCM (20 ml) at room temperature. The reaction was allowed to react for a total of 3 hours (or until TLC analysis confirmed complete bromination). Acetone (5 ml) was added and the solvents were removed using a rotary evaporator. Trituration using ethanol and subsequent filtration yielded a white solid (2.12 g, 88.3 %).
^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.69 (quint, 8H), 0.81 (t, 12H), 1.08-1.21 (m, 40H), 1.95-2.05 (m, 8H), 7.46-7.47 (m, 2H), 7.48 (s, 2H), 7.57 (s, 2H), 7.58 (d, 2H, *J* = 8.0 Hz), 7.62 (dd, 2H, *J* = 1.2 Hz, 8.0 Hz), 7.73 (d, 2H, *J* = 8.0 Hz).
MS m/z (APCI): 937.6 (M^+).

7,7”-Dibromo-2,2’:7’,2”-ter(9,9-dioctylfluorene) (8).

Bromine (0.28 g, 1.75 mmol) was added slowly to a solution of 2,2’:7’,2”-ter(9,9-dioctylfluorene) (**6**, 0.93 g, 0.80 mmol) in dry DCM (15 ml) at room temperature. The reaction was allowed to react overnight (or until TLC analysis confirmed complete bromination). Acetone (5 ml) was added and the solvents were

removed using a rotary evaporator. Trituration using ethanol and subsequent filtration yielded a white solid (0.92 g, 86.8 %).
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.71 (quint, 12H), 0.77-0.83 (overlapping t, 18H), 1.09-1.21 (m, 60H), 1.97-2.11 (m, 12H), 7.46 (s, 2H), 7.49 (s, 2H), 7.59-7.66 (m, 10H), 7.75 (d, 2H, *J* = 8.0 Hz), 7.81 (d, 2H, *J* = 8.0 Hz).
MS m/z (APCI): 1326.1 (M^+).

1-(4-Bromophenyl)-1,2,2-triphenylethylene (10).

n-Butyl lithium (2.5 M in hexanes, 7.35 ml, 0.0184 mol) was slowly added to a solution of diphenylmethane (**9**, 3.09 g, 0.0184 mol) in dry THF (40 ml) with the aid of a ice/salt/water bath. The resulting orange-red reaction mixture was stirred for 2 hours to complete the formation of the lithium salt. Subsequently, the lithium salt was slowly added to a cooled solution of 4-bromobenzophenone (4.00 g, 0.0153 mol) in dry THF (40 ml) and the resulting reaction mixture was warmed to room temperature and stirred for a further 4 hours. Subsequently, most of the THF was removed using a rotary evaporator, followed by a standard aqueous workup using dichloromethane, affording the corresponding alcohol. The crude product was azeotropically dried using toluene and used directly in the next step without purification.
The tertiary alcohol was dissolved in toluene (100 ml) and refluxed with *p*-toluene sulphonic acid (1.00 g) for 6 hours, using a Dean-Stark trap to assist water removal. The reaction mixture was cooled to room temperature and water was added to remove the *p*-toluene sulphonic acid. The toluene layer was concentrated under reduced pressure, with concomitant drying, and the crude product (first adsorbed on silica gel-dry loading) purified by gravity column chromatography (silica gel) using petroleum ether to yield a white powder (4.59 g, 72.9 %, calculated from 4-bromobenzophenone).
^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ (ppm) 6.97 (d, 2H, *J* = 8.8 Hz), 7.02-7.06 (m, 6H), 7.11-7.17 (m, 9H), 7.30 (d, 2H, *J* = 8.8 Hz).
MS m/z (EI): 410 (M-1) 412 (M+1).

4-(1,2,2-Triphenylvinyl)phenylboronic acid (11).

n-Butyllithium (2.5 M in hexanes, 6 ml, 0.015 mol) was added slowly to a solution of 1-(4-bromophenyl)-1,2,2-triphenylethylene (**10**, 4.11 g, 0.01 mol) in dry THF (150 ml) at approximately -78 ^{o}C. The resulting reaction mixture was stirred at the same temperature for three hours and subsequently tri(isopropyl)borate (3.76 g, 0.02 mol) was added to quench the lithium salt. The reaction mixture was warmed to room temperature and stirred overnight. Dilute HCl (20% v/v, 200 ml) was added and stirred for one hour. After the THF had evaporated overnight the resulting white precipitate was filtered and washed with water (1 x 200 ml), The crude boronic acid was purified by gravity column chromatography (silica gel) using DCM and acetone (10:1) to yield a white powder (3.02 g, 80.3 %).
^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ (ppm) 6.99-7.11 (m, 19H), 7.84 (d, 2H).

IR ν_{max}/cm^{-1}: 3368 (br), 3075, 3052, 3023, 2923, 1953, 1816, 1760, 1702, 1604, 1364, 1075, 1023, 822, 757, 699.

F1-TPE

2,7-Dibromo-9,9-dioctylfluorene (**2**, 0.44 g, 0.81 mmol), 4-(1,2,2-triphenylvinyl)phenylboronic acid (**11**, 0.70 g, 0.0019 mol), tetrabutylammonium hydrogen sulfate (0.03 g, 0.09 mmol) and K_2CO_3 (0.55 g, 0.0040 mol) were added to a toluene:H_2O (20 ml:10 ml) mixture and the system was evacuated, with the aid of a vacuum pump, and filled with nitrogen three times. $Pd(PPh_3)_4$ (0.05 g, 0.04 mmol) was added and again the reaction vessel was evacuated and purged with nitrogen. The reaction was heated at 90 ^{o}C for 24 hours. Water (20 ml) and toluene (10 ml) were added and the toluene layer separated and subsequently removed using a rotary evaporator. The crude product was purified by gravity column chromatography (silica gel) using gradient elution (hexane 100 % to DCM:hexane 20 %:80 %) to yield a yellow-green solid (0.43 g, 51.2 %).
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.65 (quint, 4H), 0.79 (t, 6H), 1.03-1.18 (m, 20H), 1.96-2.00 (m, 4H), 7.06-7.14 (m, 34H), 7.43 (d, 4H, *J* = 8.4 Hz), 7.52 (m, 4H), 7.70 (d, 2H, *J* = 8.0 Hz).
MS m/z (APCI): 1051.9 (M^+).
Elemental analysis, expected (%): C 92.52, H 7.48, obtained (%): C 92.27, H 7.33.

F2-TPE

7,7’-Dibromo-2,2'-bis(9,9-dioctylfluorene) (**7**, 1.00 g, 0.0011 mol), 4-(1,2,2-triphenylvinyl)phenylboronic acid (**11,** 0.92 g, 0.0025 mol), tetrabutylammonium hydrogen sulfate (0.04 g, 0.11 mmol) and K_2CO_3 (0.74 g, 0.0053 mol) were added to a toluene:H_2O (20 ml:10 ml) mixture and the system was evacuated, with the aid of a vacuum pump, and filled with nitrogen 3 times. $Pd(PPh_3)_4$ (0.06 g, 0.05 mmol) was added and again the reaction vessel was evacuated and purged with nitrogen. The reaction was heated at 90 ^{o}C for 24 hours. Water (20 ml) and toluene (10 ml) were added and the toluene layer separated and subsequently removed using a rotary evaporator. The crude product was purified by gravity column chromatography (silica gel) using gradient elution (hexane 100 % to DCM:hexane 20 %:80 %) to yield a yellow-green solid (0.46 g, 29.9 %).
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.77-0.81 (m, 20H), 1.07-1.19 (m, 40H), 2.01-2.05 (m, 8H), 7.04-7.16 (m, 34H), 7.45 (d, 4H, *J* = 8.4 Hz), 7.54 (overlapping d, 2H), 7.56 (d, 2H, *J* = 1.2 Hz), 7.61 (overlapping d, 2H), 7.64 (dd, 2H, *J* = 1.2 Hz, 7.6 Hz), 7.73 (m, 4H).
MS m/z (APCI): 1440.9 (M^+).
Elemental analysis, expected (%): C 91.74, H 8.26, obtained (%): C 91.67, H 8.24.

F3-TPE

7,7’-Dibromo-2,2’:7’,2’’-ter(9,9-dioctylfluorene) (**8**, 0.34 g, 0.26 mmol), 4-(1,2,2-triphenylvinyl)phenylboronic acid (**11,** 0.22 g, 0.59 mmol), tetrabutylammonium hydrogen sulfate (0.009 g, 0.03 mmol) and K_2CO_3 (0.18 g, 0.0013 mol) were added to a toluene:H_2O (10 ml:5 ml) mixture and the system was evacuated, with the aid of a vacuum pump, and filled with nitrogen 3 times. $Pd(PPh_3)_4$ (0.015 g, 0.015 mmol) was added and again the reaction vessel was evacuated and purged with nitrogen. The reaction was heated at 90 ^{o}C for 24 hours. Water (20 ml) and toluene (10 ml) were added and the toluene layer separated and subsequently removed using a rotary evaporator. The crude product was purified by gravity column chromatography (silica gel) using gradient elution (hexane 100 % to DCM:hexane 20 %:80 %) to yield a yellow-green solid (0.26 g, 55.3 %).
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.77-0.80 (m, 30H), 1.07-1.19 (m, 60H), 2.03-2.11 (m, 12H), 7.05-7.14 (m, 34H), 7.44 (d, 4H, *J* = 8.4 Hz), 7.54 (overlapping d, 2H), 7.56 (overlapping d, 2H), 7.61-7.66 (m, 8H), 7.73 (d, 2H, *J* = 8.4 Hz), 7.77 (d, 2H, *J* = 7.6 Hz), 7.80 (d, 2H, *J* = 7.6 Hz).
MS m/z (APCI): 1828.6 (M^+).
Elemental analysis, expected (%): C 91.29, H 8.71, obtained (%): C 91.11, H 8.75.

2-Bromo-7-iodo-9H-fluorene (13)

2-Bromo-9H-fluorene (**12**, 4.90 g, 0.0200 mol), iodine (2.13 g, 0.0084 mol), and potassium iodate (1.02 g, 0.0048 mol) were placed into a 250 ml flask. Water (4 ml), glacial acetic acid (85 ml) were added and the flask was heated in a 90 ^{o}C oil bath under a nitrogen atmosphere. After 2h of stirring，the reaction mixture was cooled to room temperature, at which point a light yellow precipitate formed. After filtration，the precipitate was washed with acetic acid and water, then recrystallised from a DCM/methanol mixture to yield a white crystalline solid (6.00 g, 81.1 %).
Melting point: 181.5-182.8 ^{o}C.
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.84 (s, 2H), 7.48-7.51 (m, 2H), 7.60 (d, 1H, *J* = 8.0 Hz), 7.66 (s, 1H), 7.70 (d, 1H, *J* = 8.0 Hz), 7.87 (s, 1H),
MS m/z (APCI): 372.1 (M+1) 370.2 (M-1).

2-Bromo-9,9-dioctyl-7-iodo-9H-fluorene (14)

NaOH (50 % aqueous solution, 5 mL) was added drop-wise to a suspension of 2-bromo-7-iodo-9H-fluorene (**13**, 5.00 g, 0.0135 mol) in DMSO (50 ml) under a nitrogen atmosphere. A bright red solution was formed, which darkened quickly with time to a maroon colour. The solution was stirred vigorously as 1-bromooctane (6.50 g, 0.0337 mol) was added and the solution turned purple. After 1 day stirring at room temperature the reaction mixture was poured into hexane (500 ml), washed with water (100 ml), brine (100 ml) and more water (100 ml). The crude product was further extracted by washing the water layers with additional hexane (100 ml), then repeating the above procedures. The combined organic layers were dried ($MgSO_4$), filtered, and concentrated under reduced pressure to yield a viscous yellow oil. The oil was dissolved in a minimum amount of gently warmed isopropanol and allowed to cool slowly to room temperature to yield amber crystals (7.48 g, 93.3 %).

^{1}HNMR($CDCl_3$): δ (ppm) 0.59 (quint, 4H), 0.85 (t, 6H), 1.05-1.26 (m, 20H), 1.88-1.92 (m, 4H), 7.40 (d, 1H, *J* = 7.6 Hz), 7.44 (s, 1H), 7.46 (d, 1H, *J* = 1.6 Hz), 7.52 (d, 1H, *J* = 8.0 Hz), 7.65 (s, 1H), 7.66 (d, 1H, *J* = 1.6 Hz).

MS m/z (APCI): 596.2 (M+1) 594.3 (M-1).

2-Bromo-9,9-dioctyl-7-(4-(1,2,2-triphenylethylenyl)phenyl)-9H-fluorene (15)

To a mixture of 2-bromo-9,9-dioctyl-7-iodo-9H-fluorene (**14**, 1.62 g, 0.0027 mol), 4-(1,2,2-triphenylvinyl)phenylboronic acid (**11**, 1.00 g, 0.0027 mol), K_2CO_3 (0.75 g, 0.0054 mol), toluene (20 ml), water (10 ml) and tetrabutylammonium hydrogen sulfate (0.09 g, 0.27 mmol) was added and the system was flushed with nitrogen. $Pd(PPh_3)_4$ (0.16 g, 0.14 mmol) was added and the reaction mixture was stirred under nitrogen for 20 hours at 90 ^{o}C. After cooling down, the reaction mixture was extracted with toluene, washed with water three times, dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude product was chromatographed on silica gel eluting with DCM/hexane (1:10) to yield a yellow-green solid (1.44 g, 66.1 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.61 (quint, 4H), 0.81 (t, 6H), 1.09-1.25 (m, 20H), 1.90-1.98 (m, 4H), 7.03-7.18 (m, 17H), 7.41-7.56 (m, 7H), 7.66 (d, 1H, *J* = 7.6 Hz).

MS m/z (APCI): 801.4 (M+1) 799.5 (M-1).

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolane-2-yl)-9,9-dioctyl-7-(4-(1,2,2-triphenyl ethylenyl)phenyl)-9H-fluorene (16)

2-Bromo-9,9-dioctyl-7-(4-(1,2,2-triphenylethylenyl)phenyl)-9H-fluorene (**15**, 1.20 g, 0.0015 mol) and bis(pinacolato)diboron (0.48 g, 0.0019 mol) were mixed together with potassium acetate (0.39 g, 0.0040 mmol) in dry dioxane (15 ml) under a nitrogen atmosphere. $PdCl_2$(dppf) catalyst (0.05 g, 0.08 mmol) was added and the reaction mixture was stirred under a nitrogen atmosphere for 16 hours at 70 ^{o}C, and a further 16 hours at 90 ^{o}C. After cooling down, the reaction mixture was extracted with DCM, washed with water three times, dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude product was chromatographed on silica gel eluting with DCM/hexane (3:7) to yield a yellow-green solid (1.05 g, 82.7 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.60 (quint, 4H), 0.81 (t, 6H), 1.08-1.25 (m, 20H), 1.40 (s, 12H), 1.96-2.02 (m, 4H), 7.05-7.16 (m, 17H), 7.43 (d, 2H, *J* = 8.4 Hz), 7.53 (d, 2H, *J* = 9.2 Hz), 7.69-7.74 (m, 3H), 7.81 (d, 1H, *J* = 7.2 Hz).

MS m/z (APCI): 847.7(M^+).

F4-TPE

7,7’-Dibromo-2,2'-bis(9,9-dioctylfluorene) (**7**, 0.10 g, 0.11 mmol), 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-9,9-dioctyl-7-(4-(1,2,2-triphenylethylenyl)phenyl)-9H-fluorene (**16,** 0.22 g, 0.26 mmol), tetrabutylammonium hydrogen sulfate (4.0 mg, 0.011 mmol) and K_2CO_3 (0.07 g, 0.53 mmol) were added to a

toluene:H_2O (5 ml:2.5 ml) mixture and the system was evacuated, with the aid of a vacuum pump, and filled with nitrogen 3 times. $Pd(PPh_3)_4$ (6.2 mg, 0.0053 mmol) was added and again the reaction vessel was evacuated and purged with nitrogen. The reaction was heated at 90 ^oC for 24 hours. Water (20 ml) and toluene (10 ml) were added and the toluene layer separated and subsequently removed using a rotary evaporator. The crude product was purified by gravity column chromatography (silica gel) eluting with DCM:hexane (1:9) to yield a yellow-green solid (0.16 g, 66.7 %).
^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.73-0.87 (m, 40H), 1.08-1.25 (m, 80H), 2.04-2.13 (m, 16H), 7.05-7.18 (m, 34H), 7.46 (d, 4H, *J* = 8.4 Hz), 7.55-7.70 (m, 16H), 7.75-7.82 (m, 8H).
MS m/z (MALDI-TOF): 2217.1 (M^+).
Elemental analysis, expected (%): C 91.00, H 9.00, obtained (%): C 90.91, H 8.96.

F5-TPE

7,7’-Dibromo-2,2’:7’,2’’-ter(9,9-dioctylfluorene) (**8**, 0.14 g, 0.11 mmol), 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-9,9-dioctyl-7-(4-(1,2,2-triphenylethylenyl)phenyl)-9H-fluorene (**16,** 0.20 g, 0.23 mmol), tetrabutylammonium hydrogen sulfate (4.0 mg, 0.011 mmol) and K_2CO_3 (0.07 g, 0.53 mmol) were added to a toluene:H_2O (5 ml:2.5 ml) mixture and the system was evacuated, with the aid of a vacuum pump, and filled with nitrogen 3 times. $Pd(PPh_3)_4$ (6.18 g, 0.00535 mmol) was added and again the reaction vessel was evacuated and purged with nitrogen. The reaction was heated at 90 ^oC for 24 hours. Water (20 ml) and toluene (10 ml) were added and the toluene layer separated and subsequently removed using a rotary evaporator. The crude product was purified by gravity column chromatography (silica gel) eluting with DCM:hexane (1:9) to yield a yellow-greeen solid (0.20 g, 71.4 %).
^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.76-0.85 (m, 50H), 1.09-1.26 (m, 100H), 2.05-2.12 (m, 20H), 7.06-7.17 (m, 34H), 7.46 (d, 4H, *J* = 8.0 Hz), 7.56-7.71 (m, 20 H), 7.75-7.85 (m, 10H).
MS m/z (MALDI-TOF):2605.3 (M^+).
Elemental analysis, expected (%): C 90.79, H 9.21, obtained (%): C 90.59, H 9.09.

9-(4-Bromophenyl)-10-phenylphenanthrene (17)

A solution of 1-(4-bromophenyl)-1,2,2-triphenylethylene (**10**, 1.00 g, 0.0024 mol) in dry DCM (200 ml) was cooled with the aid of an ice/salt/water bath. After 15 minutes methanesulphonic acid (20 ml) was added and stirred for a further 5 minutes. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (0.61 g, 0.0027 mol) was added slowly in powder form over a period of 30 minutes and the reaction mixture was stirred for a further 6 hours under a nitrogen atmosphere. The work-up procedure involved washing the DCM with a saturated aqueous solution of sodium bicarbonate (100 ml) to remove the reduced hydroquinone and washing further with water (2 x 100 ml).

The organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude solid was adsorbed on silica gel and chromatographed using silica gel and petroleum ether as the eluent. For the sake of speed 20% DCM in petroleum ether was finally used as the eluent to yield a yellowish powder, which was further washed with ethanol to yield a white powder (0.77 g, 77 %).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (d, 2H, *J* = 8.8 Hz), 7.15-7.35 (m, 5H), 7.40-7.44 (m, 2H), 7.53-7.60 (m, 4H), 7.70-7.75 (m, 2H), 8.82 (d, 2H).
MS m/z (GC-MS): 9-(4-chlorophenyl)-10-phenylphenanthrene; 11.9 mins, 9 %, M^+=364.1 and 9-(4-bromophenyl)-10-phenylphenanthrene; 12.9 mins, 91 %, (M+1) 410.1 and M(-1)=408.1.

2,2'-(9,9-Dioctyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18)

A solution of 2,7-dibromo-9,9-dioctylfluorene (**2**, 10.0 g, 0.0182 mol) in dry THF (200 ml) was cold to approximately -78 °C with the aid of a solid CO_2/acetone bath. After stirring for 10 minutes n-butyl lithium (2.5 M, 16.0 ml, 0.0401 mol) was added slowly over a period of 20 minutes. The reaction mixture was stirred at approximately -78 °C for a further one hour, quenched with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7.80 g, 0.0419 mol) and allowed to warm to room temperature with subsequent stirring overnight. Water (100 ml) was added and the organics extracted into diethyl ether (2 x 150 ml). The ethereal extracts were washed with water (1 x 200 ml), dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude product was purified by gravity column chromatography (silica gel) using gradient elution (DCM:hexane 10%:90%, 20%:80%, 30%:70%, 50%:50% and 100% DCM) and finally recrystallised from ethanol to yield white crystalline needles (4.08 g, 34.9 %).
^{1}H NMR (400 MHz, $CDCl_3$): δ 0.55 (quint, 4H), 0.80 (t, 6H), 1.04-1.20 (m, 20H), 1.39 (s, 24H), 1.97-2.01 (m, 4H), 7.71-7.74 (m, 4H), 7.80 (d, 2H, *J* = 8.0 Hz).
MS m/z (ACPI): 642.6 (M^+).

F1-PP

2,2'-(9,9-Dioctyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**18**, 0.46 g, 0.72 mmol), 9-(4-bromophenyl)-10-phenylphenanthrene (**17**, 0.65 g, 0.0016 mol) and K_3PO_4 (0.76 g, 0.0036 mmol) were added to dry DMF (10 ml) and the system was evacuated, with the aid of a vacuum pump, and filled with nitrogen three times. $Pd(PPh_3)_4$ (0.04 g, 0.04 mmol) was added and again the reaction vessel was evacuated and purged with nitrogen. The reaction was heated at 100 °C for 2 days. Water (20 ml) and DCM (10 ml) were added and the DCM layer separated and subsequently removed using a rotary evaporator. The crude product was adsorbed on silica gel and purified by gravity column chromatography (silica gel) using DCM:hexane (2:8) to yield a light yellow solid, which was further washed with DCM to yield a white powder (0.20 g, 26.7 %).

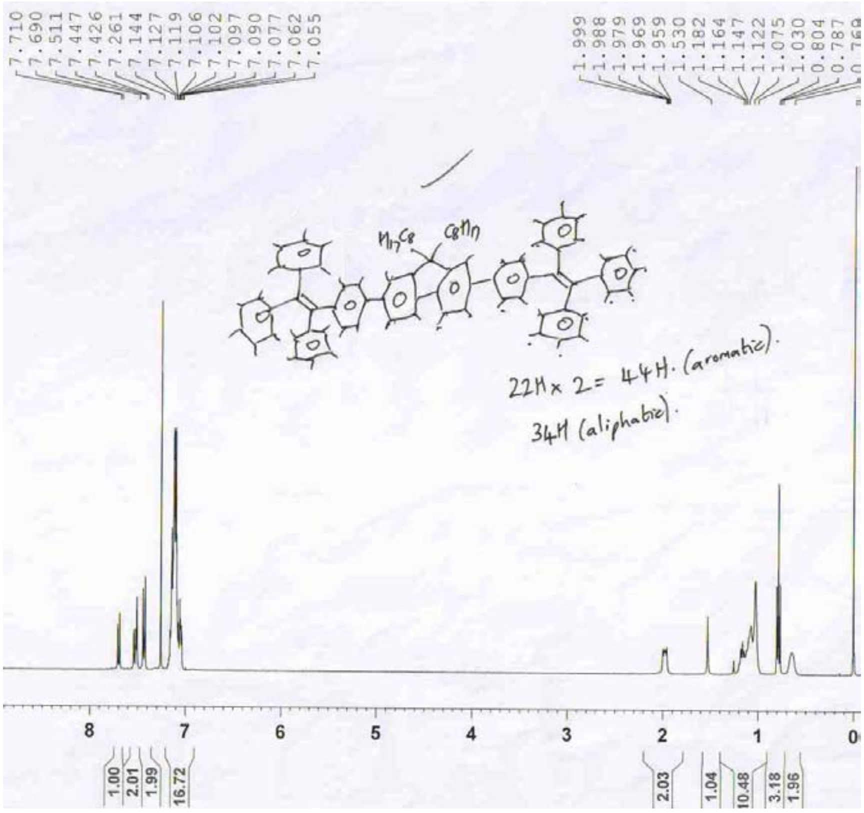
^{1}H NMR (400 MHz, $CDCl_3$): δ 0.61-0.74 (m, 4H), 0.80 (t, 6H), 1.08-1.22 (m, 20H), 2.06-2.10 (m, 4H), 7.20-7.38 (m, 14H), 7.46-7.75 (m, 20H), 7.80 (d, 2H, *J* = 8.0 Hz), 8.85 (d, 4H, *J* = 8.3 Hz).

MS m/z (APCI): 1047.9 (M^+).

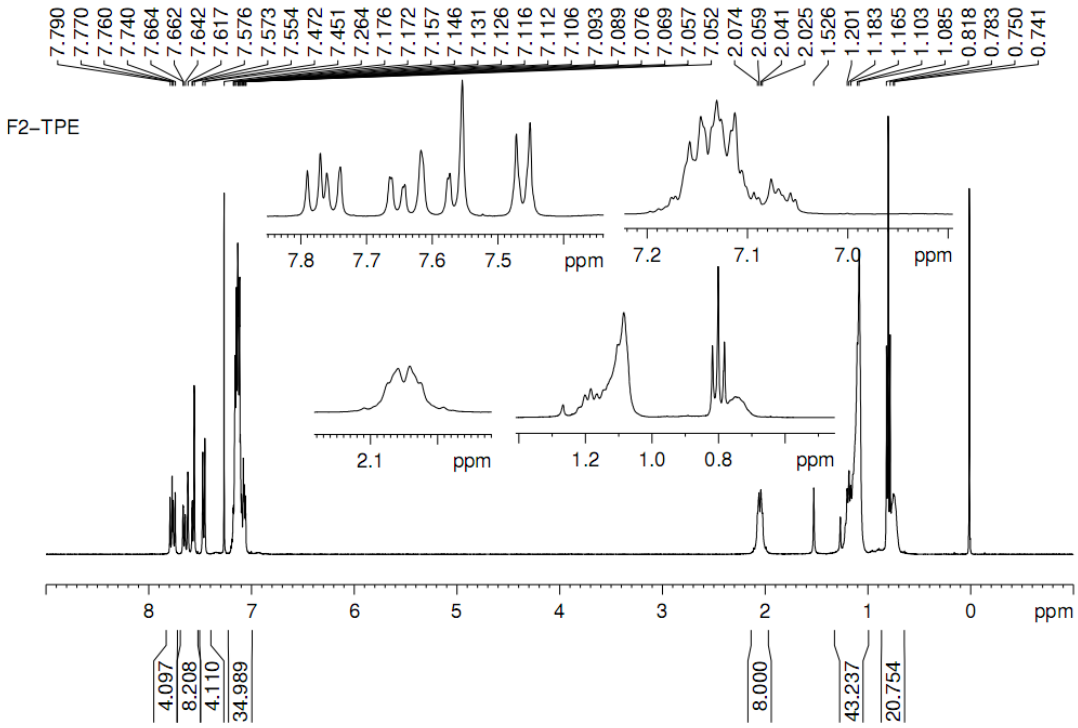
HPLC = 96.4 % (2:8, DCM:hexane, CN column).

2. ^{1}HNMR SPECTRA OF F(1-5)TPE and F1-PP.

F1-TPE



F2-TPE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7.093
7.089
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7.057
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2.059
2.041
2.025
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1.201
1.183
1.165
1.103
1.085
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0.783
0.750
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7.7
7.6
7.5
ppm
7.2
7.1
7.0
ppm
2.1
ppm
1.2
1.0
0.8
ppm
8
7
6
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ppm
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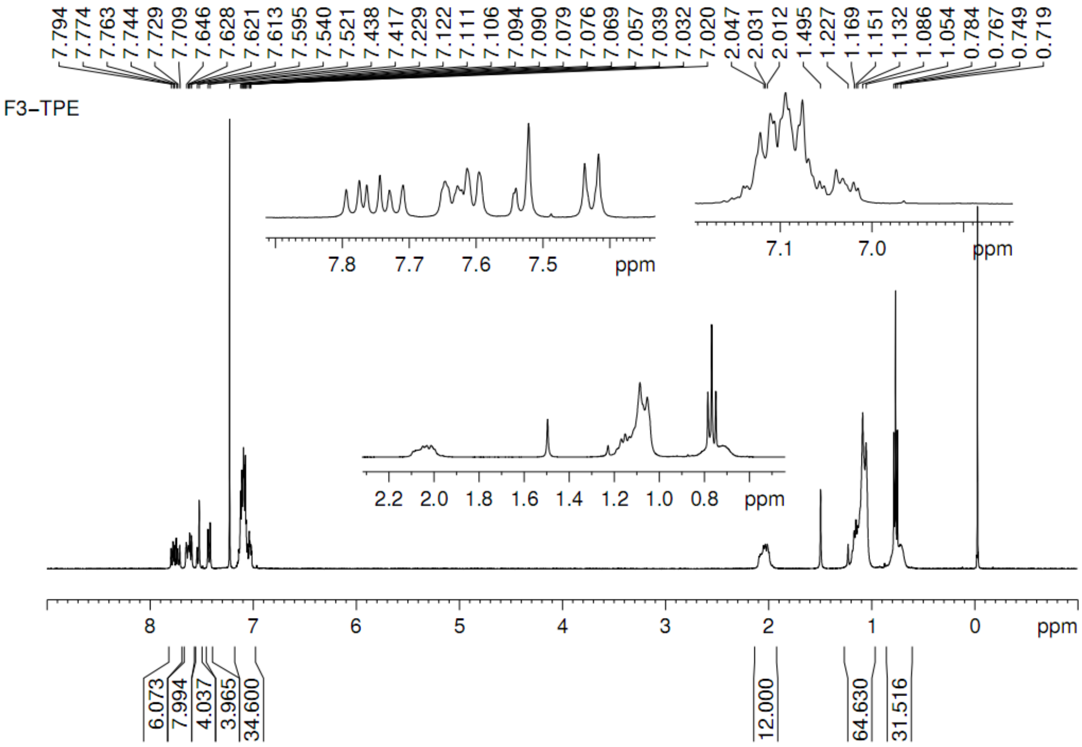
F3-TPE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7.076
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7.032
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1.169
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1.054
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7.7
7.6
7.5
ppm
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7.0
ppm
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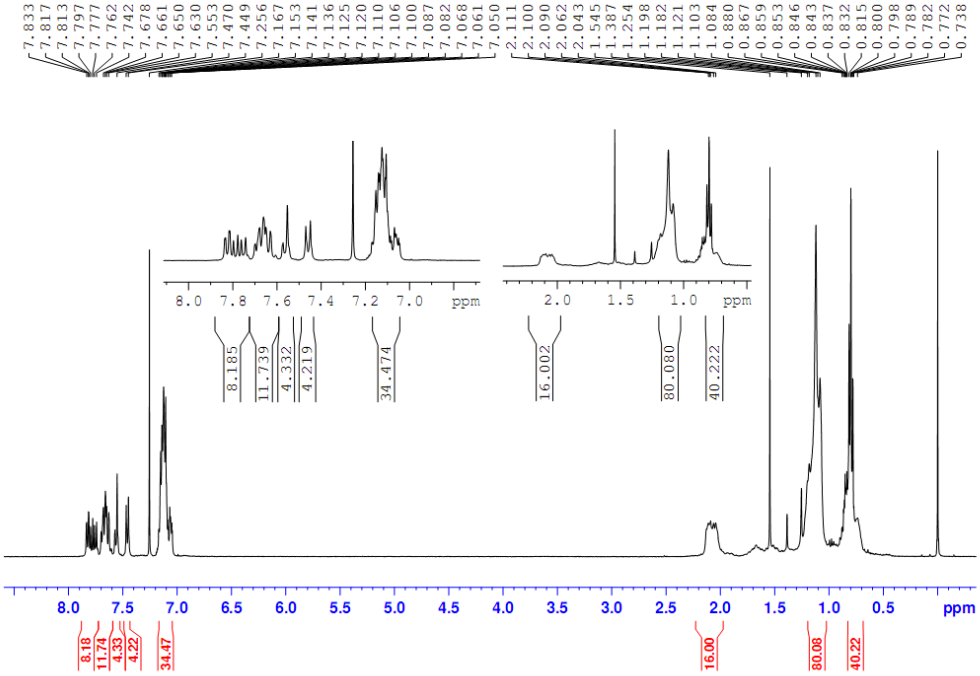
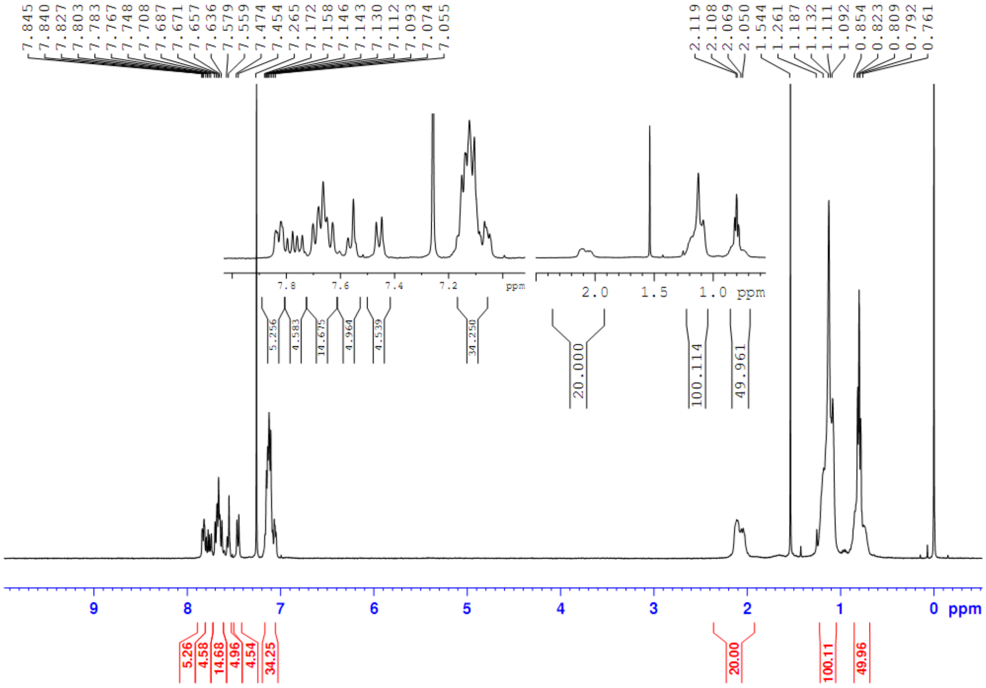
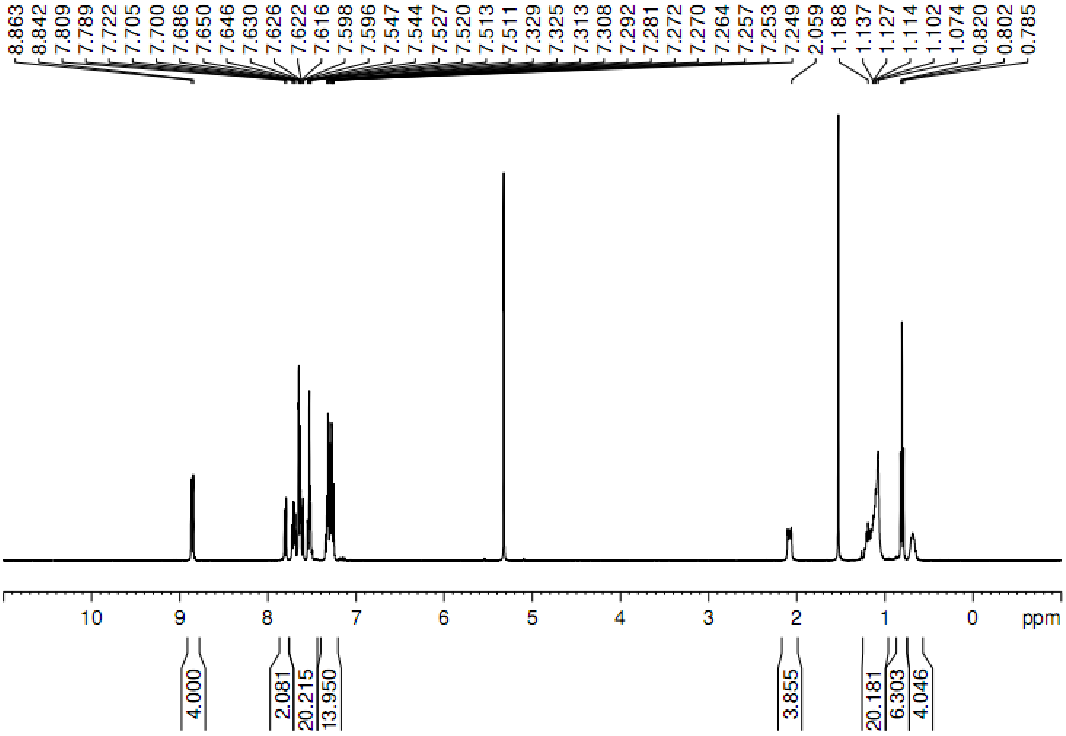
F4-TPE



F5-TPE



F1-PP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7.249
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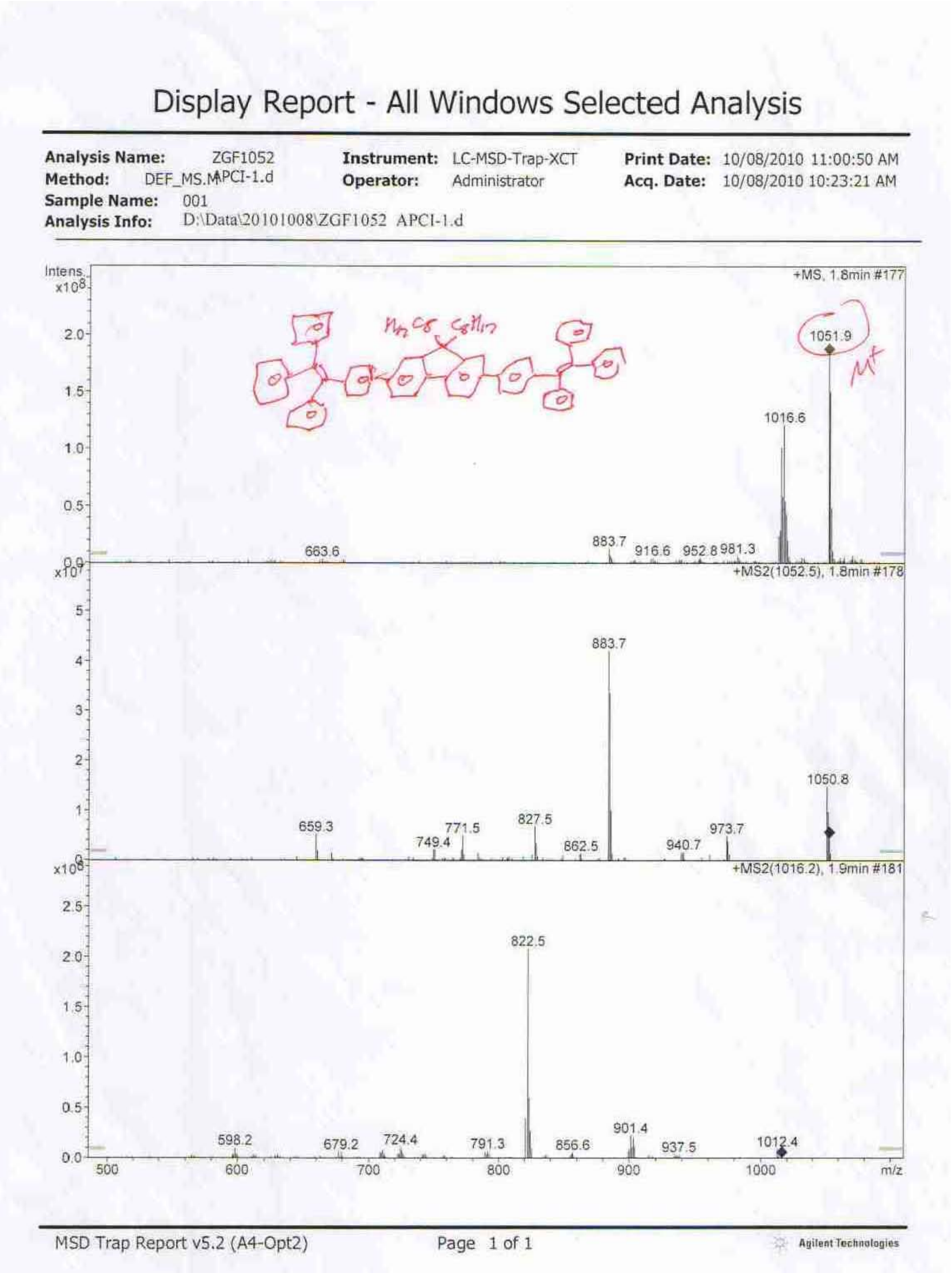
3. MASS SPECTRA OF F(1-5)TPE and F1-PP.

F1-TPE



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Operator: Administrator
Print Date: 10/08/2010 11:00:50 AM
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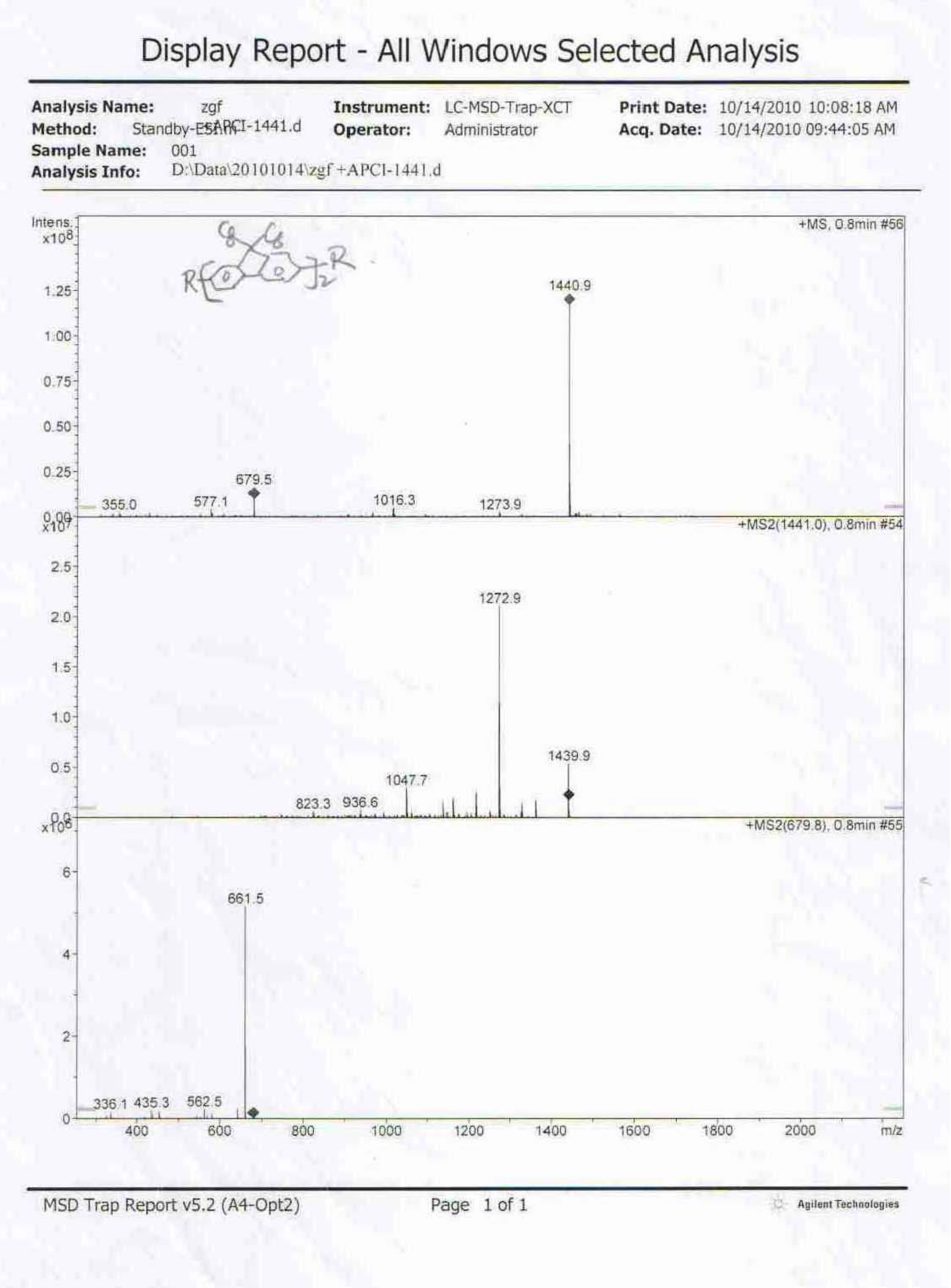
MSD Trap Report v5.2 (A4-Opt2) Page 1 of 1 Agilent Technologies

F2-TPE



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Operator: Administrator
Print Date: 10/14/2010 10:08:18 AM
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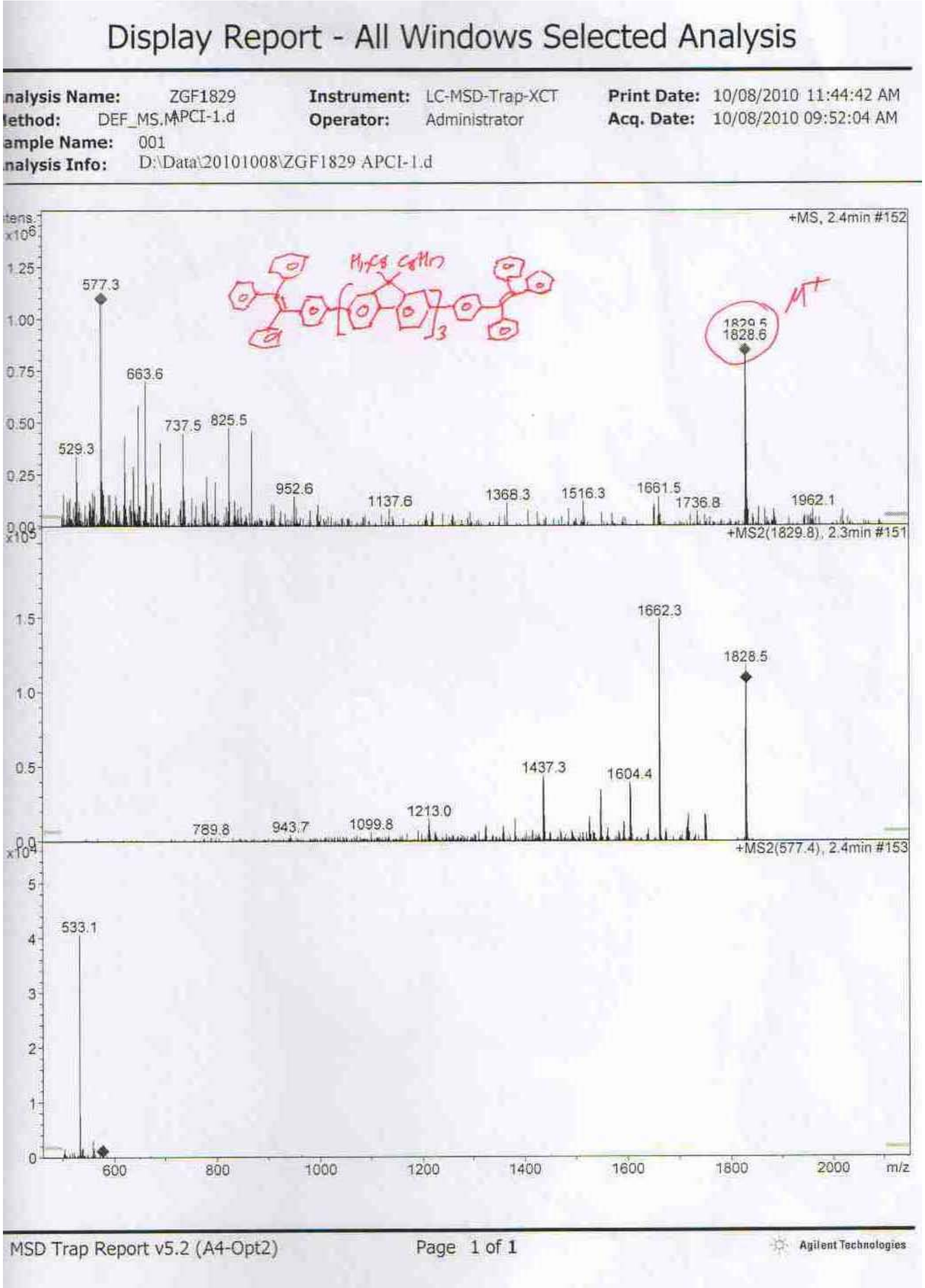
MSD Trap Report v5.2 (A4-Opt2)   Page 1 of 1   Agilent Technologies

F3-TPE



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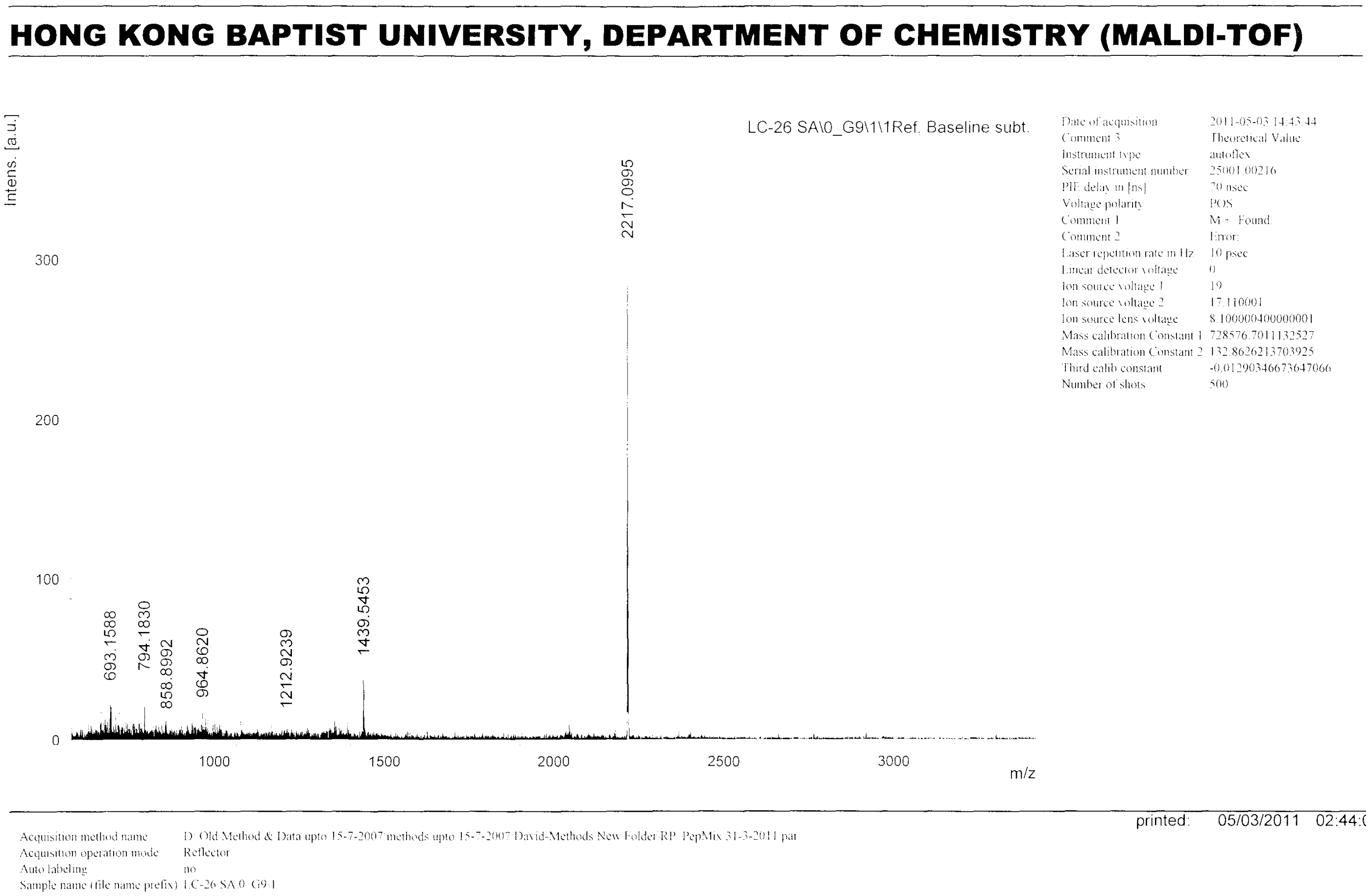
MSD Trap Report v5.2 (A4-Opt2)

Page 1 of 1

F4-TPE



HONG KONG BAPTIST UNIVERSITY, DEPARTMENT OF CHEMISTRY (MALDI-TOF)

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Comment 2	Error:
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Ion source lens voltage	8.100000400000001
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Number of shots	500

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Acquisition method name	D: Old Method & Data upto 15-7-2007 methods upto 15-7-2007 David-Methods New Folder RP PepMix 31-3-2011 par
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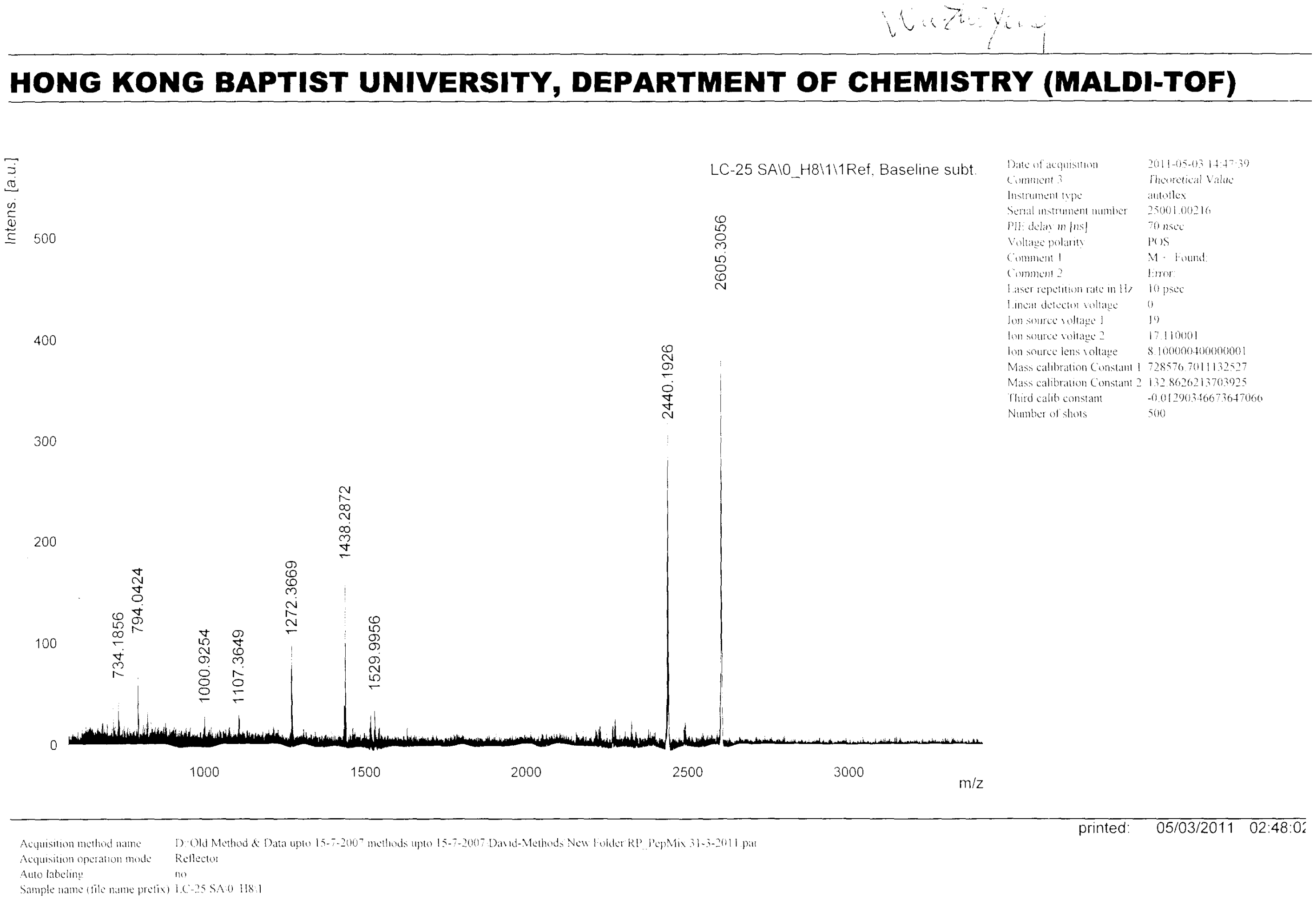
F5-TPE



HONG KONG BAPTIST UNIVERSITY, DEPARTMENT OF CHEMISTRY (MALDI-TOF)

LC-25 SA\0_H8\1\1Ref, Baseline subt.

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Linear detector voltage	0
Ion source voltage 1	19
Ion source voltage 2	17.110001
Ion source lens voltage	8.100000400000001
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Number of shots	500

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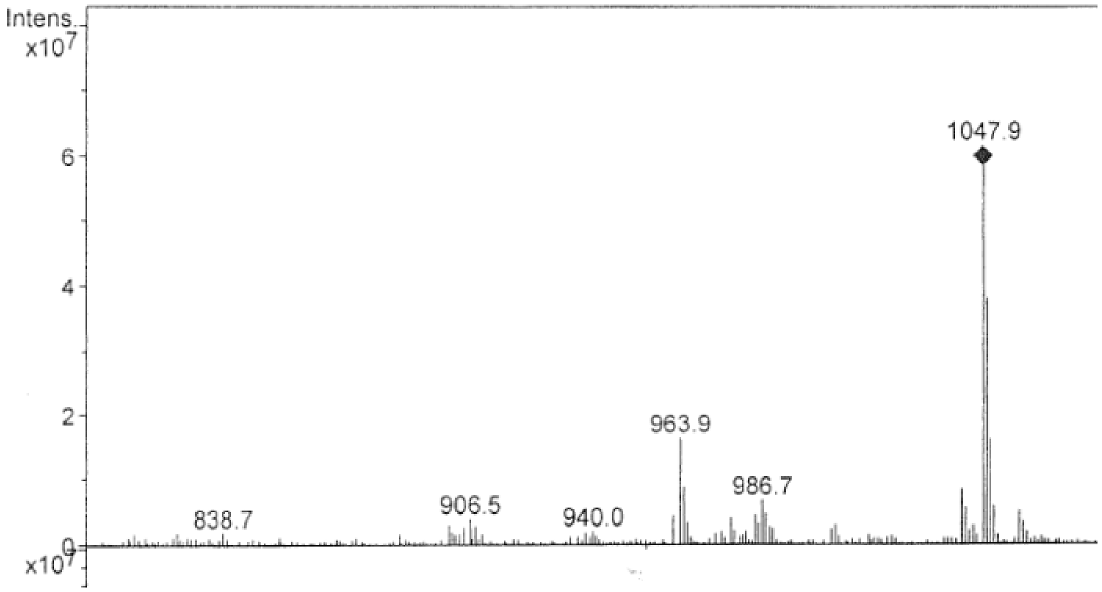
F1-PP



4. VAPOUR SENSING PHOTOS

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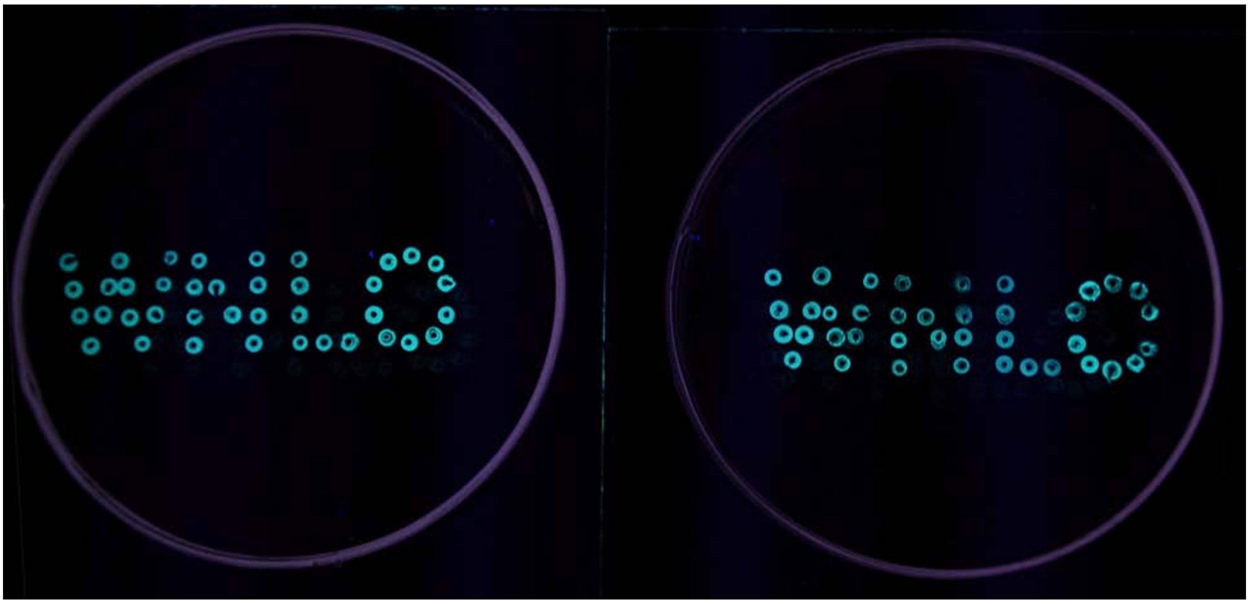

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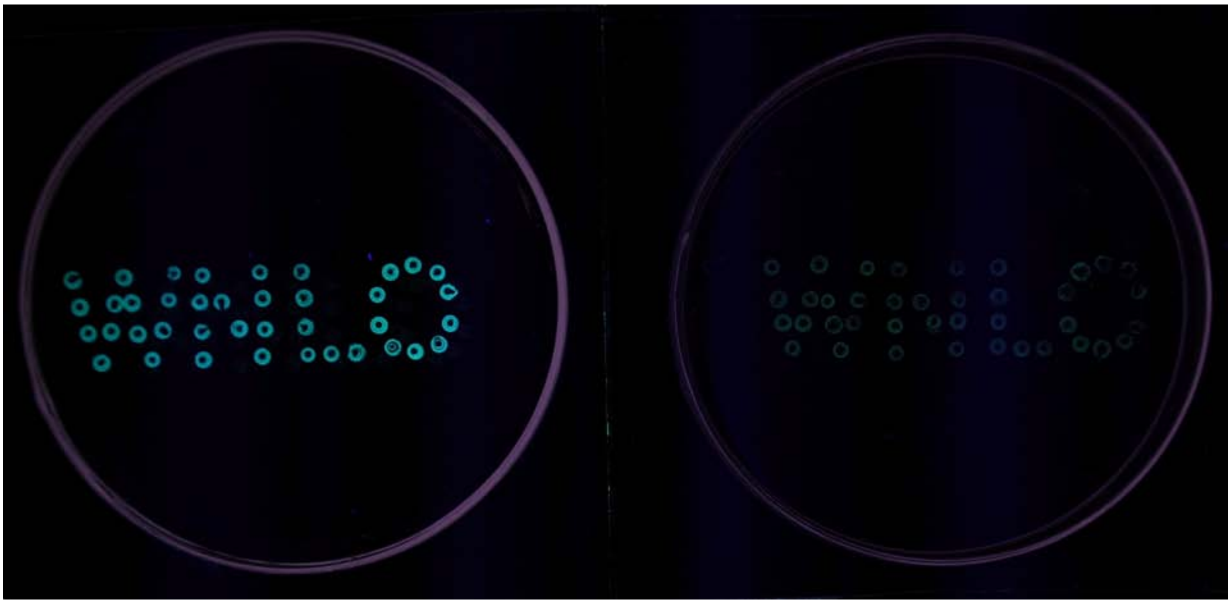

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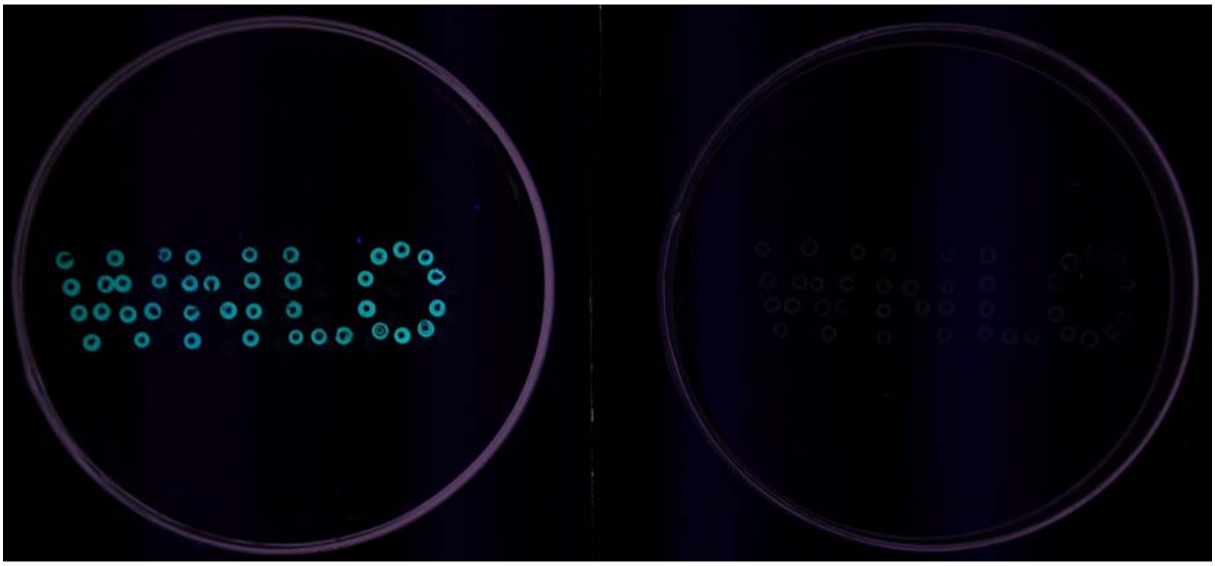

5. REFERENCES

1. S. O. Mihigo, W. Mammo, M. Bezabih, K. A. Marobela and B. M. Abegaz, *Bioorg. Med. Chem.*, 2010, **18**, 2464.
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4. S. J. Liu, Q. Zhao, R. F. Chen, Y. Deng, Q. L. Fan, F. Y. Li, L. H. Wang, C. H. Huang and W. Huang, *Chem. Eur. J.*, 2006, **12**, 4351.