Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Main and secondary relaxations of non-polymeric high-T_g glass formers as revealed by dielectric spectroscopy

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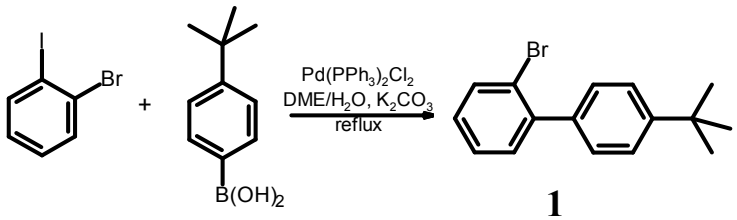
Synthetic route



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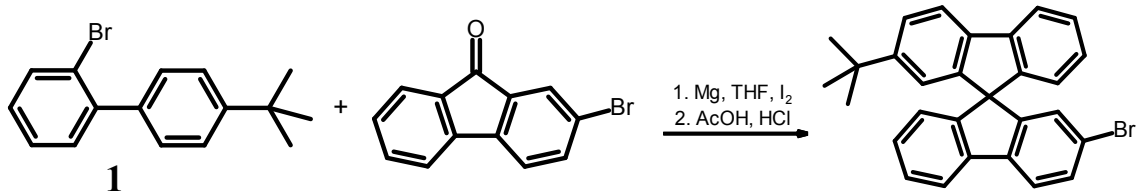

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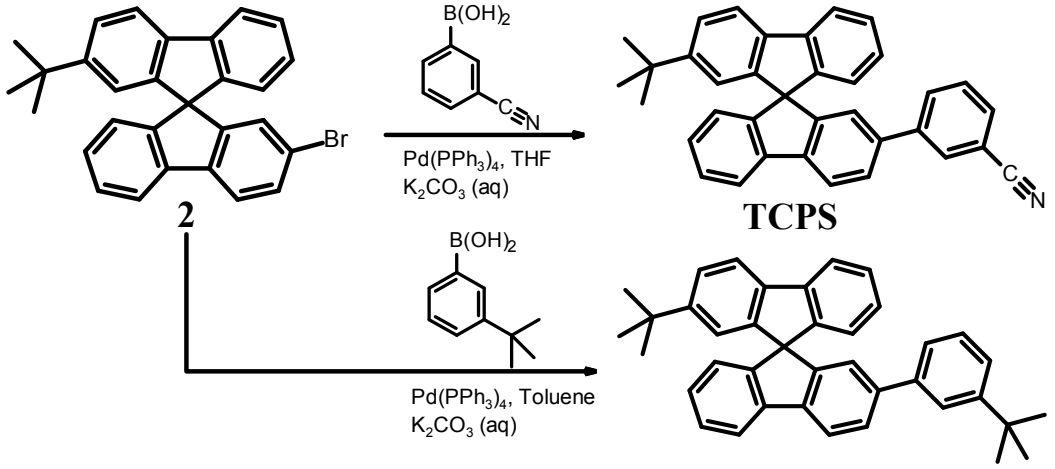
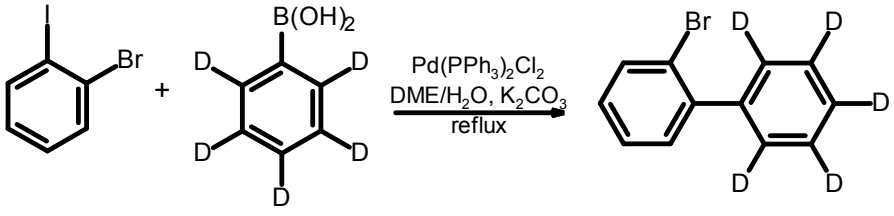


2 TCPS m-TPTS



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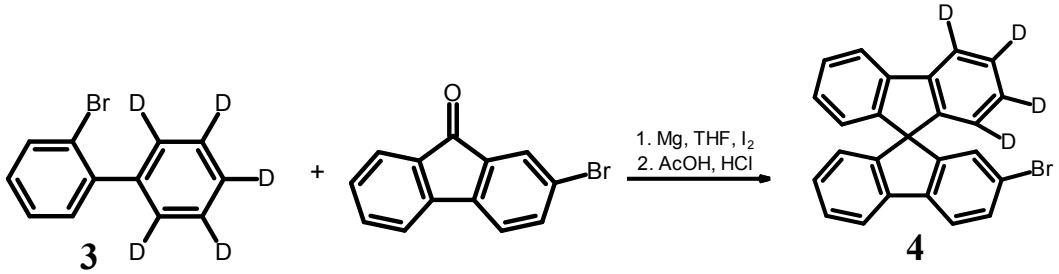
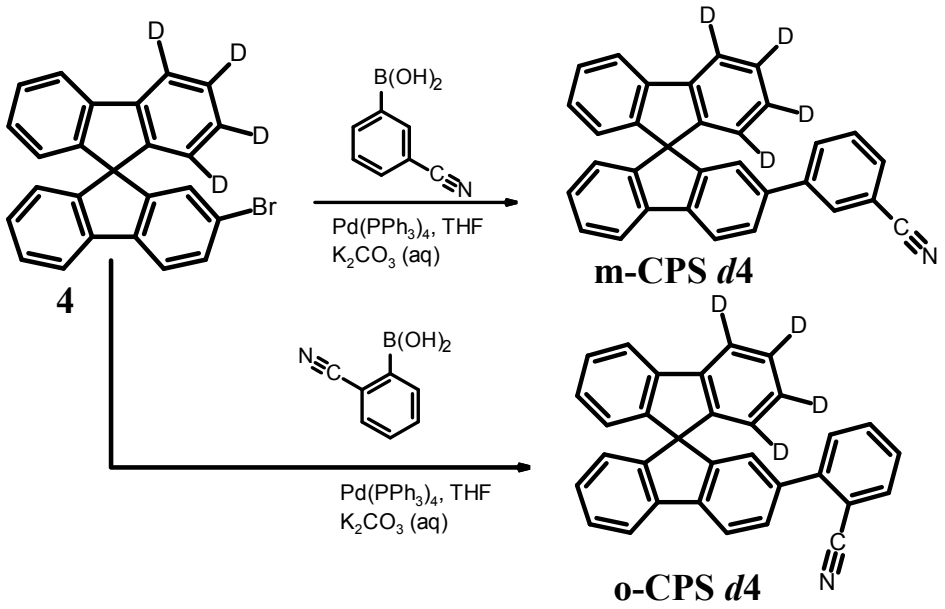


3 4



Synthetic procedures and ^{1}H-NMR data

Synthesis of **1**: 7.00 g (24.8 mmol) Iodobromobenzene and 5.291 g (29.7 mmol) of 4-*tert*butyl-phenylboronic acid are solved in 60 mL of DME and 10 mL of H_2O. 8.55 g of K_2CO_3 are added, then the mixture is flushed with Argon under stirring for 30 minutes. 260 mg of $PdCl_2(PPh_3)_2$ are added and Argon is flushed for another 30 minutes. Afterwards the mixture is heated to 80 °C for 18 h.

After cooling, DME is removed under reduced pressure, to the residue is given 80 mL of H_2O and 40 mL of Ether. The phases are separated, the aqueous phase is washed with Ether, the combined organic phases are dried over $MgSO_4$ and the solvent is removed under reduced pressure. The crude product is further purified by column chromatography with cyclohexane to yield 6.15 g (86 %) of a colourless liquid with a distinct odour.

1H NMR (300 MHz, CDCl3): δ = 1.40 (s, 9H, *t*-Bu-H), 7.21 (m, 1H, Ar-H), 7.38 (m, 4H, Ar-H), 7.47 (dt, 2H, Ar-H), 7.69 (m, 1H, Ar-H)

Synthesis of **2**: 6.15 g (21.4 mmol) of **1** are mixed with 625 mg of Mg and one spatula tip of I_2 in 50 mL of dry THF and heated under reflux. 4.66 g (18 mmol) 2-bromo-fluorenone are dissolved in 15 mL of dry THF. After 5 h, the Grignard reagent is transferred to the fluorenone solution with a syringe and stirred under reflux for further 17 h. Then a few drops of HCl are given to the solution upon which it clarifies. THF is removed under reduced pressure, the remaining material is dissolved in 50 mL AcOH and 2 mL of 32 % HCl and heated under reflux

for 4 h. The precipitated product is then filtered, washed with hexane and EtOH, and dried to yield 5.04 g (62 %) of a colourless powder.

1H NMR (300 MHz, CDCl3): δ = 1H NMR (300 MHz, CDCl3): δ = 1.20 (s, 9H, *t*-Bu-H), 6.67 (m, 1H, Ar-H), 6.74 (m, 1H, Ar-H), 6.87 (dd, 1H, Ar-H), 7.12 (m, 2H, Ar-H), 7.37 (qd, 2H, Ar-H), 7.48 (m, 2H, Ar-H), 7.77 (m, 4H, Ar-H)

Synthesis of **TCPS**: 570 mg of **2** (1.3 mmol) are mixed with 240 mg 3-cyanophenylboronic acid (1.62 mmol, 1.25 n) in 100 mL of THF. 60 mL 2 M K_2CO_3 solution are added and the mixture is stirred under Ar stream for 30 minutes. 120 mg of $Pd(PPh_3)_4$ are added and the mixture is stirred under Ar for another 30 minutes and subsequently heated to reflux for 17 h.

After cooling the mixture is filtrated, the phases are separated, the organic phase is washed with brine, dried over $MgSO_4$ and the solvent is removed under reduced pressure. The crude product is further purified by column chromatography (cyclohexane / ethyl acetate 5:1) to yield 538 mg (85 %) of an off-white powder.

1H NMR (300 MHz, CDCl3): δ = 1.19 (s, 9H, *t*-Bu-H), 6.71 (m, 1H, Ar-H), 6,77 (m, 2H, Ar-H), 6.92 (dd, 1H, Ar-H), 7.13 (m, 2H, Ar-H), 7.43 (m, 4H, Ar-H), 7.54 (td, 1H, Ar-H), 7.64 (m, 2H, Ar-H), 7.72 (m, 1H, Ar-H), 7.80 – 7.99 (m, 4H, Ar-H)

Synthesis of **m-TPTS**: 4.5 g (10 mmol) of **2** are dissolved in 100 mL Toluene with 1.73 g (12.48 mmol) 3-tertbutylphenyl boronic acid. 60 mL 2M K_2CO_3 solution are added and the mixture is bubbled with Ar for 30 minutes. 336 mg $Pd(PPh_3)_4$ are added and Ar is bubbled for another 30 minutes. The mixture is then stirred at 100 °C for 17 h. After the reaction is complete, the phases are separated and the aqueous phase is washed with toluene. The combined organic phases are dried over $MgSO_4$ and the solvent is evaporated under reduced pressure. The crude product is the purified via column chromatography (cyclohexane / ethyl acetate 5:1 and 100:1) to yield 2.07 g (41 %) of a white powder.

1H NMR (300 MHz, CDCl3): δ = 1.19 (s, 9H, *t*-Bu-H), 1.32 (s, 9H, *t*-Bu-H), 6.75 (m, 3H, Ar-H), 6.94 (dd, 1H, Ar-H), 7.10 (m, 2H, Ar-H), 7.18 – 7.48 (m, 7H, Ar-H), 7.64 (dd, 1H, Ar-H), 7.77 – 7.95 (m, 4H, Ar-H)

Synthesis of **3**: 3.81 g 2-Iodobromobenzene and 2.14 g of phenyl-*d*5-boronic acid are dissolved in 40 mL of DME and 5 mL of H_2O. 3.64 g of K_2CO_3 are added, then the mixture is flushed with Argon under stirring for 30 minutes. 118 mg of $PdCl_2(PPh_3)_4$ are added and Argon is flushed for another 30 minutes. Afterwards the mixture is heated to 80 °C for 5 h.

After cooling, DME is removed under reduced pressure, to the residue is given 50 mL of H_2O and 30 mL of Ether. The phases are separated, the aqueous phase is washed with Ether, the combined organic phases are dried over $MgSO_4$ and the solvent is removed under reduced pressure. The crude product is further purified by column chromatography with hexane to yield 2.122 g (68 %) of a colourless liquid with a distinct odour.

1H NMR (300 MHz, CDCl3): δ = 7.23 (m, 1H, Ar-H), 7.33 – 7.42 (m, 2H, Ar-H), 7.70 (m, 1H, Ar-H).

Synthesis of **4**: 2.2 g of **3** are dissolved in 25 mL of dry THF. 0.271 g of Mg and a spatula tip of I_2 are added. The mixture is stirred under reflux for 3 h. 2.41 g of 2-Bromofluorenone are dissolved in 5 mL dry THF. The Grignard reagent is carefully transferred to the fluorenone solution using a syringe. The mixture is stirred for another 18 hours under reflux.

Afterwards, 2 mL of AcOH are added to the mixture, after which the opaque suspension clears. THF is removed under reduced pressure and to the mixture are added 20 mL of AcOH and 1 mL of HCl (32 %). The mixture is stirred under reflux for another 5 h. After cooling, DCM and water are added, the phases are separated and the aqueous phase is washed twice with DCM. The combined organic phase are dried over $MgSO_4$ and the solvent is removed under reduced pressure to yield 2.505 g (68 %) of a white solid.

1H NMR (300 MHz, CDCl3): δ = 6.74 (m, 2H, Ar-H), 6.87 (dd, 1H, Ar-H), 7.15 (dt, 2H, Ar-H), 7.40 (m, 2H, Ar-H), 7.50 (dd, 1H, Ar-H), 7.72 (dd, 1H, Ar-H), 7.85 (m, 2H, Ar-H),

Synthesis of **o-CPS *d*4** and **m-CPS *d*4**: The synthetic procedure to obtain both compounds from **4** is according to the undeuterated compounds and can be found elsewhere.[1]

o-CPS *d*4: 1H NMR (300 MHz, CDCl3): δ = 6.80 (m, 2H, Ar-H), 6.87 (dd, 1H, Ar-H), 7.16 (qt, 2H, Ar-H), 7.30 – 7.44 (m, 4H, Ar-H), 7.51 (m, 1H, Ar-H), 7.67 (dd, 2H, Ar-H), 7.89 (m, 2H, Ar-H), 7.98 (dd, 1H, Ar-H)

m-CPS *d*4: 1H NMR (300 MHz, CDCl3): δ = 6.78 (m, 2H, Ar-H), 6.92 (dd, 1H, Ar-H), 7.15 (m, 2H, Ar-H), 7.42 (m, 3H, Ar-H), 7.53 (td, 1H, Ar-H), 7.58 – 7.73 (m, 3H, Ar-H), 7.90 (m, 2H, Ar-H), 7.96 (dd, 1H, Ar-H)

References:

1. F. Krohn, C. Neuber, E. A. Rössler and H.-W. Schmidt, *J. Phys. Chem. B.*, 2019, **123**, 10286-10293.