Supporting Information

Organic Glasses of High Glass Transition Temperatures Due to Substitution with Nitrile Groups

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Experimental procedure and characterization

2-cyano-9,9'-spirobi[9H]fluorene (5) and 2,7-dicyano-9,9'-spirobi[9H]fluorene (6) were prepared according to literature procedures. [1] 2,7-dibromo-9,9'-spirobi[9H]fluorene was prepared according to literature procedures. [2]

General procedure for Suzuki-Miyaura cross coupling: 5 mmol of bromo-substituted 9,9'-spirobi[9H]fluorene are dissolved in 100 mL THF with 1.25 equivalents of the respective phenyl boronic acid. 60 mL 2 M K₂CO₃ are added and argon is flushed through the solution for 30 min. 2 mole-% (according to the boronic acid) of Pd(PPh₃)₄ are added to the mixture and argon is flushed for another 30 min. Subsequently, the mixture is heated to 80 °C for 17 h. After cooling, the phases are separated, the organic phase is washed with brine, dried over MgSO₄, and the solvent is removed under reduced pressure. The crude product is further purified by column chromatography (cyclohexane/ethyl acetate).

General procedure for a Rosenmund-von-Braun reaction: 1 g of bromo-substituted 9,9'-spirobi[9H]fluorene are dissolved in 15 mL of dry DMF under inert atmosphere. Two equivalents of CuCN are added and the mixture is heated to 170 °C for 17 h. After cooling, 40 mL H₂O, 4 mL of 32 % HCl and 5 g FeCl₃ are added and the mixture is kept at 70 °C for another 30 min. After cooling, the mixture is extracted three times with toluene, the organic phases are combined, dried over MgSO₄, and the solvent is
evaporated under reduced pressure. The crude product is further purified by column chromatography (cyclohexane/ethyl acetate).

2,7-dibromo-2',7'-dicyano-9,9'-spirobi[9\text{H}]fluorene: 2 g (5.47 mmol) of 2,7-dicyano-9,9'-Spirobi[9\text{H}]fluorene (6) are dissolved in 20 mL DCM with 45 mg (5 mole-%) FeCl₃. 3.5 g (22 mmol) of Br₂ are dissolved in another 4 mL DCM and slowly added to the educts. The mixture is subsequently heated to reflux for 24 h. After cooling, 10 % aqueous Na₂SO₃ is added to the mixture which is subsequently extracted three times with DCM. The combined organic phases are dried over MgSO₄ and the solvent is evaporated under reduced pressure to yield 2.11 g (74 %) of an off-white powder. Mp: 326 °C (under decomposition), ¹H NMR (300 MHz, CDCl₃): \( \delta = 6.77 \) (d, 2H, Ar-H), 7.06 (m, 2H, Ar-H), 7.59 (dd, 2H, Ar-H), 7.73 (d, 1H, Ar-H), 7.77 (dd, 1H, Ar-H), 8.00 (dd, 1H, Ar-H)

2-phenyl-9,9'-spirobi[9\text{H}]fluorene (2): The product was obtained as a white solid, yield: 82 %, ¹H NMR (300 MHz, CDCl₃): \( \delta = 6.74 \) (m, 1H, Ar-H), 6.78 (m, 2H, Ar-H), 6.94 (dd, 1H, Ar-H), 7.08 – 7.15 (m, 3H, Ar-H), 7.20 – 7.44 (m, 7H, Ar-H), 7.62 (dd, 1H, Ar-H), 7.83 – 7.89 (m, 3H, Ar-H), 7.91 (dd, 1H, Ar-H),

2,7-diphenyl-9,9'-spirobi[9\text{H}]fluorene (3): After recrystallization, the product was obtained as white crystals, yield: 50 %, Mp: 258 °C, ¹H NMR (300 MHz, CDCl₃): \( \delta = 6.82 \) (m, 2H, Ar-H), 6.94 (m, 2H, Ar-H), 7.12 (dt, 2H, Ar-H), 7.20 – 7.45 (m, 12H, Ar-H), 7.65 (dd, 1H, Ar-H), 7.86 (m, 2H, Ar-H), 7.92 (m, 2H, Ar-H).
General procedure for the bromination of 7a-c: 1.04 g of 4a-c (2.49 mmol) are dissolved in 18 mL of DCM with a spatula tip of I₂. 1.5 g (9.4 mmol) of Br₂ are dissolved in 3 mL of DCM and slowly added to the educts. The mixture is stirred at room temperature for 72 h. After the reaction is complete, 10 % aqueous Na₂SO₃ is added to the mixture, which is subsequently extracted three times with DCM. The combined organic phases are dried over MgSO₄ and the solvent is evaporated under reduced pressure.

2-(2-cyanophenyl)-9,9'-spirobi[9H]fluorene (7-ortho): The product remained as a white powder. Yield: 73 %. Mp: 179 °C, ¹H NMR (300 MHz, CDCl₃): δ = 6.73-6.86 (m, 4H, Ar-H), 7.10-7.18 (m, 3H, Ar-H), 7.28-7.43 (m, 5H, Ar-H), 7.49 (m, 1H, Ar-H), 7.65 (dd, 2H, Ar-H), 7.81-7.91 (m, 3H, Ar-H), 7.95 (d, 1H, Ar-H)

2-(3-cyanophenyl)-9,9'-Spirobi[9H]fluorene (7-meta): After recrystallization in CHCl₃/MeOH, the product remained as off-white crystals. Yield: 78 %, mp: 191 °C, ¹H NMR (300 MHz, CDCl₃): δ = 6.72-6.79 (m, 3H, Ar-H), 6.89 (d, 1H, Ar-H), 7.90-7.17 (m, 3H, Ar-H), 7.36-7.44 (m, 4H, Ar-H), 7.52 (dt, 1H, Ar-H), 7.58 (dd, 1H, Ar-H), 7.64 (dt, 1H, Ar-H), 7.67 (dt, 1H, Ar-H), 7.88 (d, 2H, Ar-H), 7.94 (d, 1H, Ar-H)

2-(4-cyanophenyl)-9,9'-spirobi[9H]fluorene (7-para): The product remained as white flakes. Yield: 78 %, mp: 221 °C, ¹H NMR (300 MHz, CDCl₃): δ = 6.75 (m, 3H, Ar-H), 6.93 (d, 1H, Ar-H), 7.08-7.18 (m, 3H, Ar-H), 7.35-7.44 (m, 3H, Ar-H), 7.51 (dt, 2H, Ar-H), 7.56-7.64 (m, 3H, Ar-H), 7.64 (dt, 1H, Ar-H), 7.84-7.90 (m, 3H, Ar-H), 7.95 (d, 1H, Ar-H)
2-(2-cyanophenyl)-2',7,7'tribromo-9,9'-spirobi[9H]fluorene: The product was obtained as off-white crystals. Yield: 96 %, \( ^1H \text{NMR (300 MHz, CDCl}_3\): \delta = 6.85 \text{ (dd, 2H, Ar-H), 6.90 \text{ (d, 2H, Ar-H), 7.33-7.39 \text{ (m, 2H, Ar-H), 7.50 – 7.59 \text{ (m, 4H, Ar-H), 7.65 – 7.78 \text{ (m, 5H, Ar-H), 7.94 \text{ (d, 1H, Ar-H)}}} \)

2-(3-cyanophenyl)-2',7,7'tribromo-9,9'-spirobi[9H]fluorene: The product remained as an off-white powder, yield: 99 %, \( ^1H \text{NMR (300 MHz, CDCl}_3\): \delta = 6.86 \text{ (m, 4H, Ar-H), 7.45 \text{ (dt, 1H, Ar-H), 7.50-7.78 \text{ (m, 10H, Ar-H), 7.91 \text{ (dd, 1H, Ar-H)}}} \)

2-(4-cyanophenyl)-2',7,7'tribromo-9,9'-spirobi[9H]fluorene: The product was obtained as an off-white solid, yield: 98 %, \( ^1H \text{NMR (300 MHz, CDCl}_3\): \delta = 6.86-6.93 \text{ (m, 3H, Ar-H), 7.52-7.80 \text{ (m, 11H, Ar-H), 7.94 \text{ (m, 1H, Ar-H)}}} \)

2-(2-cyanophenyl)-2',7,7'-tricyano-9,9'-spirobi[9H]fluorene (8-ortho): The product was obtained as a white powder, yield: 34 %, mp: 313 °C, \( ^1H \text{NMR (300 MHz, CDCl}_3\): \delta = 6.89 \text{ (d, 1H, Ar-H), 6.98 \text{ (d, 1H, Ar-H), 7.11 \text{ (d, 2H, Ar-H), 7.40 \text{ (m, 2H, Ar-H) 7.57 \text{ (m, 1H, Ar-H) 7.68 \text{ (dd, 1H, Ar-H), 7.73 – 7.82 \text{ (m, 4H, Ar-H), 7.99 – 8.10 \text{ (m, 4H, Ar-H)}}} \)

2-(3-cyanophenyl)-2',7,7'-tricyano-9,9'-spirobi[9H]fluorene (8-meta): The product remained as a white solid, yield: 62 %, mp: 320 °C, \( ^1H \text{NMR (300 MHz, CDCl}_3\): \delta = 6.86 \text{ (dd, 1H, Ar-H), 6.96 \text{ (dd, 1H, Ar-H), 7.07 \text{ (dd, 2H, Ar-H), 7.48 \text{ (m, 1H, Ar-H), 7.59 \text{ (dt, 1H, Ar-H), 7.66-7.70 \text{ (m, 2H, Ar-H), 7.74 \text{ (dd, 1H, Ar-H), 7.77-7.83 \text{ (m, 3H, Ar-H), 8.01-8.09 \text{ (m, 4H, Ar-H)}}} \)

2-(4-cyanophenyl)-2',7,7'-tricyano-9,9'-spirobi[9H]fluorene (8-para): The product remained as an off-white powder, yield: 37 %, mp: 347 °C \( ^1H \text{NMR (300 MHz, CDCl}_3\): \delta =
δ = 6.92 (dd, 2H, Ar-H), 7.07 (d, 2H, Ar-H), 7.53 (d, 2H, Ar-H), 7.65 (d, 2H, Ar-H) 7.73 – 7.82 (m, 4H, Ar-H), 7.99 – 8.09 (m, 4H, Ar-H)

2,7-bis-(2-cyanophenyl)-9,9'-spirobi[9H]fluorene (**9-ortho**): After recrystallization, the product was obtained as white crystals, yield: 68 %, mp: 316 °C, ¹H NMR (300 MHz, CDCl₃): δ = 6.85 – 6.90 (m, 4H, Ar-H), 7.17 (dt, 2H, Ar-H), 7.30 – 7.42 (m, 6H, Ar-H), 7.46 – 7.54 (m, 4H, Ar-H), 7.63 – 7.70 (m, 4H, Ar-H), 7.84 (m, 2H, Ar-H), 8.00 (dd, 2H, Ar-H)

2,7-bis-(3-cyanophenyl)-9,9'-spirobi[9H]fluorene (**9-meta**): The product remained as white crystals, yield: 26 %, mp: °C, ¹H NMR (300 MHz, CDCl₃): δ = 6.80 (m, 2H, Ar-H), 6.91 (dd, 2H, Ar-H), 7.15 (td, 2H, Ar-H), 7.38-7.46 (m, 4H, Ar-H), 7.53 (td, 2H, Ar-H), 7.59-7.72 (m, 6H, Ar-H), 7.91 (m, 2H, Ar-H), 7.98 (dd, 2H, Ar-H)

2,7-bis-(4-cyanophenyl)-9,9'-spirobi[9H]fluorene (**9-para**): The product was obtained as an off-white solid, yield: 80 %, mp: 310 °C, ¹H NMR (300 MHz, CDCl₃): δ = 6.80 (dt, 1H, Ar-H), 6.94 (dd, 1H, Ar-H), 7.14 (m, 1H, Ar-H), 7.41 (m, 1H, Ar-H), 7.52 (m, 2H, Ar-H), 7.60 (m, 2H, Ar-H), 7.65 (dd, 1H, Ar-H), 7.89 (m, 1H, Ar-H), 7.98 (dd, 1H, Ar-H)

2,7-bis-(2-cyanophenyl)-2',7'-dicyano-9,9'-spirobi[9H]fluorene (**10-ortho**): After recrystallization, the product was obtained as an off-white solid, yield: 67 %, mp: 327 °C, ¹H NMR (300 MHz, CDCl₃): δ = 6.87 (d, 2H, Ar-H), 7.21 (d, 2H, Ar-H), 7.34-7.43 (m, 4H, Ar-H), 7.56 (td, 2H, Ar-H), 7.65 – 7.76 (m, 6H, Ar-H), 7.98 (d, 2H, Ar-H), 8.06 (d, 2H, Ar-H)
2,7-bis-(3-cyanophenyl)-2',7'-dicyano-9,9'-spirobi[9\(H\)]fluorene \(10\text{-meta}\): After recrystallization, a white powder was obtained, yield: 40 %, mp: 340 °C, \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 6.82\) (d, 2H, Ar-H), 7.13 (d, 2H, Ar-H), 7.47 (td, 2H, Ar-H), 7.58 (dt, 2H, Ar-H), 7.70 (m, 6H, Ar-H), 7.79 (dd, 2H, Ar-H), 8.05 (m, 4H, Ar-H)

2,7-bis-(4-cyanophenyl)-2',7'-dicyano-9,9'-spirobi[9\(H\)]fluorene \(10\text{-para}\): After recrystallization, off-white crystals were obtained, yield: 36 %, mp: 340 °C, \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 6.84\) (d, 2H, Ar-H), 7.13 (d, 2H, Ar-H), 7.53 (dt, 4H, Ar-H), 7.64 (dt, 4H, Ar-H), 7.70 – 7.80 (m, 4H, Ar-H), 8.04 (d, 4H, Ar-H)

References
