White Light Emitting Hybrid Nanoarchitectures Based on Functionalized Quantum Dots

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Synthesis and characterization of the organic blue emitter DHTFBA

The synthetic sequence adopted is outlined in Scheme 1.

Synthesis of 2-(9,9,9',9'-tetrahexyl-9H,9'H-2,2'-bifluoren-7-yl)-1,3,2-dioxaborinane 3. In a 100 mL three necked round bottom flask, 2,2'-(9,9'-dihexyl-9H-fluorene-2,7-diyl)bis(1,3,2-dioxaborinane) 1 (3.18 g, 6.3 mmol) and 2-bromo-9,9-dihexyl-9H-fluorene 2 (1.31 g, 3.2 mmol) were dissolved under a nitrogen atmosphere in a degassed mixture of toluene (20 ml) and ethanol (5 ml). Pd(PPh3)4 (0.11 g, 0.1 mmol) and degassed aq. 2M Na2CO3 (16 ml) were then added to the solution and the resulting mixture was stirred at reflux for 12h. The reaction mixture was then cooled at room temperature, quenched by aqueous saturated NH4Cl (100 ml) and extracted with ethyl acetate (3 x 70 ml). The organic collected phase was dried over anhydrous sodium sulfate and the distillation of the solvent under reduced pressure yielded a crude product which was purified by column chromatography on silica gel using a mixture of dichloromethane and methanol (99.5:0.5 vol) as the eluent. The pure product was isolated as a pale yellow solid (1.90 g, 80%). Mp 51-52 °C (EtOH).

1H NMR (500 MHz, CDCl3): □□7.84-7.78 (m, 4H), 7.77-7.73 (m, 2H), 7.66 (dt J1= 7.9, J2=1.5 Hz, 2H), 7.65-7.62 (bs, 2H), 7.41-7.30 (m, 3H), 4.23 (t, J= 5.5, 4H), 2.17-1.97 (m, 10H), 1.21-0.98 (m, 24H), 0.85-0.65 (m, 20H).

13C NMR (125 MHz, CDCl3): □□152.03, 151.42, 151.00, 150.02, 143.19, 140.79, 140.78, 140.55, 140.33, 140.28, 132.53, 127.90, 126.93, 126.75, 126.02, 125.96, 122.89, 121.47, 121.44, 120.17, 119.83, 119.68, 118.90, 62.00, 55.15, 55.09, 40.35, 31.48, 31.45, 29.70, 29.67, 27.49, 23.77, 22.57, 22.53, 13.98, 13.97.

FT-IR (KBr): 2926, 2855, 1608, 1458, 1310, 1276, 821, 740 cm-1

Anal. Calcd.for C53H71BO2: C, 84.77; H, 9.53. Found: C, 84.63; H, 9.47.

Synthesis of methyl-4-(9,9-dihexyl-9H-fluoren-2-yl)benzoate 5. In a 100 mL three necked round bottom flask, 2-bromo-9,9-dihexyl-9H-fluorene 2 (1.90 g, 4.6 mmol) and methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate 4 (1.20 g, 4.6 mmol) were dissolved under a nitrogen atmosphere in a degassed mixture of toluene (30 ml) and ethanol (7.5 ml). Pd(PPh3)4 (0.16 g, 0.14 mmol) and degassed aq. 2M Na2CO3 (23 ml) were added to the solution and the resulting mixture was stirred at reflux for 12h. The reaction mixture was then cooled at room temperature, quenched by aq. saturated NH4Cl (100 ml) and extracted with ethyl acetate (3 x 60 ml). The crude product obtained after drying the organic extract over anhydrous sodium sulfate and distilling the solvent under reduced pressure was purified by column chromatography on silica gel, using a mixture of hexane and dichloromethane (7:3 vol) as the eluent. The pure product was isolated as a white solid (1.61 g, 75%). Mp 77-78 °C (CH3CN).

1H NMR (500 MHz, CDCl3): □□8.14 (d, J = 8.3 Hz, 2H), 7.78 (d, J = 7.8 Hz, 1H), 7.76-7.7.72 (m, 3H), 7.61 (dd, J1= 7.8, J2= 1.6, 1H), 7.70-7.57 (bs, 1H), 7.39-7.31 (m, 3H), 3.96 (s, 3H), 2.08-1.96 (m, 4H), 1.17-1.00 (m, 12H), 0.76 (t, J = 7.1 Hz, 6H), 0.73-0.62 (m, 4H).

13C NMR (125 MHz, CDCl3): □□167.03, 151.56, 151.04, 146.15, 141.34, 140.46, 138.70, 130.09, 128.64, 127.31, 127.02, 126.84, 126.16, 122.92, 121.52, 120.03, 119.89, 55.22, 52.09, 52.08, 40.36, 31.45, 29.66, 23.74, 22.54, 13.96.

FT-IR (KBr): 2923, 2855, 1726, 1605, 1279, 1110, 828, 763, 735 cm-1

Anal. Calcd. for C33H40O2: C, 84.57; H, 8.60. Found: C, 84.50; H, 8.70.

Synthesis of methyl-4-(9,9-dihexyl-7-iodo-9H-fluoren-2-yl)benzoate 6. In a 100 mL three necked round bottom flask, methyl 4-(9,9-dihexyl-9H-fluoren-2-yl)benzoate 5 (1.51 g, 3.2 mmol) was dissolved in dry dichloromethane (40 mL) under a nitrogen atmosphere. ICl (1M in CH2Cl2) (3.87 mL, 3.87 mmol) was added and the resulting solution was stirred at reflux for 4h. The reaction mixture was then cooled at room temperature, diluted with dichloromethane (100 mL) and washed with aq. saturated Na2CO3 (50 mL) and water (50 mL). After drying the organic collected extracts over anhydrous sodium sulfate and removing the solvent at reduced pressure, the crude product was purified by column chromatography on silica gel, using a mixture of hexane and dichloromethane (7:3 vol) as the eluent. The pure product was isolated as a white solid (1.69 g, 88%). Mp 106-107 °C (CH3CN).

1H NMR (500 MHz, CDCl3): □□8.14 (d, J = 8.4 Hz, 2H), 7.77-7.66 (m, 5H), 7.61 (dd, J1= 7.9, J2= 1.6 Hz, 1H), 7.58-7.54 (bs, 1H), 7.47 (d, J = 7.9, 1H), 3.96 (s, 3H), 2.05-1.90 (m, 4H), 1.18-1.00 (m, 12H), 0.77 (t, J = 7.3 Hz, 6H), 0.70-0.60 (m, 4H).

13C NMR (125 MHz, CDCl3): □□166.96, 153.43, 150.98, 145.87, 140.26, 140.12, 139.39, 135.95, 132.12, 130.11, 130.06, 128.80, 127.03, 126.98, 126.37, 121.58, 121.48, 120.20, 92.86, 55.49, 52.11, 40.21, 31.41, 29.57, 23.69, 22.53, 13.96.

FT-IR (KBr): 2926, 2855, 1718, 1606, 1435, 1283, 1189, 812, 775 cm-1

Anal. Calcd. for C33H39IO2: C, 66.66; H, 6.61. Found: C, 66.65; H, 6.63.

Synthesis of methyl-4-ter(9,9-dihexylfluoren-2-yl)-benzoate DHTFBMe. In a 100 mL three necked round bottom flask, 2-(9,9,9',9'-tetrahexyl-9H,9'H-2,2'-bifluoren-7-yl)-1,3,2-dioxaborinane 3 (0.70 g, 0.9 mmol) and methyl 4-(9,9-dihexyl-7-iodo-9H-fluoren-2-yl)benzoate 6 (0.61 g, 1.0 mmol) were dissolved under a nitrogen atmosphere in a mixture of degassed toluene (20 ml) and ethanol (5 mL). Pd(PPh3)4 (0.03 g, 0.03 mmol) and degassed aq. 2M Na2CO3 (5 ml) were added to the solution and the resulting mixture was stirred at reflux for 12h. The reaction mixture was then cooled at room temperature, quenched by aqueous saturated NH4Cl (80 ml) and extracted with dichloromethane (3 x 60 ml). After drying the extract over anhydrous sodium sulfate and removing the solvent at reduced pressure, the crude product was purified by column chromatography over silica gel using a mixture of hexane and dichloromethane (7:3 vol) as the eluent. The pure product was isolated as a white solid (0.64 g, 60%). Mp 76-79 °C (MeOH).

1H NMR (500 MHz, CDCl3): □□8.15 (d, J = 8.6 Hz, 2H), 7.87-7.74 (m, 8H), 7.72-7.59 (m, 10H), 7.41-7.28 (m, 3H), 3.97 (s, 3H), 2.16-1.98 (m, 12H), 1.20-1.02 (m, 36H), 0.87-0.65 (m, 30H).

13C NMR (125 MHz, CDCl3): □□167.06, 151.88, 151.83, 151.80, 151.76, 151.46, 150.99, 146.14, 141.04, 140.89, 140.78, 140.58, 140.47, 140.37, 140.33, 140.10, 139.92, 139.65, 138.69, 130.12, 128.78, 128.65, 127.19, 127.03, 126.97, 126.77, 126.30, 126.21, 126.15, 126.02, 122.91, 121.60, 121.51, 121.42, 120.16, 120.12, 119.95, 119.87, 119.70, 55.38, 55.32, 55.16, 52.12, 40.36, 40.33, 31.47, 31.44, 31.43, 29.69, 29.65, 23.83, 23.82, 23.78, 22.55, 22.54, 22.53, 14.00, 13.99.

FT-IR (KBr): 2960, 2924, 2854, 1723, 1605, 1453, 1261, 1099, 1019, 799 cm-1

Anal. Calcd. for C83H104O2: C, 87.93; H, 9.25. Found: C, 87.60; H, 9.48.

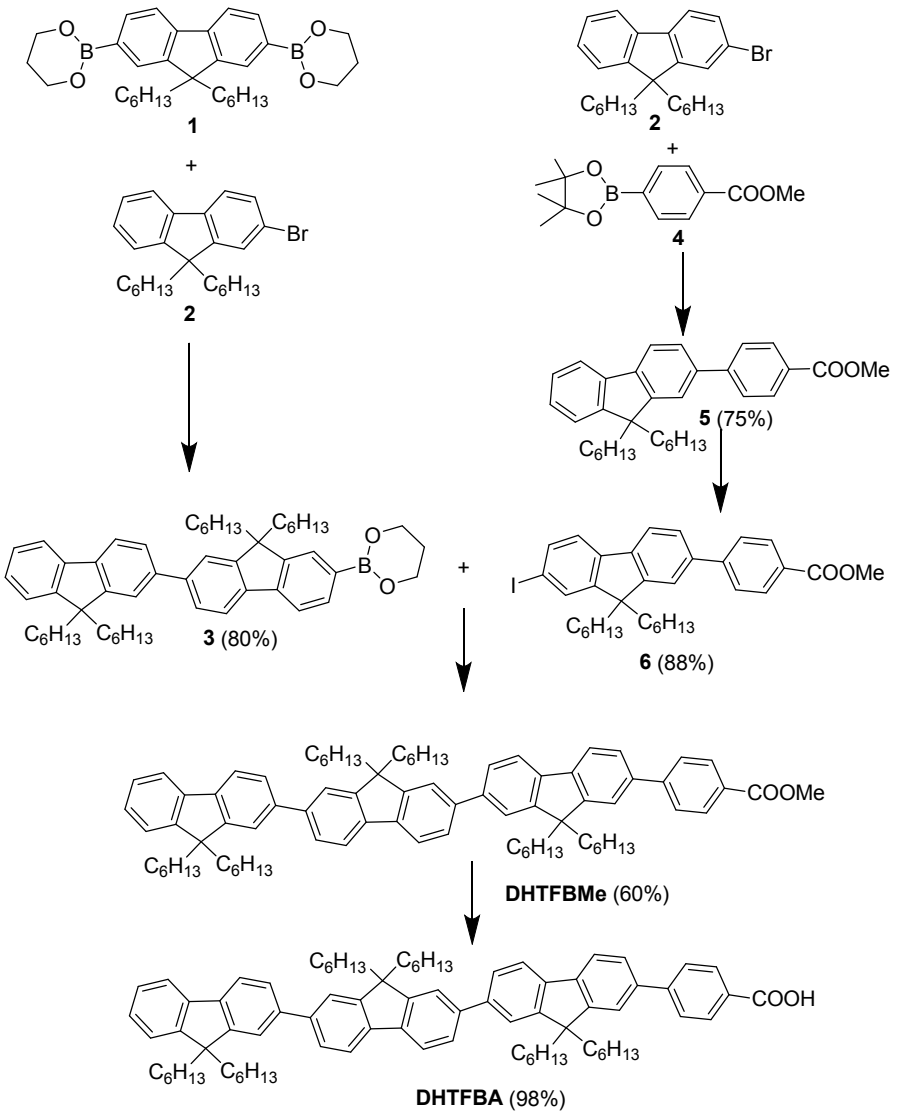
Synthesis of 4-ter(9,9-dihexylfluoren-2-yl)-benzoic acid DHTFBA. In a 100 ml round bottom flask, 7 (0.56 g, 0.5 mmol) and LiOH.H2O (0.21 g, 0.5 mmol) were stirred overnight in a mixture of THF (15 ml), methanol (10 ml) and water (10 ml) at 50°C. The precipitate was then filtered and washed with water and methanol to yield the pure product DHTFBA as a pale yellow solid (0.54 g, 98%). Mp 95-97 °C (EtOH).

1H NMR (500 MHz, CDCl3): □□8.31 d (d, J = 7.0 Hz, 2H), 8.00-7.60 (m, 18H), 7.50-7.30 (m, 3H), 2.40-1-90 (bs, 12H), 1.30-1.00 (bs, 36H), 1.00-0.60 (bs, 30H).

13C NMR (125 MHz, CDCl3): □□172.15, 151.90, 151.86, 151.80, 151.76, 151.45, 150.97, 146.88, 141.17, 140.93, 140.77, 140.58, 140.46, 140.36, 140.35, 140.33, 140.11, 139.92, 139.63, 138.59, 130.78, 128.76, 127.17, 127.11, 126.98, 126.78, 126.37, 126.24, 126.16, 126.03, 122.89, 121.62, 121.49, 121.40, 120.21, 120.18, 119.97, 119.88, 119.70, 55.39, 55.32, 55.15, 40.37, 31.46, 31.44, 31.43, 29.70, 29.68, 29.65, 29.64, 23.83, 23.77, 22.54, 22.54, 22.53, 14.00.

FT-IR (KBr): 3420, 2925, 2854, 1689, 1606, 1460, 1286, 815, 779, 740 cm-1

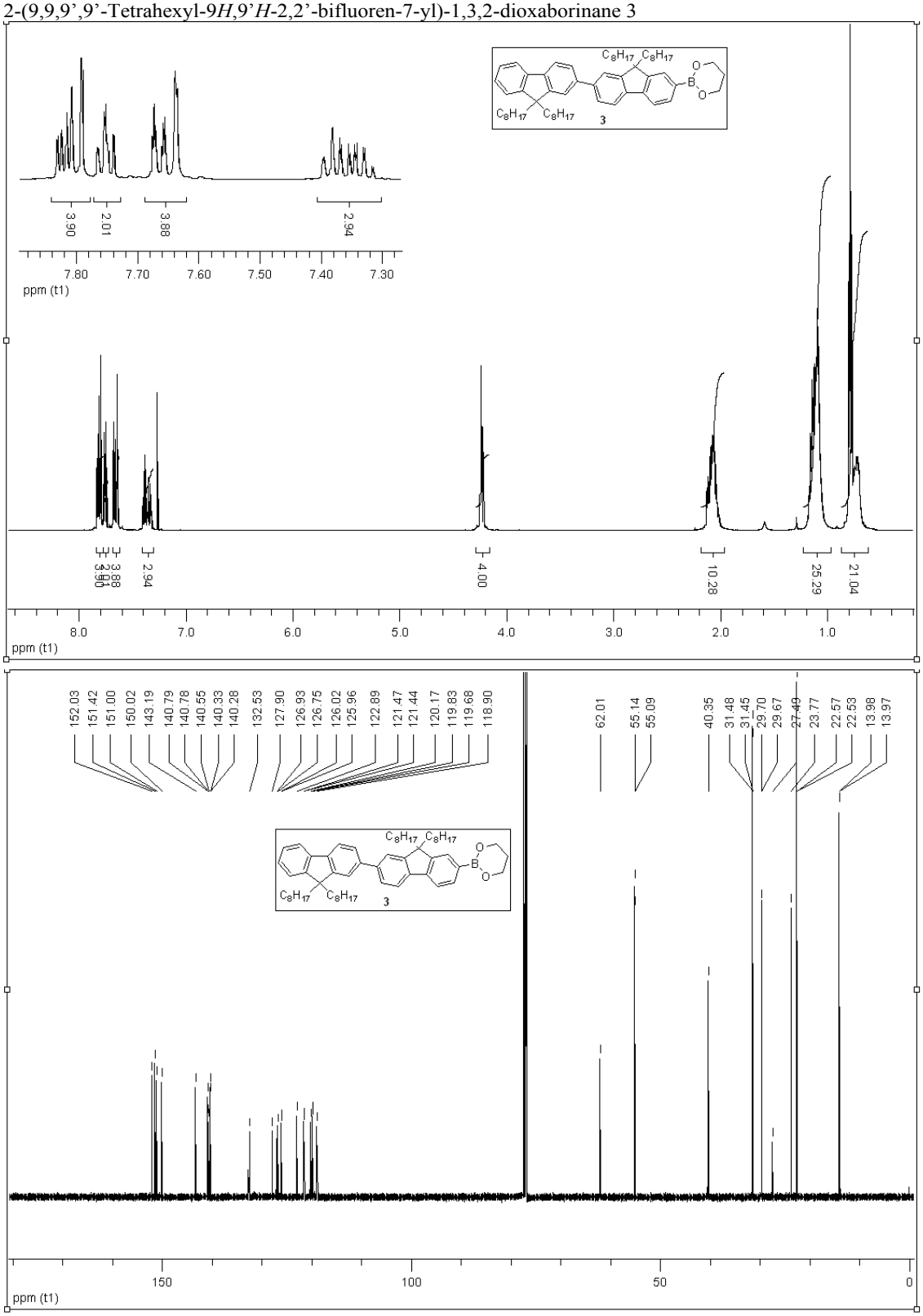
Anal. Calcd. for C82H102O2: C, 87.96; H, 9.18. Found: C, 87.74; H, 9.30.



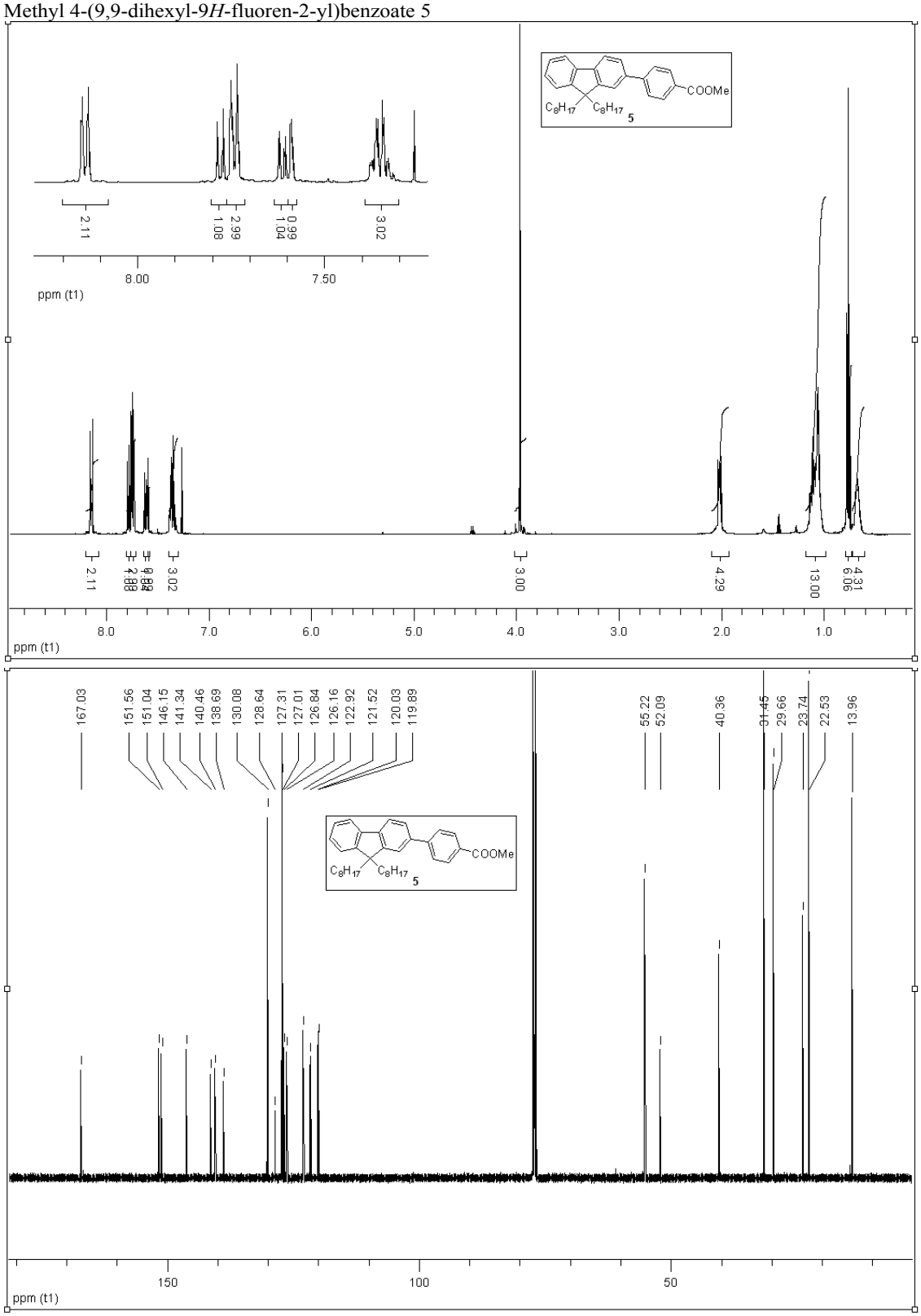
Scheme S1. Synthetic route to **DHTFBA**

Figure S1. NMR Spectra of the synthesized organic compounds.

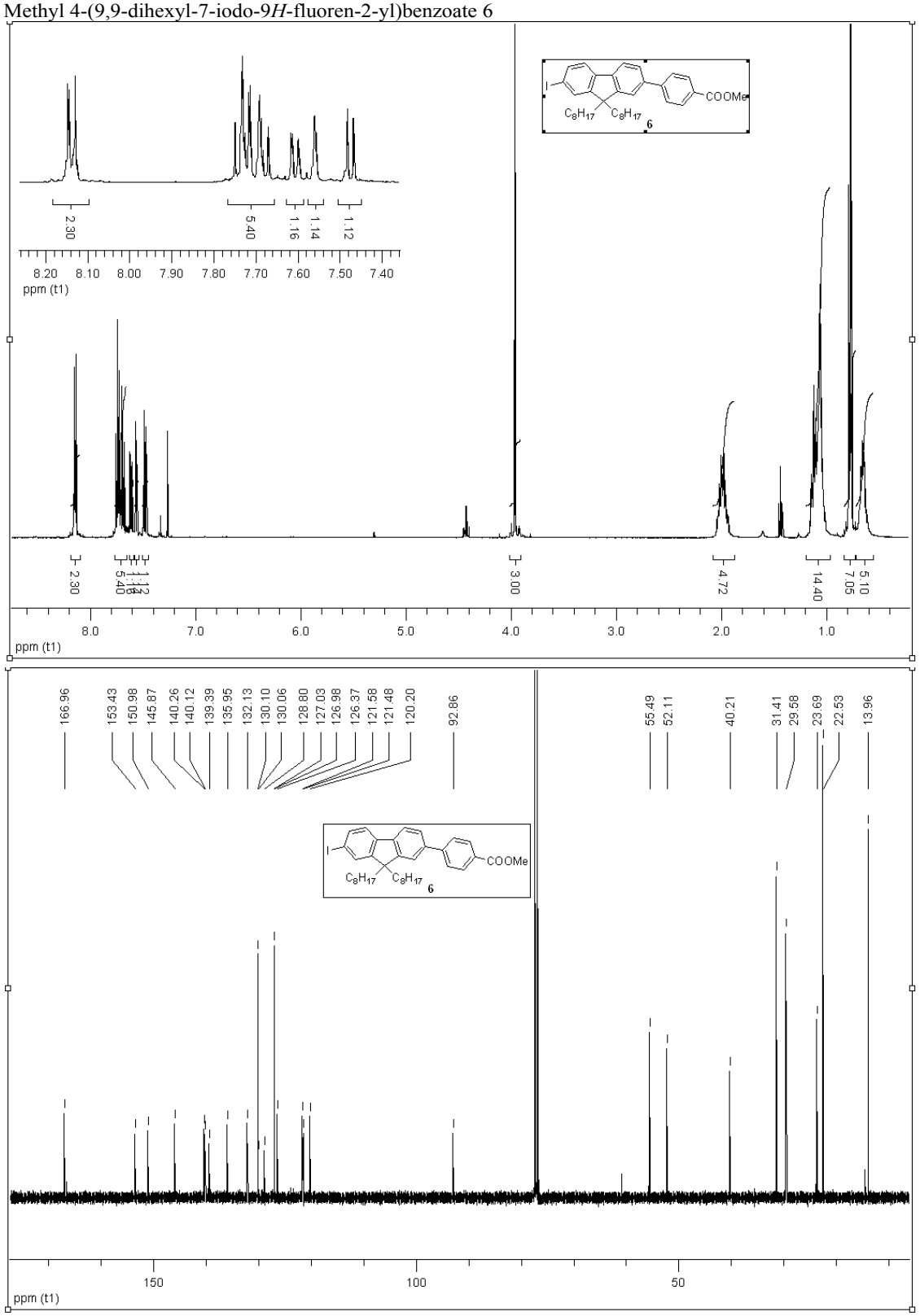
2-(9,9,9',9'-Tetrahexyl-9*H*,9'*H*-2,2'-bifluoren-7-yl)-1,3,2-dioxaborinane 3



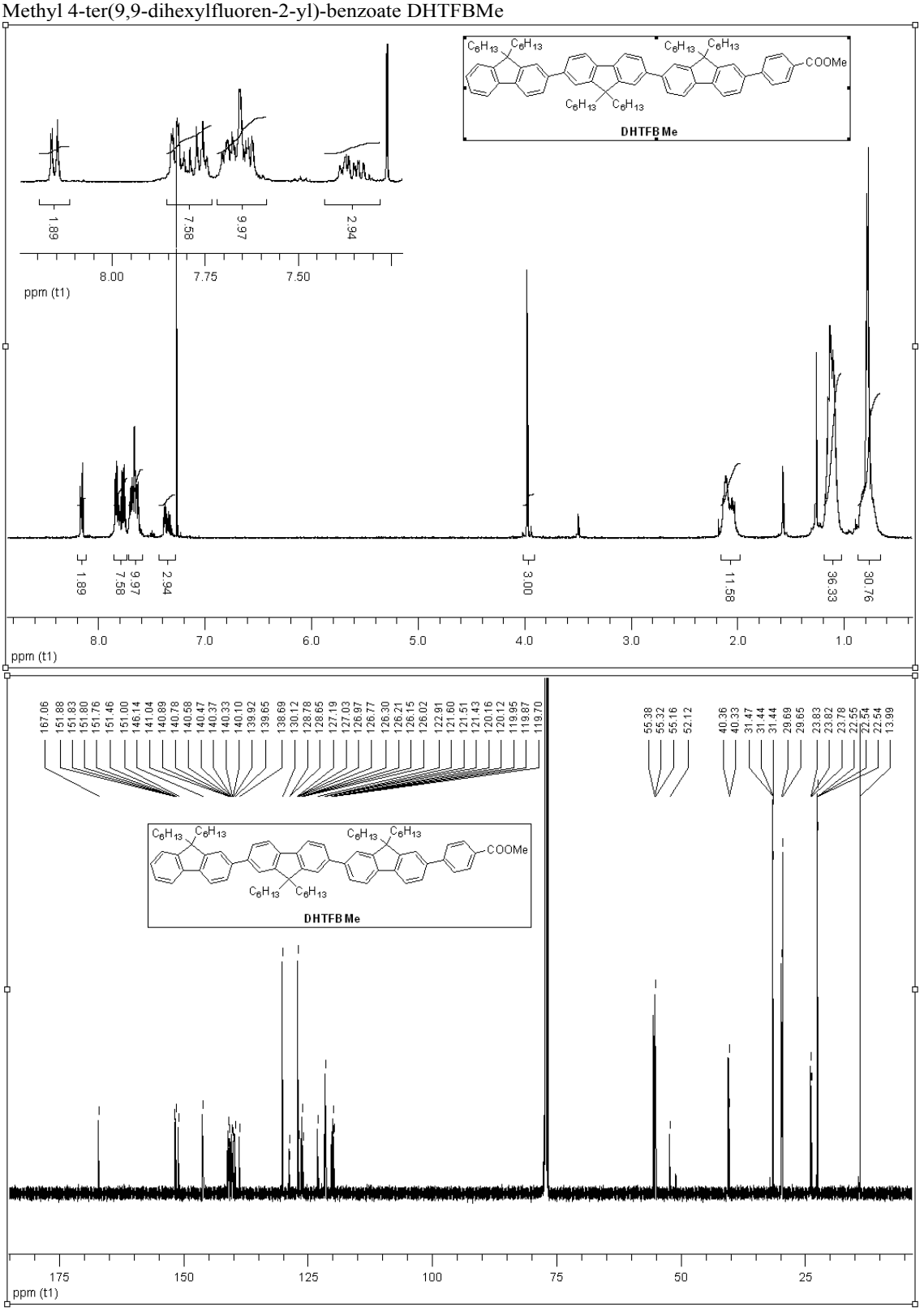
Methyl 4-(9,9-dihexyl-9*H*-fluoren-2-yl)benzoate 5



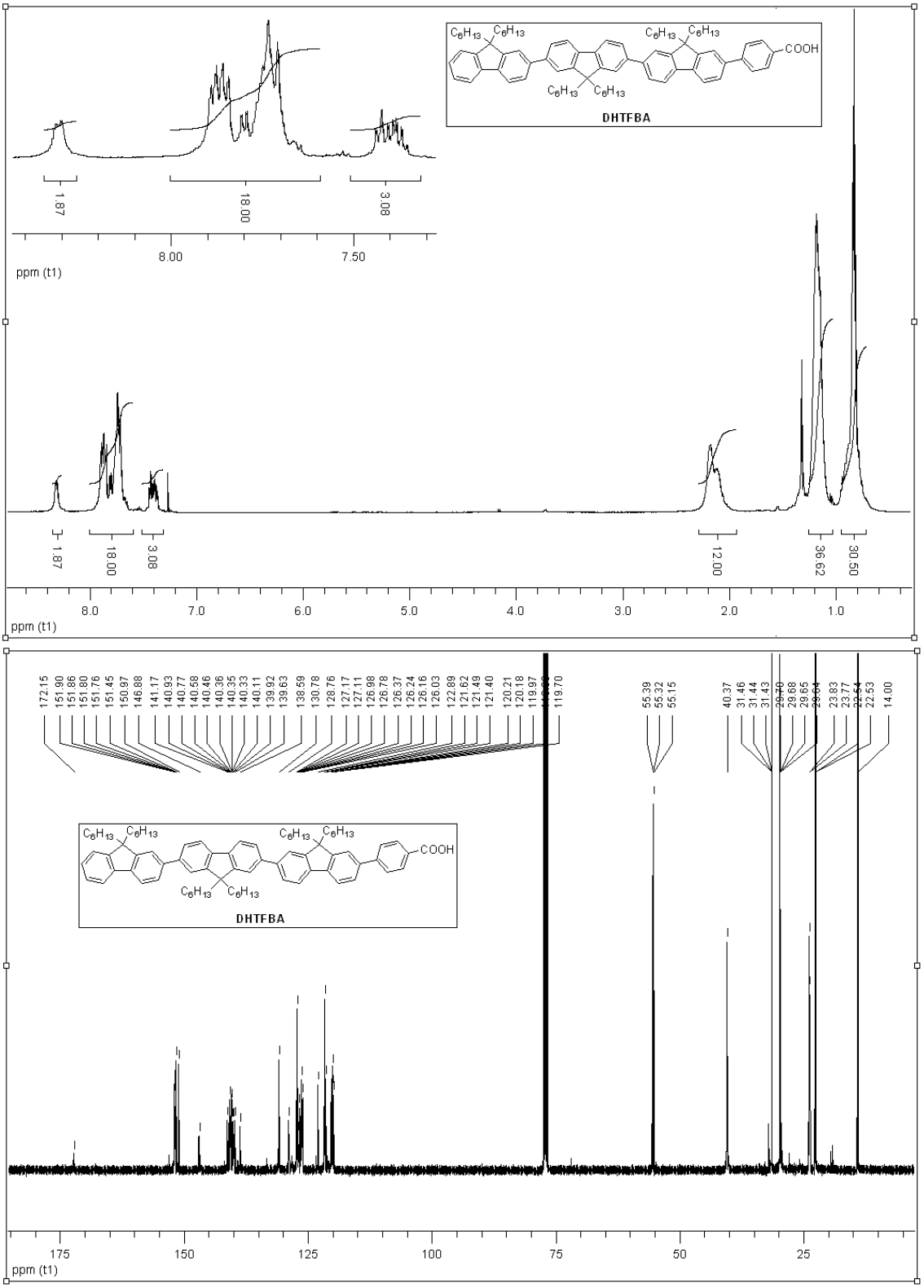
Methyl 4-(9,9-dihexyl-7-iodo-9*H*-fluoren-2-yl)benzoate 6



Methyl 4-ter(9,9-dihexylfluoren-2-yl)-benzoate DHTFBMe



4-Ter(9,9-dihexylfluoren-2-yl)-benzoic acid DHTFBA



Absorption and photoluminescence (PL) spectra of **DHTFBA** in chloroform solution are shown in Figure S2 .

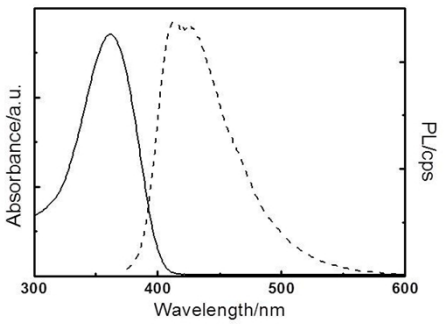


Figure S2. Absorption (solid line) and PL spectra (dash line) (excitation wavelength λ_{exc} = 325 nm) of **DHTFBA** in $CHCl_3$

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The fluorophore shows an absorption spectrum centered at 361 nm (calculated absorption molar coefficient $\varepsilon = 6.5 \cdot 10^5$ $Lmol^{-1}cm^{-1}$). The emission profile is characterized by two components at 415 nm and 428 nm (Figure S2), respectively. The first component is attributed to electron-hole recombination whereas the high wavelength component is due to its vibronic replica.

Synthesis and characterization of CdSe@ZnS quantum dots (QDs) Core-shell structures of CdSe@ZnS QDs were synthesized following a literature reported approach with minor modification.[1] In particular, for the core synthesis CdO (1.127 g), as cadmium precursor, and a mixture of hexadecylamine (12.00 g, HDA), trioctyl-phosphine oxide (12.00 g, TOPO) and *t*-butylphosphonic acid (0.28 g) were introduced in a 50mL three-neck flask, warmed up at 100°C under inert atmosphere until TOPO and HDA melt, and degassed for 1h. The temperature was then risen up to 300 °C and a mixture of selenium (0.39 g, Se) and tributyl-phosphine (4.40 g) was injected to start the formation of CdSe nuclei; their subsequent growth was carried out at 270 °C. The longer the reaction time the bigger the particle size, thus resulting in a red shift of the excitonic band edge transition in the absorbance spectra and of the photoluminescence wavelength in the emission spectra. Therefore, by properly choosing the reaction time it was possible to select the CdSe nanocrystal size and optical properties. The CdSe nanocrystal growth was stopped by cooling down the reaction mixture to 100°C and stirred for 1 hour for thermal annealing. The shell growth was carried out by a drop-wise injection of a stock solution of ZnS precursors containing TBP, Et_2Zn (1M solution in heptane) and hexamethyldisilathiane (HMTS) in the same reaction flask at 155°C. CdSe@ZnS core-shell QDs, as red powder, were then collected by centrifugation at 635 g for 10 min after the addition methanol as the non solvent and dispersed in chloroform (4 ml). Three batches of CdSe nanocrystals were prepared, with nanocrystal average size 3 nm, 3.6 nm and 3.7 nm and the ZnS shell grown, thus resulting in three CdSe@ZnS QD samples. These QDs show absorption peaks at 552 nm (green line CdSe core size 3 nm), 573 nm (yellow line, CdSe core size 3.6 nm) and 578 nm (red line, CdSe core size 3.7 nm), respectively, corresponding to excitonic band edge transition, while the continuum of states is present at high energy.
The absorption spectra of the three differently sized QD batch solutions are reported in Figure S3.

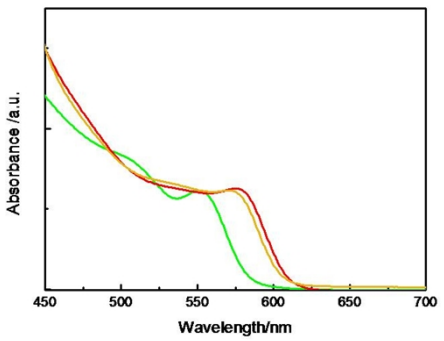

Figure S3. Absorption spectra of QDs with excitonic features at 552 nm (green line), 573 nm (yellow line) and 578 nm (red line). The related emission spectra are reported in Figure 2A.

Growth of a silica shell on CdSe@ZnS QD nanocrystals. Silica coated CdSe@ZnS nanocrystals were prepared by water in oil microemulsion approach.[2] In detail, a volume of 40 µl of QD solution ($2 \cdot 10^{-4}$ M) in chloroform has been diluted to 6 mL with cyclohexane and stirred at 28°C. Consecutively, 750 µl of IGEPAL CO520, 350 µl of ammonia solution and TEOS in the range of 20-50 µl have been added and the reaction mixture has been stirred overnight at 28°C. Addition of 3mL of methanol and centrifugation at 635 g for 10 min has allowed the disruption of the micelles and the collection of the NPs, which have been thoroughly purified by two cycles of redispersion in 15 mL of ethanol and centrifugation at 7800 g for 10 min (Beckman J2-21). The collected orange colored precipitate has been suspended in ethanol (2 ml), resulting in a concentration of $5 \cdot 10^{-6}$M (nearly 10^{14} NPs).

Synthesis and characterization of QD@SiO_2 nanoparticles functionalized with APTES. Surface functionalization of the QD@SiO_2 with amino groups was carried out by adding APTES (20, 70 and 120 microliters, respectively) and equal volume of aqueous NH4OH to a dilute suspension of the nanobead (0.4 ml of as prepared QD@SiO_2 diluted to 2 mL with ethanol). After 1 day of reaction at 28°C, the sample was purified from the excess of reactants and side products by three cycles of centrifugation and redispersion in ethanol. Finally, the purified collected precipitate has been redispersed in 1.5 mL of ethanol (≈10-6M).FTIR spectrum of the QD@SiO_2 (Figure S4 panel A, a) before and after functionalization with 20 µL ((Figure S4 panel B, b) and 120 µL (Figure S4 panel C, c) of APTES are reported in Figure S4. The FTIR spectra reported in panel B and C show a clear decrease in intensity of the band (3600 cm-1-3200 cm-1) ascribed to the stretching of SiO-H groups as the APTES used to functionalize the surface increases. In addition, the retention (Figure S6 panel a, b, c) of the characteristic peak ascribed to the vibration of Si-O of the siloxane network (1300 cm-1-1000 cm-1) allows to undoubtedly exclude the cross linking between free APTES in solution and non completely hydrolyzed APTES

bound to the surface of the nanoparticle, which would alternatively result in a broad band in the range of 1000-1200 cm-1 as reported elsewhere.3

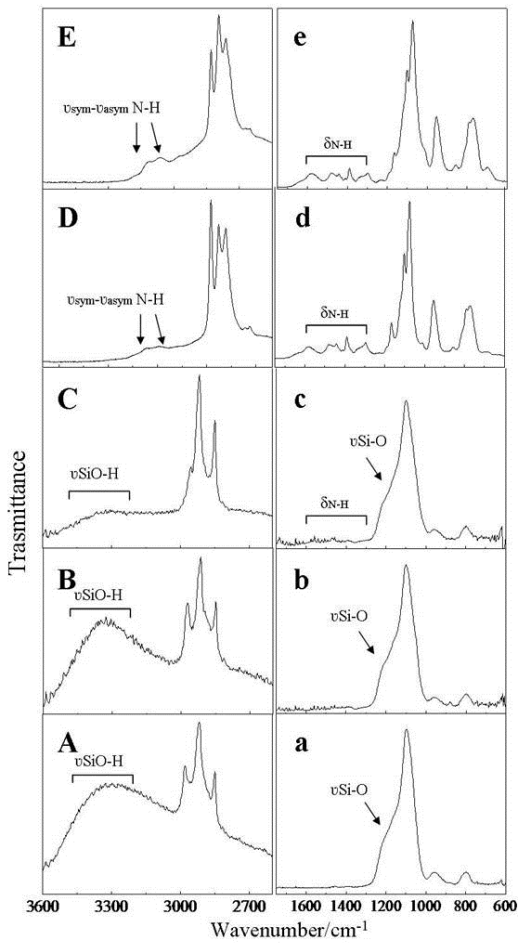

Figure S4. FTIR spectra of QD@SiO_2 nanoparticles before (A, a) and after functionalization with 20 µL (B, b) and 120 µL (C, c) of APTES; FTIR spectra of APTES (D, d) and a overnight reacted solution of APTES, ammonia solution in ethanol (E, e).

The signals ascribed to the bending of N-H (1500 cm^{-1} - 1600cm^{-1}) which are clearly visible in the spectra of free APTES (Figure S4 panel d), start to appear in the spectra of 120 µL APTES functionalized QD@SiO_2 nanoparticles reported in Figure S4 panel c. The FTIR spectrum of a blank experiment based on an overnight reaction of a solution of APTES and ammonia in ethanol in the absence of QD@SiO_2 was recorded (Figure S4 panel E, e) and compared with that of the pure APTES (Figure S4, panel D, d). The spectrum does not show any appreciable change in APTES vibrational modes, with the clear double band of the symmetric and asymmetric stretching of N-H (3300 cm^{-1}-3400 cm^{-1}) and the structured band in the range of 1100 cm^{-1}- 900 cm^{-1}. These evidences suggest that, at this experimental condition, polymerization phenomenon can be neglected.

The density of NH_2 groups on the QD@SiO_2 surface was estimated via ninhydrin assay.[4]

Ninhydrin (110 mg) has been dispersed in 16 mL of ethanol (0.68% w/v) and 4 mL of 2,6 lutidine have been added (ninhydrin final concentration $3 \cdot 10^{-5}$M). Preliminary calibration experiments have been performed by adding an excess of the ninhydrin solution to APTES standard solutions ranging from 50µM to 15 mM. Upon heating in a thermostatic bath at 90°C for 5 min, in the presence of primary amine, the solution color changes from pale yellow (free ninhydrin) to blue due to the formation of Rehumanns blue by-product, thus providing an evidence of the presence of the amine groups.

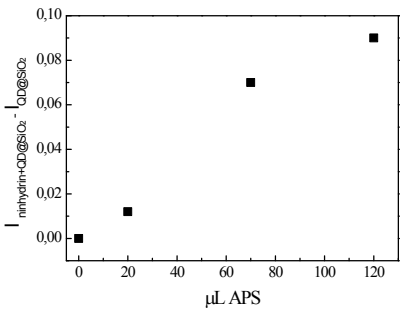

Figure S5. Scatter plot of the absorbance intensity at 570 nm, as measured by the ninhydrin test, per volume of APTES used to functionalize the QD@SiO_2. The absorbance intensity was corrected by considering the contribution at 570 nm of QD@SiO_2 absorbance.

The absorption intensity at 570 nm, characteristic of the Ruhemann's blue by-product, monitored by UV-Vis absorbance spectroscopy, allows to plot a calibration line and to determine the extinction coefficient (ξ_{570nm} = 49 L/mol·cm). Similarly, the ninhydrin test was performed on the prepared QD@SiO_2 and on the QD@SiO_2 samples prepared by using different volume of APTES (20 µL, 70 µL and 120 µL).In particular a molar excess of ninhydrin was added to each nanoparticle suspension, diluted 1:4 v/v and UV-Vis spectrophotometric characterization carried out. The absorbance intensity at 570 nm of the QD@SiO_2 sample and of the three amine groups-functionalized QD@SiO_2 samples, corrected by considering the contribution of the QD@SiO_2, are reported in Figure S5. From the ninhydrin test the concentration of NH_2 groups can be determined ranging from 1mM to 10mM, as the APTES increases from 20 µL to 120 µL. The theoretically estimated density of NH_2 groups at the surface of the beads ranges from 4 to 40 groups/nm^2, respectively.

Fabrication of single hybrid nanostructures DHTFBA-functionalized QD@SiO_2 NPs. Conjugation reaction of the organic fluorophore DHTFBA were carried out with each of the three batches of APTES-functionalized QD@SiO_2 (20 µL, 70 µL, 120 µL of APTES). In particular 1 ml of each nanoparticle sample was mixed with an excess of DHTFBA (0.1 mL of a 10^{-2} M solution) and BOP (8 mg) and DIPEA (5 µL) conjugation reactants were added and let it stirred at room temperature for 48 hours. The DHTFBA-functionalized QD@SiO_2 NPs were collected by centrifugation at 7800 g for 10 min (Beckman J2-21), purified by three cycles of redispersion in ethanol/centrifugation and dispersed in ethanol for further spectroscopic characterization and evaluation of the color points in the CIE.

Aging of DHTFBA-functionalized QD@SiO_2.

The aging effect of the white emitting **DHTFBA-**functionalized QD@SiO_2 sample was evaluated by measuring the color point

after several months. The result (Figure S6) shows that, although slightly changed, the color point of the suspension still falls in the white color region of the CIE 1931 diagram. The shift was mainly attributed to a partial oxidation of the QDs.

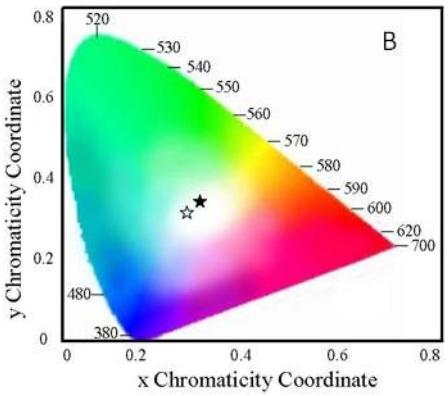

Figure S6. CIE diagram of white emitting DHTFBA-functionalized QD@SiO_2 sample: as prepared (filled star) and after few months of aging (empty star).

References

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