Electronic Supplementary Information (ESI)

High-contrast mechanochromic benzothiadiazole derivatives based on a triphenylamine or a carbazole unit

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Table of Contents

1. Experimental Section...........................................................................................S3

2. Copies of NMR spectra and Mass spectra..............................................................S7
1. Experimental Section

Materials and measurements

General: The starting materials 4,7-dibromobenzo[c][1,2,5]thiadiazole, 4-(diphenylamino)phenylboronic acid, 4,7-dibromo-5,6-difluorobenzo[c][1,2,5]thiadiazole and 4-(9H-carbazol-9-yl)phenylboronic acid purchased from J&K Chemical were used as received. Manipulations were carried out under an argon atmosphere by using standard Schlenk techniques, unless otherwise stated. $^1$H NMR (400 MHz) and $^{13}$C NMR (100.6 MHz) spectra were collected on American Varian Mercury Plus 400 spectrometer (400 MHz). $^1$H NMR spectra are reported as followed: chemical shift in ppm ($\delta$) relative to the chemical shift of TMS at 0.00 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet and m = multiplet), and coupling constant (Hz). $^{13}$C NMR chemical shifts reported in ppm ($\delta$) relative to the central line of triplet for CDCl$_3$ at 77 ppm. Elemental analyses (C, H, N) were carried out with a PE CHN 2400 analyzer. EI-MS was obtained using Thermo scientific DSQ II. Fluorescence spectra were recorded on the Fluoromax-P luminescence spectrometer (HORIBA JOBIN YVON INC.). Absolute luminescence quantum yields were measured by HAMAMATSU ABSOLUTE PL QUANTUM YIELD SPECTROMETER C11347. The fluorescence lifetimes were measured by HAMAMATSU COMPACT FLUORESCENCE LIFETIME SPECTROMETER C11367. XRD studies
were recorded on a Shimadzu XRD-6000 diffractometer using Ni-filtered and graphite-monochromated Cu Kα radiation (λ = 1.54 Å, 40 kV, 30 mA). Column chromatographic separations were carried out on silica gel (200-300 mesh). TLC was performed by using commercially prepared 100-400 mesh silica gel plates (GF254) and visualization was effected at 254 nm.

Scheme S1. Synthesis of the compounds 1, 2, 3 and 4.

General procedure for the synthesis

Synthesis of 1: A mixture of 4,7-dibromobenzo[c][1,2,5]thiadiazole (5.1 mmol, 1.5 g), 4-(diphenylamino)phenylboronic acid (5.1 mmol, 1.47 g), K₂CO₃ (2 mol/L, 6 ml, aqueous solution), TBAB (3.7 mmol, 1.2 g), Pd(PPh₃)₄ (0.4 mmol, 0.46 g) were stirred in toluene (70 ml) for 24 h under an argon atmosphere at 80°C, after completion of present reaction,
the mixture was extracted with dichloromethane (3×60 mL), The combined organic layers were washed with brine, dried (MgSO₄), and concentrated in vacuo. The residues were purified by column chromatography, affording the red solid product in a yield of 61.5%. 1: 

1H NMR (400 MHz, CDCl₃): δ (ppm) = 7.89 (d, J = 8 Hz, 1H), 7.80 (d, J = 8 Hz, 2H), 7.54 (d, J = 8 Hz, 1H), 7.29 (t, J = 8 Hz, 4H), 7.20-7.17 (m, 6H), 7.08 (t, J = 6 Hz, 2H). 13C NMR (100 MHz, CDCl₃): δ (ppm) = 154.0, 153.2, 148.5, 147.4, 133.6, 132.4, 129.9, 129.4, 127.3, 125.1, 124.2, 123.5, 122.6, 112.2. EI-MS: m/z = 457.10. Anal. Calcd. for C₂₄H₁₆BrN₃S: C, 62.89; H, 3.52; N, 9.17. Found: C, 62.81; H, 3.47; N, 9.26.

Synthesis of 2: A mixture of 4,7-dibromo-5,6-difluorobenzo[c][1,2,5]thiadiazole (5.1 mmol, 1.68 g), 4-(diphenylamino)phenylboronic acid (5.1 mmol, 1.47 g), K₂CO₃ (2 mol/L, 6 ml, aqueous solution), TBAB (3.7 mmol, 1.2 g), Pd(PPh₃)₄ (0.4 mmol, 0.46 g) were stirred in toluene (70 ml) for 24 h under an argon atmosphere at 80°C, after completion of present reaction, the mixture was extracted with dichloromethane (3×60 mL), The combined organic layers were washed with brine, dried (MgSO₄), and concentrated in vacuo. The residues were purified by column chromatography, affording the red solid product in a yield of 63.2%. Because of the limited solubility of 2, and thus 13C NMR spectrum of 2 was not obtained. 2: 1H NMR (400
MHz, CDCl$_3$): $\delta$ (ppm) = 7.66 (d, $J = 8$ Hz, 2H), 7.31 (t, $J = 8$ Hz, 4H), 7.19 (t, $J = 8$ Hz, 6H), 7.10 (t, $J = 8$ Hz, 2H). EI-MS: m/z = 495.05. Anal. Calcd. for C$_{24}$H$_{14}$BrF$_2$N$_3$S: C, 58.31; H, 2.85; N, 8.50. Found: C, 58.25; H, 2.89; N, 8.43.

Synthesis of 3: A mixture of 4,7-dibromobenzo[c][1,2,5]thiadiazole (5.1 mmol, 1.5 g), 4-(9H-carbazol-9-yl) phenylboronic acid (5.1 mmol, 1.46 g), K$_2$CO$_3$ (2 mol/L, 6 ml, aqueous solution), TBAB (3.7 mmol, 1.2 g), Pd(PPh$_3$)$_4$ (0.4 mmol, 0.46 g) were stirred in toluene (70 ml) for 24 h under an argon atmosphere at 80°C, after completion of present reaction, the mixture was extracted with dichloromethane (3×60 mL), The combined organic layers were washed with brine, dried (MgSO$_4$), and concentrated in vacuo. The residues were purified by column chromatography, affording the yellow solid product in a yield of 63.1%.

3:$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 8.16 (t, $J = 8$ Hz, 4H), 7.98 (d, $J = 8$ Hz, 1H), 7.75 (d, $J = 8$ Hz, 2H), 7.68 (d, $J = 8$ Hz, 1H), 7.55 (d, $J = 8$ Hz, 2H), 7.44 (t, $J = 8$ Hz, 2H), 7.32 (t, $J = 6$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) = 154.0, 153.1, 140.7, 138.2, 135.5, 133.0, 132.3, 130.6, 128.4, 127.1, 126.0, 123.6, 120.4, 120.2, 113.6, 109.9. EI-MS: m/z = 457.10. Anal. Calcd. for C$_{24}$H$_{14}$BrN$_3$S: C, 63.16; H, 3.09; N, 9.21. Found: C, 63.21; H, 3.02; N, 9.25.

Synthesis of 4: A mixture of 4,7-dibromo-5,6-difluorobenzo[c][1,2,5]thiadiazole (5.1 mmol, 1.68 g), 4-(9H-carbazol-9-
yl) phenylboronic acid (5.1 mmol, 1.46 g), K$_2$CO$_3$ (2 mol/L, 6 ml, aqueous solution), TBAB (3.7 mmol, 1.2 g), Pd(PPh$_3$)$_4$ (0.4 mmol, 0.46 g) were stirred in toluene (70 ml) for 24 h under an argon atmosphere at 80°C, after completion of present reaction, the mixture was extracted with dichloromethane (3 × 60 mL). The combined organic layers were washed with brine, dried (MgSO$_4$), and concentrated in vacuo. The residues were purified by column chromatography, affording the yellow solid product in a yield of 62.8%. Because of the limited solubility of 4, and thus $^{13}$C NMR spectrum of 4 was not obtained. 4: $^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) = 8.17 (d, $J$ = 8 Hz, 2H), 8.05 (d, $J$ = 8 Hz, 2H), 7.80 (d, $J$ = 8 Hz, 2H), 7.58 (d, $J$ = 8 Hz, 2H), 7.46 (t, $J$ = 6 Hz, 2H), 7.33 (t, $J$ = 8 Hz, 2H). EI-MS: m/z = 493.00. Anal. Calcd. for C$_{24}$H$_{12}$BrF$_2$N$_3$S: C, 58.55; H, 2.46; N, 8.53. Found: C, 58.50; H, 2.43; N, 8.57.

2. Copies of NMR spectra and Mass spectra