Supplementary Material (ESI) for Chemical Communications

Accelerated hole transfer across a molecular double barrier

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Synthetic procedures and product characterization data

The synthetic strategies followed to obtain donor-bridge-acceptor molecules **1** – **4** are summarized graphically by Figure S1. The syntheses of the four rhenium(I) complexes rely on a set of buildings blocks that can be synthesized as illustrated in Figure S2.

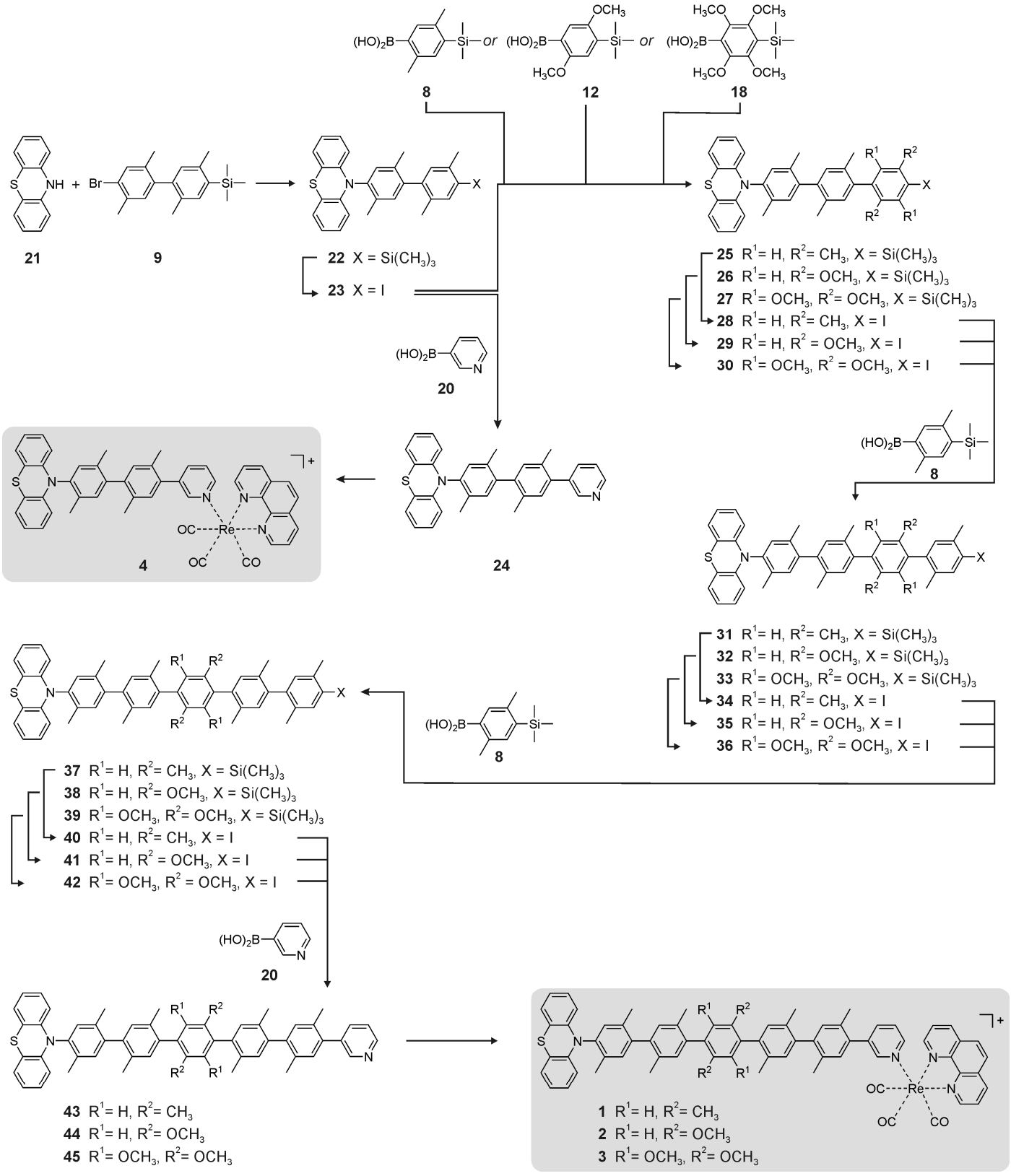

Figure S1. Synthesis of dyads **1** – **4**.

The following abbreviations are used in this experimental section: PTZ for phenothiazine, xy for *p*-xylene, dmb for *p*-dimethoxybenzene, tmb for 1,2,4,5-tetramethoxybenzene, py for pyridine, phen for 1,10-phenanthroline.

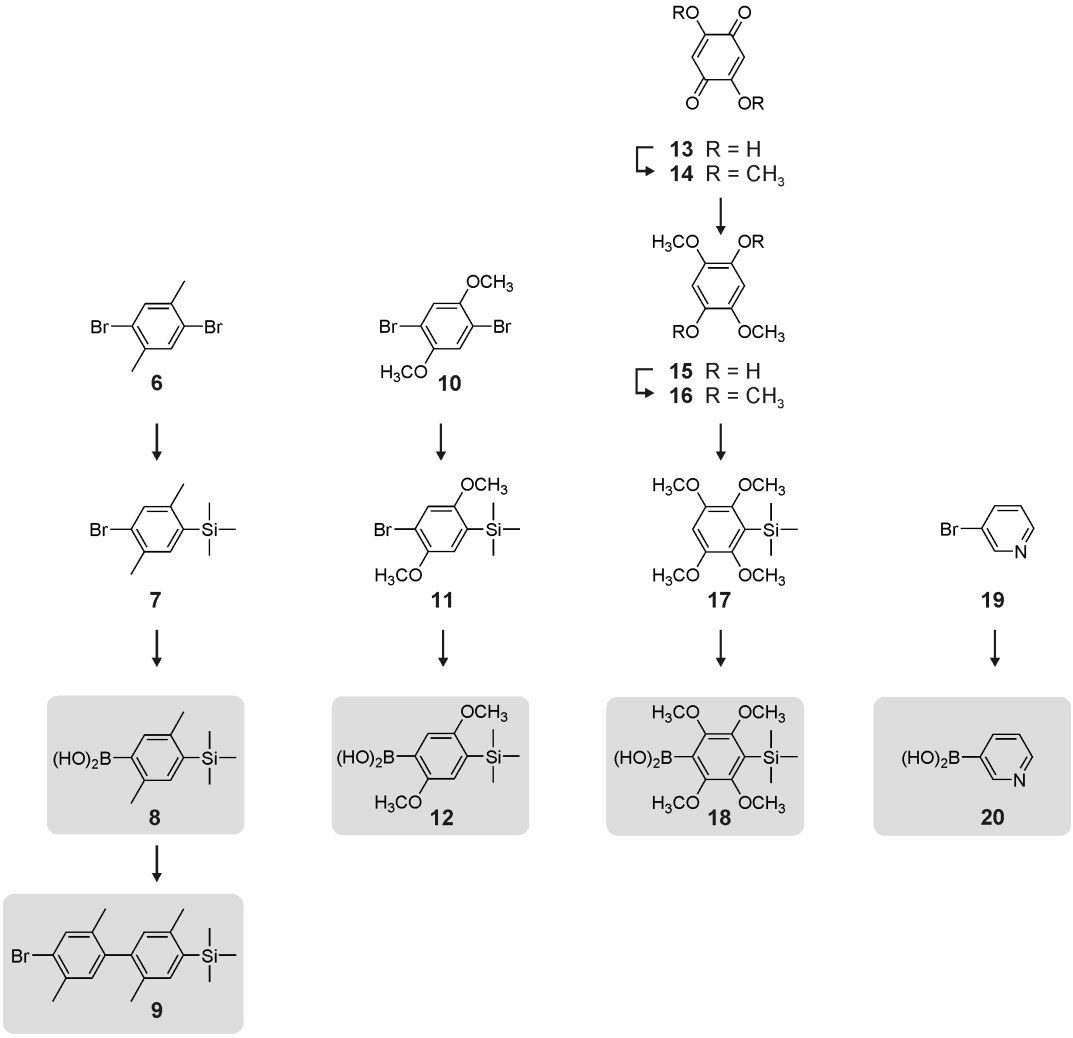

Figure S2. Synthesis of the building blocks used in Figure S1.

Molecule **1** ([PTZ-xy_5-Re]$^+OSO_2CF_3^-$). A solution of ligand **42** (50 mg, 0.063 mmol) and [Re(1,10-phenanthroline)$(CO)_3(OSO_2CF_3)$] (34 mg, 0.056 mmol) in a mixture of chloroform and methanol (2:8) was heated to reflux under nitrogen atmosphere over night. After cooling to room temperature, the solvent was evaporated under reduced pressure and the remaining solid was purified by chromatography on a silica gel column. Using a dichloromethane-methanol (98:2) mixture, the pure product complex was obtained in 61% yield (53 mg) as a yellow solid. For product characterization data, see reference 1.

Molecule **2** ([PTZ-xy_2-dmb-xy_2-Re]$^+OSO_2CF_3^-$). A solution of pyridine ligand **43** (70 mg, 0.084 mmol) and Re(1,10-phenanthroline)$(CO)_3(OSO_2CF_3)$ (51 mg, 0.084 mmol) in a mixture of chloroform and methanol (2:8) was heated to reflux under nitrogen atmosphere over night. After cooling to room temperature and subsequent solvent evaporation under reduced pressure, the crude product was purified by column chromatography on a silica gel stationary phase. Using a dichloromethane-methanol mixture (98:2) as an eluent, the desired product could be obtained in 53% yield (64 mg). ^{1}H NMR ($CDCl_3$): δ = 1.94 (s, 6 H, CH_3), 2.12 (s, 6 H, CH_3), 2.17 (s, 3 H, CH_3), 2.19 (s, 3 H, CH_3), 2.22 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3), 6.13 (dd, *J* = 7.6, 1.2 Hz, 2 H, PTZ), 6.74 (s, 1 H), 6.78 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.86 (m, 4 H), 6.98 (dd, *J* = 7.6, 1.6 Hz, 2 H, PTZ), 7.01 (s, 1 H), 7.11 (s, 1 H), 7.12 (s, 1 H), 7.21 (s, 1 H), 7.23

(s, 1 H), 7.47 (m, 1 H, py), 7.75 (m, 1 H, py), 8.11(m, 1 H, py), 8.22 (dd, *J* = 8.0, 5.2 Hz, 1 H, phen), 8.29 (s, 2 H, phen), 8.39 (d, *J* = 1.6 Hz, 1 H, py), 8.93 (dd, *J* = 8.0, 0.8 Hz, 2 H, phen), 9.60 (d, *J* = 5.2 Hz, 2 H, phen) ppm. HRMS (ESI): calcd. for $C_{72}H_{60}N_4O_5SRe^+$ 1279.3762; found 1279.3836. $C_{73}H_{60}N_4O_8F_3S_2Re \cdot 2\ CH_3OH$ (1492.70): calcd. C 60.35, H 4.59, N 3.75; found C 60.16, H 4.46, N 3.63.

Molecule **3** ($[PTZ\text{-}xy_2\text{-}tmb\text{-}xy_2\text{-}Re]^+OSO_2CF_3^-$). A solution of pyridine ligand **44** (51 mg, 0.057 mmol) and Re(1,10-phenanthroline)$(CO)_3(OSO_2CF_3)$ (35 mg, 0.057 mmol) in a mixture of chloroform and methanol (2:8) was heated to reflux under nitrogen atmosphere over night. After cooling to room temperature, the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on a silica gel stationary phase using a dichloromethane-methanol mixture (98:2) as an eluent. This procedure gave the desired product in 73% yield (62 mg). ^{1}H NMR ($CDCl_3$): δ = 1.93 (s, 3 H, CH_3), 2.09 (s, 3 H, CH_3), 2.11 (s, 3 H, CH_3), 2.15-2.25 (m, 15 H, CH_3), 3.59 (s, 6 H, OCH_3), 3.67 (s, 6 H, OCH_3), 6.13 (dd, *J* = 7.6, 1.2 Hz, 2 H, PTZ), 6.74 (s, 1 H, xy), 6.79 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.87 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.95 (dd, *J* = 7.6, 1.2 Hz, 2 H, PTZ), 7.03 (s, 1 H, xy), 7.12 (s, 1 H, xy), 7.21 (s, 1 H, xy), 7.23 (s, 1 H, xy), 7.31 (s, 1 H, xy), 7.45 (m, 2 H), 7.76 (m, 1 H, py), 8.16 (m, 1 H, py), 8.23 (m, 3 H), 8.29 (s, 2 H, phen), 8.36 (d, *J* = 1.6 Hz, 1 H, py), 8.94 (dd, *J* = 7.6, 0.8 Hz, 2 H, phen), 9.61 (d, *J* = 5.2 Hz, 2 H, phen) ppm. MS (ESI): calcd. for $C_{74}H_{64}N_4O_7SRe^+$ 1339.4047, found 1339.4035. $C_{75}H_{64}N_4O_{10}F_3S_2Re \cdot CHCl_3$ (1608.74): calcd. C 56.77, H 4.07, N 3.48; found C 56.94, H 3.65, N 3.65.

Molecule **4** ($[PTZ\text{-}xy_2\text{-}Re]^+OSO_2CF_3^-$) was synthesized from ligand **24** and [Re(1,10-phenanthroline)$(CO)_3(OSO_2CF_3)$] as described in reference 1.

Molecule **5** ($[Re(phen)(CO)_3(pyridine)]^+OSO_2CF_3^-$) was synthesized as described in reference 1.

Molecule **6** (1,4-dibromo-2,5-dimethylbenzene). This molecule was purchased from the Sigma-Aldrich chemical company.

Molecule **7** (1-bromo-2,5-dimethyl-4-(trimethylsilyl)benzene). The synthesis of this molecule is described in reference 1.

Molecule **8** (2,5-dimethyl-4-(trimethylsilyl)phenylboronic acid). The synthesis of this molecule is described in reference 1.

Molecule **9** (4′-bromo-2,2′,5,5′-tetramethylbiphenyl-4-yl)trimethylsilane). To a deoxygenated suspension of dibromide **6** (11.88 g, 45.0 mmol) and boronic acid **7** (2.00 g, 9.0 mmol) and sodium carbonate (2.86 g, 2.7 mmol) in a mixture of toluene, ethanol, water (85:10:5) was added tetrakistriphenylphosphinepalladium(0) (312 mg, 0.27 mmol). The yellow reaction mixture was degassed for an additional 10 minutes and then heated to reflux under nitrogen over night. After cooling to room temperature, the mixture was extracted with dichloromethane, and the combined organic phases were evaporated to dryness. The majority of the excess dibromide **5** was removed by sublimation, before subjecting the brown remaining solid to column chromatography on a silica gel stationary phase. The desired coupling product **9** was eluted from the column using a dichloromethane/methanol mixture (98:2). It was obtained as a colorless oil in 88% yield. ^{1}H NMR ($CDCl_3$): δ = 0.39 (s, 9 H, $Si(CH_3)_3$), 2.11 (s, 3 H, CH_3), 2.14 (s, 3 H, CH_3), 2.18 (s, 3 H, CH_3), 2.48 (s, 3 H, CH_3), 6.11 (dd, *J* = 8.0, 1.2 Hz, 2 H, PTZ), 6.95 (m, 2 H, PTZ), 6.96 (d, *J* = 7.6 Hz, 2 H, PTZ), 7.01 (s, 1 H, xy), 7.20 (s, 1 H, xy), 7.22 (s, 1 H, xy), 7.38 (s, 1 H, xy) ppm.

Molecule **10** (1,4-dibromo-2,5-dimethoxybenzene). This molecule was synthesized from commercially available 1,4-dimethoxybenzene (Fluka chemical company) as described in reference 2.

Molecule **11** (1-bromo-2,5-dimethoxy-4-(trimethylsilyl)benzene) was synthesized as described in reference 2.

Molecule **12** (4-bromo-2,5-dimethoxyphenylboronic acid) was synthesized as described in reference 2.

Molecule **13** (2,5-dihydroxy-1,4-benzoquinone) was bought from the Sigma-Aldrich chemical company.

Molecule **14** (2,5-dimethoxy-1,4-benzoquinone). Acetyl chloride (2.0 ml, 28.0 mmol) was added to a suspension of 2,5-dihydroxy-1,4-benzoquinone **13** (5.0 g, 35.7 mmol) in methanol (50 ml) at room temperature. After heating the reaction mixture to 90°C under nitrogen atmosphere during 3 days, the resulting brown suspension was filtered, and the solid was washed with cold methanol until the washing solution was colorless. The filtered solid was dried under vacuum to give the product in 89% yield (5.3 g, 31.8 mmol). ^{1}H NMR ($CDCl_3$): δ = 3.87 (s, 6 H, OCH_3), 5.89 (s, 2 H) ppm.

Molecule **15** (2,5-dimethoxy-1,4-dihydroxybenzene).[3] 2,5-dimethoxy-1,4-benzoquinone **14** (5.3 g, 31.8 mmol) was suspended in ethanol (50 ml). While cooling the suspension in an ice bath, sodium borohydride (4.3 g, 113.7 mmol) was added in small portions over a period of 20 minutes. After reacting the mixture for 4 hours at room temperature, aqueous hydrochloric acid was added slowly (1 M, 50 ml). After addition of water (60 ml), the solution was extracted with dichloromethane and diethyl ether. Drying of the extracts with anhydrous sodium sulfate and subsequent solvent evaporation afforded the product in essentially quantitative yield (5.3 g, 31.8 mmol). ^{1}H NMR ($CDCl_3$): δ = 3.87 (s, 6 H, OCH_3), 5.60 (s, 2 H) ppm.

Molecule **16** (1,2,4,5-tetramethoxybenzene).[4] To a suspension of 2,5-dimethoxy-1,4-dihydroxybenzene **15** (5.3 g, 31.8 mmol) in ethanol (30 ml) was added dimethylsulfate (13.1 ml, 138.1 mmol) while cooling the reaction mixture in an ice bath. After careful addition of $NaHSO_3$ (0.89 g, 8.6 mmol) and aqueous solution of sodium hydroxide (9.2 g NaOH in 18 ml H_2O), the bubbling mixture was reacted for 30 minutes at 0 °C, before heating it to 80°C during 36 hours. Then, water was added (100 ml) and the product was extracted with dichloromethane (three 100 ml portions). After complete evaporation of the organic solvents, the crude product was re-dissolved in dichloromethane and washed twice with 2 M aqueous sodium hydroxide solution (100 ml). The washing solutions were re-extracted with dichloromethane, and the combined organic phases were finally dried with anhydrous sodium sulfate, and the solvent was evaporated. This gave the product in 82% yield (5.1 g, 25.7 mmol). ^{1}H NMR ($CDCl_3$): δ = 3.87 (s, 12 H, OCH_3), 6.62 (s, 2 H) ppm.

Molecule **17** (1,2,4,5-tetramethoxy-3-(trimethylsilyl)benzene.[4] A suspension of molecule **16** (4.25 g, 21.4 mmol) in hexane (150 ml) was deoxygenated during 15 minutes by bubbling with nitrogen. Then, N,N,N′,N′-tetramethyl-*p*-phenylenediamine (3.9 g, 25.8 mmol) and 1.6 M solution of *n*-butyllithium in hexane (16.1 ml, 25.8 mmol) were added at room temperature. This reaction mixture was protected from light and stirred for 14 hours at room temperature, before cooling it to 0 °C. Following addition of chlorotrimethylsilane (4.0 ml, 31.6 mmol), the solution was allowed to warm to room temperature and after 2 hours, de-ionized water (100 ml) was added. The aqueous phase was extracted with dichloromethane, and the combined organic phases were evaporated to afford the crude product as a brown oil. This was purified by column chromatography on silica gel using a pentane-dichloromethane (9:1) eluent mixture. Thereby molecule **17** was obtained as in the form of a pale yellow oil in 78% yield (4.5 g, 16.6 mmol). ^{1}H NMR ($CDCl_3$): δ = 0.35 (s, 9 H, $Si(CH_3)_3$), 3.77 (s, 6 H, OCH_3), 3.86 (s, 6 H, OCH_3), 6.61 (s, 1 H) ppm.

Molecule **18** (2,3,5,6-tetramethoxy-4-(trimethylsilyl)phenylboronic acid).[5] A solution of molecule **17** (2.78 g, 10.3 mmol) in hexane (130 ml) was deoxygenated by bubbling nitrogen gas during 15 minutes. To this solution were added N,N,N′,N′-tetramethyl-*p*-phenylenediamine (2.2 g, 14.6 mmol) and a 1.6 M solution of *n*-butyllithium in hexane (8.4 ml, 13.4 mmol) at room temperature. This reaction mixture was protected from light and stirred at room temperature during 14 hours. Prior to addition of triisopropylborate (3.5 ml, 15.2 mmol), the reaction mixture was cooled to 0 °C, and subsequently it was allowed to warm up to room temperature. After stirring for 24 hours at this temperature, 2 M aqueous hydrochloric acid was added (120 ml) and the resulting two phases were separated from one another. The

aqueous phase was extracted with dichloromethane, and the combined organic phases were evaporated to dryness. The resulting brown oil was purified by column chromatography on silica gel using first pure dichloromethane, then methanol-dichloromethane mixtures with increasing methanol proportions (up to 1:20) as eluents. This gave the pure boronic acid in 84% yield (2.72 g). ^{1}H NMR ($CDCl_3$): δ = 0.36 (s, 9 H, $Si(CH_3)_3$), 3.79 (s, 6 H, OCH_3), 3.90 (s, 6 H, OCH_3) ppm.

Molecule **19** (2-bromopyridine) was bought from the Fluka chemical company.

Molecule **20** (3-pyridineboronic acid) was synthesized as described in reference 6.

Molecule **21** (phenothiazine) was purchased from Fluka.

Molecule **22** (PTZ-xy$_2$-TMS). To a two-neck flask containing phenothiazine **21** (1.32 g, 6.6 mmol), bixylyl **9** (2.40 g, 6.6 mmol), potassium tertiobutanolate (1.12 g, 10.0 mmol) and Pd(dibenzylidene-acetone)$_2$ (76 mg, 0.13 mmol) were added freshly distilled toluene (25 ml) and a 1 M solution of P(*tert.*-butylphosphine)$_3$ (0.13 ml, 0.13 mmol) under nitrogen atmosphere. The yellow suspension was heated to 60 °C while following reaction progress by thin layer chromatography. Once the phenothiazine starting material had all disappeared, the solvent was evaporated and the crude brown product was purified by column chromatography on a silica gel stationary phase using a pentane/dichloromethane (98:2) eluent mixture. This afforded the pure N-C coupling product **22** as a pale yellow solid in 89% yield (2.84 g). ^{1}H NMR ($CDCl_3$): δ = 0.39 (s, 9 H, $Si(CH_3)_3$), 2.11 (s, 3 H, CH_3), 2.14 (s, 3 H, CH_3), 2.18 (s, 3 H, CH_3), 2.48 (s, 3 H, CH_3), 6.11 (d, *J* = 8.0 Hz, 2 H, PTZ), 6.91 (m, 2 H, PTZ), 6.94 (m, 2 H, PTZ, 6.96 (d, *J* = 7.6 Hz, 2 H, PTZ), 7.01 (s, 1 H, xy), 7.20 (s, 1 H, xy), 7.22 (s, 1 H, xy), 7.38 (s, 1 H, PTZ) ppm.

Molecule **23** (PTZ-xy$_2$-I). To a suspension of molecule **22** (2.70 g, 5.6 mmol) in a mixture of dichloromethane (10 ml) and acetonitrile (30 ml) at 0 °C was added slowly a solution of iodine monochloride (1.83 g, 11.3 mmol) in dichloromethane (5 ml). The reaction mixture was allowed to warm to room temperature and stirred during 20 hours. After hydrolysis with aqueous $Na_2S_2O_3$ solution (20 ml), the reaction mixture was extracted with dichloromethane. The combined organic phases were evaporated to dryness, and the crude brown product was purified by column chromatography on silica gel. A pentane-dichloromethane mixture (98:2) was used to elude the product in essentially quantitative yield (3.00 g). ^{1}H NMR ($CDCl_3$): δ = 2.08 (s, 6 H, CH_3), 2.18 (s, 3 H, CH_3), 2.45 (s, 3 H, CH_3), 6.08 (dd, *J* = 8.0, 1.2 Hz, 2 H, PTZ), 6.77 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.84 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.96 (dd, *J* = 7.6, 1.6 Hz, 2 H, PTZ), 7.08 (s, 1 H, xy), 7.15 (s, 1 H, xy), 7.22 (s, 1 H, xy), 7.77 (s, 1 H, xy) ppm.

Molecule **24** (PTZ-xy$_2$-py) was synthesized from iodo compound **23** and 3-pyridineboronic acid **20** as described in reference 1.

Molecule **25** (PTZ-xy$_3$-TMS). To a deoxygenated suspension of iodo compound **23** (2.20 g, 4.1 mmol), 2,5-dimethyl-4-(trimethylsilyl)phenylboronic acid **8** (101 mg, 4.5 mmol) and sodium carbonate (1.31 g, 12.4 mmol) in a mixture of toluene, ethanol and water (85:10:5) was added tetrakistriphenylphosphinepalladium(0) catalyst (95 mg, 0.08 mmol). The reaction mixture was degassed for an additional 10 minutes by bubbling nitrogen gas before heating it to reflux under nitrogen atmosphere over night. After cooling to room temperature, the coupling product was extracted with dichloromethane. The combined organic phases were evaporated to dryness, and the remaining dark brown solid was subjected to column chromatography on a silica gel stationary phase. The product was eluted using a pentane-dichloromethane mixture (98:2). This procedure afforded molecule **25** in 80% yield (1.20 g) as a pale yellow solid. ^{1}H NMR ($CDCl_3$): δ = 0.38 (s, 9 H, $Si(CH_3)_3$), 2.09-2.16 (m, 12 H, CH_3)), 2.29 (s, 2 H, CH_3), 2.47 (s, 3 H, CH_3); 6.13 (dd, *J* = 8.0, 1.2 Hz, 2 H, PTZ), 6.77 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.84 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.96 (dd, *J* = 7.6, 1.6 Hz, 2 H, PTZ), 7.00 (s, 1 H, xy), 7.05 (d, *J* = 4.4 Hz, 1 H, xy), 7.09 (d, *J* =4.4 Hz, 1 H, xy), 7.24 (s, 1 H, xy), 7.26 (s, 1 H, xy), 7.36 (s, 1 H, xy) ppm.

Molecule **26** (PTZ-xy_2-dmb-TMS). To a suspension of iodo compound **23** (1.33 g, 2.5 mmol), 2,5-dimethoxy-4-(trimethylsilyl)phenylboronic acid **12** (762 mg, 3.0 mmol) and sodium carbonate (794 mg, 8.4 mmol) in a mixture of toluene, ethanol, water (85:10:5) was added tetrakistriphenylphosphinepalladium(0) (144 mg, 0.125 mmol). Prior to heating at reflux under nitrogen atmosphere over night, the yellow suspension was degassed by bubbling nitrogen gas. After cooling to room temperature, the mixture was extracted with dichloromethane, and the combined organic phases were evaporated to dryness. The remaining dark brown solid was purified by column chromatography on silica gel, and product elusion occurred using a pentane-dichloromethane mixture (98:2). This procedure gave the desired coupling product **26** in 95% yield (1.34 g). ^{1}H NMR ($CDCl_3$): δ = 0.35 (s, 9 H, $Si(CH_3)_3$), 2.14 (s, 3 H, CH_3), 2.17 (s, 3 H, CH_3), 2.20 (s, 6 H, CH_3), 3.78 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3), 6.13 (dd, *J* = 8.0, 1.2 Hz, 2 H, PTZ), 6.75 (s, 1 H), 6.78 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.86 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.97 (dd, *J* = 7.6, 1.2 Hz, 2 H, PTZ), 7.01 (s, 1 H), 7.10 (s, 1 H), 7.15 (s, 1 H), 7.24 (s, 1 H), 7.27 (s, 1 H) ppm.

Molecule **27** (PTZ-xy_2-tmb-TMS). To a suspension of iodo compound **23** (628 mg, 1.2 mmol), 2,3,5,6-tetramethyl-4-(trimethylsilyl)phenylboronic acid **18** (370 mg, 1.2 mmol) and sodium carbonate (375 mg, 3.5 mmol) in a mixture of toluene, ethanol, water (85:10:5) was added tetrakistriphenylphosphinepalladium(0) (68 mg, 0.06 mmol). The yellow suspension was deoxygenated by bubbling nitrogen gas prior to heating to reflux under nitrogen atmosphere over night. After cooling to room temperature, the mixture was extracted with dichloromethane, and the combined organic phases were evaporated to dryness. The crude product was purified by column chromatography on silica gel using a pentane-dichloromethane eluent mixture (98:2). This afforded pure **27** in 48% yield as a pale yellow solid. ^{1}H NMR ($CDCl_3$): δ = 0.40 (s, 9 H, $Si(CH_3)_3$, 2.13 (s, 3 H, CH_3), 2.14 (s, 3 H, CH_3), 2.19 (s, 3 H, CH_3), 2.20 (s, 3 H, CH_3), 3.50 (s, 3 H, OCH_3), 3.57 (s, 3 H, OCH_3), 3.86 (s, 6 H, OCH_3), 6.13 (dd, *J* = 8.0, 1.2 Hz, 2 H, PTZ), 6.82 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.84 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.97 (dd, *J* = 7.6, 1.6 Hz, 2 H, PTZ), 7.12 (s, 1 H, xy), 7.15 (s, 1 H, xy), 7.23 (s, 1 H, xy), 7.28 (s, 1 H, xy) ppm.

Molecule **28** (PTZ-xy_3-I). A solution of iodine monochloride (1.33 g, 8.2 mmol) in dichloromethane (5 ml) was added slowly to a suspension of the trimethylsilyl-protected compound **25** (2.40 g, 4.1 mmol) in a mixture of dichloromethane (10 ml) and acetonitrile (30 ml) at 0 °C under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 20 hours before adding aqueous $Na_2S_2O_3$ solution. After extraction with dichloromethane, the combined organic phases were evaporated to dryness, and the crude product was purified by chromatography on a silica gel stationary phase using an eluent mixture comprised of pentane and dichloromethane (98:2). This gave pure **28** in 88% yield (2.28 g) as a yellow solid. ^{1}H NMR ($CDCl_3$): δ = 2.06 (s, 6 H, CH_3), 2.11 (s, 6 H, CH_3), 2.19 (s, 3 H, CH_3), 2.48 (s, 3 H, CH_3), 6.11 (dd, *J* = 8.0, 1.2 Hz, 2 H, PTZ), 6.77 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.84 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.98 (m, 3 H, xy), 7.07 (m, 2 H, xy), 7.24 (m, 2 H, xy), 7.75 (s, 1 H, xy) ppm.

Molecule **29** (PTZ-xy_2-dmb-I). To a suspension of molecule **26** (1.34 g, 2.1 mmol) in a dichloromethane-acetonitrile mixture (5 ml:15 ml) at 0 °C was added slowly a solution of iodine monochloride (677 mg, 4.2 mmol) in dichloromethane (3 ml). The reaction mixture was stirred at room temperature for 20 hours. After addition of aqueous $Na_2S_2O_3$ solution, the crude product was extracted with dichloromethane and purified by column chromatography on silica gel using a pentane-dichloromethane (98:2) mixture as an eluent. This gave the pure product **29** in essentially quantitative yield (1.41 g). ^{1}H NMR ($CDCl_3$): δ = 2.12 (s, 3 H, CH_3), 2.17-2.21 (m, 9 H, CH_3), 3.78 (s, 3 H, OCH_3), 3.89 (s, 3 H, OCH_3), 6.15 (dd, *J* = 8.0, 1.2 Hz, 2 H, PTZ), 6.78 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.81 (s, 1 H), 6.87 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.97 (dd, *J* = 7.6, 1.6 Hz, 2 H, PTZ), 7.13 (m, 2 H), 7.23 (m, 1 H), 7.27 (s, 1 H), 7.70 (m, 1 H, xy) ppm.

Molecule **30** (PTZ-xy_2-tmb-I). A solution of iodine monochloride (184 mg, 1.1 mmol) in dichloromethane (2 ml) was added slowly to a suspension of molecule **27** (382 mg, 0.565 mmol) in a mixture of dichloromethane (4 ml) and acetonitrile (12 ml) at 0 °C. The dark orange reaction mixture was stirred at room temperature for 20 hours before hydrolyzing with aqueous $Na_2S_2O_3$ solution. After subsequent extraction with dichloromethane and evaporation of the

combined organic phases, the crude brown product was subjected to column chromatography on silica gel using a pentane-dichloromethane mixture (98:2) as an eluent. This gave pure **30** as a yellow solid in 83% yield (340 mg). ^{1}H NMR ($CDCl_3$): δ = 2.13 (s, 3 H, CH_3), 2.14 (s, 3 H, CH_3), 2.19 (s, 3 H, CH_3), 2.20 (s, 3 H, CH_3), 3.50 (s, 3 H, OCH_3), 3.59 (s, 3 H, OCH_3), 3.85 (s, 6 H, OCH_3), 6.13 (dd, *J* = 8.0, 1.2 Hz, 2 H, PTZ), 6.82 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.84 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.97 (dd, *J* = 7.6, 1.6 Hz, 2 H, PTZ), 7.12 (s, 1 H, xy), 7.15 (s, 1 H, xy), 7.51 (s, 1 H, xy), 7.78 (s, 1 H, xy) ppm.

Molecule **31** (PTZ-xy_4-TMS). To a deoxygenated suspension of iodo compound **28** (4.00 g, 6.2 mmol), 2,5-dimethyl-4-(trimethylsilyl)phenylboronic acid **8** (1.67 g, 7.5 mmol) and sodium carbonate (2.00 g, 18.8 mmol) in a mixture of toluene, ethanol and water (85:10:5) was added tetrakistriphenylphosphinepalladium(0) (145 mg, 0.125 mmol). This reaction mixture was heated to reflux under nitrogen atmosphere over night and extracted subsequently with dichloromethane. After evaporation of the combined organic phases, the remaining dark brown solid was purified by column chromatography on a silica gel stationary phase. A pentane-dichloromethane mixture (98:2) was used as an eluent. This gave coupling product **31** as a pale yellow solid in 70% yield (3.01 g). ^{1}H NMR ($CDCl_3$): δ = 0.43 (s, 9 H, $Si(CH_3)_3$), 2.14-2.25 (m, 21 H, CH_3), 2.51 (s, 3 H, CH_3), 6.19 (dd, *J* = 8.0, 1.2 Hz, 2 H, PTZ), 6.82 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.90 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.98-7.31 (m, 8 H), 7.33 (s, 1 H, xy), 7.41 (s, 1 H, xy) ppm.

Molecule **32** (PTZ-xy_2-dmb-xy-TMS). Iodo compound **29** (1.41 g, 2.1 mmol), boronic acid **8** (663 mg, 2.6 mmol) and sodium carbonate (692 mg, 6.5 mmol) were suspended in a mixture of toluene, ethanol and water (85:10:5). After addition of tetrakistriphenylphosphinepalladium(0) (126 mg, 0.11 mol), the reaction mixture was deoxygenated thoroughly by bubbling nitrogen gas prior to heating to reflux under nitrogen atmosphere over night. After cooling to room temperature, extraction with dichloromethane and evaporation to dryness of the combined organic phases, the crude product was purified by column chromatography. A pentane-dichloromethane mixture (98:2) was used to elude the product from a silica gel stationary phase. This gave pure molecule **32** as a pale yellow solid in 73% yield (1.10 g). ^{1}H NMR ($CDCl_3$): δ = 0.38 (s, 9 H, $Si(CH_3)_3$), 2.17 (s, 3 H, CH_3), 2.19 (s, 3 H, CH_3), 2.20 (s, 3 H, CH_3), 2.23 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3), 2.50 (s, 3 H, CH_3), 3.77 (s, 3 H, OCH_3), 3.78 (s, 3 H, OCH_3), 6.14 (dd, *J* = 8.0, 1.2 Hz, 2 H, PTZ), 6.78 (m, 2 H, PTZ), 6.82 (s, 1 H), 6.86 (s, 1 H), 6.87 (ddd, *J* = 7.6, 7.6, 1.2, 2 H, PTZ), 6.97 (dd, *J* = 7.6, 1.6 Hz, 2 H, PTZ), 7.12 (s, 2 H), 7.22 (m, 1 H), 7.25 (s, 1 H), 7.29 (s, 1 H), 7.38 (s, 1 H) ppm.

Molecule **33** (PTZ-xy_2-tmb-xy-TMS). Tetrakistriphenylphosphinepalladium(0) catalyst (27 mg, 0.02 mmol) was added to a deoxygenated suspension of iodo compound **30** ((340 mg, 4.7 mmol), boronic acid **8** (125 mg, 0.56 mmol) and sodium carbonate (148 mg, 1.4 mmol) in a mixture of toluene, ethanol and water (85:10:5). After deoxygenating by bubbling nitrogen gas during 10 minutes, the reaction mixture was refluxed under nitrogen atmosphere over night. The coupling product was extracted with dichloromethane and purified by column chromatography on silica gel using a pentane-dichloromethane mixture (98:2) as an eluent. This gave pure molecule **33** as a pale yellow solid in 37% yield (280 mg). ^{1}H NMR ($CDCl_3$): δ = 0.38 (s, 9 H, $Si(CH_3)_3$), 2.15-2.21 (m, 15 H, CH_3), 2.48 (s, 3 H, CH_3), 3.58 (s, 3 H, OCH_3), 3.61 (s, 6 H, OCH_3), 3.66 (s, 3 H, OCH_3), 6.14 (dd, *J* = 8.0, 1.2 Hz, 2 H, PTZ), 6.80 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.87 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.96 (dd, *J* = 7.6, 1.2 Hz, 2 H, PTZ), 7.08 (d, *J* = 4.8 Hz, 1 H, xy), 7.15 (d, *J* = 4.8, 1 H, xy), 7.23 (m, 2 H, xy), 7.31 (s, 1 H, xy), 7.38 (s, 1 H, xy) ppm.

Molecule **34** (PTZ-xy_4-I). A solution of iodine monochloride (1.89 g, 11.6 mmol) in dichloromethane (5 ml) was added slowly to a suspension of the trimethylsilyl-protected compound **31** (4.00 g, 5.8 mmol) in a mixture of dichloromethane (10 ml) and acetonitrile (30 ml) at 0 °C. This mixture was reacted at room temperature for 20 hours, then, aqueous solution of $Na_2S_2O_3$ was added. The crude product was extracted with dichloromethane and purified on a silica gel column with a pentane-dichloromethane mixture (98:2) mobile phase. This procedure gave pure **34** as a yellow solid in 86% yield (3.72 g). ^{1}H NMR ($CDCl_3$): δ = 2.07-2.15 (m, 18 H, CH_3), 2.21 (s, 3 H, CH_3), 2.44 (s, 3 H,

CH_3), 6.13 (dd, *J* = 8.0, 1.2 Hz, 2 H, PTZ), 6.78 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.86 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.98 (m, 3 H, xy), 7.08-7.11 (m, 4 H, xy), 7.24 (s, 1 H, xy), 7.28 (s, 1 H, xy), 7.76 (s, 1 H, xy) ppm.

Molecule **35** (PTZ-xy_2-dmb-xy-I). To a suspension of compound **32** (870 mg, 1.2 mmol) in a mixture of dichloromethane (4 ml) and acetonitrile (12 ml) at 0°C was added slowly a solution of iodine monochloride (392 mg, 2.4 mmol) in dichloromethane (3 ml). The reaction mixture was stirred at room temperature over night. Then, aqueous $Na_2S_2O_3$ solution was added and the product was extracted with dichloromethane. The combined organic phases were evaporated to dryness, and the crude brown product was purified by column chromatography on silica gel using a pentane-dichloromethane (98:2) eluent mixture. This gave pure molecule **35** as a yellow solid in essentially quantitative yield (930 mg). ^{1}H NMR ($CDCl_3$): δ = 2.16 (s, 6 H, CH_3), 2.17 (s, 3 H, CH_3), 2.19 (s, 3 H, CH_3), 2.22 (s, 3 H, CH_3), 2.45 (s, 3 H, CH_3), 3.76 (s, 6 H, OCH_3), 6.12 (dd, *J* = 8.0, 1.2 Hz, 2 H, PTZ), 6.75 (s, 1 H), 6.77 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.84 (s, 1 H), 6.86 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.96 (dd, *J* = 7.6, 1.6 Hz, 2 H, PTZ), 7.11 (s, 1 H), 7.17 (m, 1 H), 7.20 (s, 1 H), 7.23 (s, 1 H), 7.27 (s, 1 H), 7.75 (s, 1 H) ppm.

Molecule **36** (PTZ-xy_2-tmb-xy-I). To a suspension of trimethylsilyl-protected molecule **33** (280 mg, 0.36 mmol) in a mixture of dichloromethane (2 ml) and acetonitrile (6 ml) at 0 °C was added a solution of iodine monochloride (116 mg, 0.72 mmol) in dichloromethane (2 ml). After stirring the dark orange suspension at room temperature during 20 hours, the mixture was hydrolyzed using aqueous $Na_2S_2O_3$ solution. The crude product was extracted with dichloromethane and purified by column chromatography on silica gel. A pentane-dichloromethane mixture (98:2) was used to elude the pure product as a yellow solid in essentially quantitative yield (300 mg). ^{1}H NMR ($CDCl_3$): δ = 2.14-2.17 (m, 15 H, CH_3), 2.45 (s, 3 H, CH_3), 3.57 (s, 3 H, OCH_3), 3.59 (s, 6 H, OCH_3), 3.64 (s, 3 H, OCH_3), 6.14 (dd, *J* = 8.0, 1.2 Hz, 2 H, PTZ), 6.78 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.86 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.95 (dd, *J* = 7.6, 1.6 Hz, 2 H, PTZ), 7.14-7.20 (m, 3 H, xy), 7.30 (s, 1 H, xy), 7.50 (s, 1 H, xy), 7.78 (s, 1 H, xy) ppm.

Molecule **37** (PTZ-xy_5-TMS). Iodo compound **34** (2.00 g, 2.70 mmol), boronic acid **8** (720 mg, 3.2 mmol) and sodium carbonate (857 mg, 8.1 mmol) were suspended in a mixture of toluene, ethanol and water (85:10:5). Prior to addition of tetrakistriphenylphosphinepalladium(0) (62 mg, 0.054 mmol), the reaction mixture was deoxygenated thoroughly by bubbling nitrogen gas. After heating to reflux under nitrogen atmosphere over night, the mixture was extracted with dichloromethane, and the crude product was purified by chromatography on silica gel with a mobile phase comprised of pentane and dichloromethane (98:2). This gave pure **37** as a pale yellow solid in 63% yield (1.34 g). ^{1}H NMR ($CDCl_3$): δ = 0.37 (s, 9 H, $Si(CH_3)_3$), 2.08-2.20 (m, 27 H, CH_3), 2.46 (s, 3 H, CH_3), 6.13 (dd, *J* = 8.0, 1.2 Hz, 2 H, PTZ), 6.77 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.86 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.97 (dd, *J* = 8.0, 1.2 Hz, 2 H, PTZ), 7.02 (m, 2 H, xy), 7.09 (m, 5 H, xy), 7.24 (s, 1 H, xy), 7.28 (s, 1 H, xy), 7.35 (s, 1 H, xy) ppm.

Molecule **38** (PTZ-xy_2-dmb-xy_2-TMS). To a suspension of iodo compound **35** (930 mg, 1.2 mmol), boronic acid **8** (347 mg, 1.6 mmol) and sodium carbonate (382 mg, 3.6 mmol) in a mixture of toluene, ethanol and water (85:10:5) was added tetrakistriphenylphosphinepalladium(0) (69 mg, 0.06 mmol). The yellow reaction mixture was deoxygenated by bubbling nitrogen gas prior to heating to reflux under nitrogen atmosphere over night. After cooling to room temperature, the mixture was extracted with dichloromethane, and the combined organic phases were evaporated to dryness. The remaining dark brown solid was purified by column chromatography on silica gel using a pentane-dichloromethane (98:2) eluent mixture. Thereby the pure product was obtained in 78% yield (250 mg). ^{1}H NMR ($CDCl_3$): δ = 0.38 (s, 9 H, $Si(CH_3)_3$), 2.11 (s, 3 H, CH_3), 2.15 (s, 3 H, CH_3), 2.18 (s, 3 H, CH_3), 2.19 (s, 3 H, CH_3), 2.20 (s, 3 H, CH_3), 2.21 (s, 6 H, CH_3), 2.26 (s, 6 H, CH_3), 2.46 (s, 3 H, CH_3), 3.81 (s, 6 H, OCH_3), 6.13 (dd, *J* = 8.0, 1.2 Hz, 2 H, PTZ), 6.78 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.88 (m, 4 H, xy), 6.97 (dd, *J* = 7.6, 1.6 Hz, 2 H, PTZ), 7.01 (s, 1 H, xy), 7.05 (m, 1 H, xy), 7.13 (s, 1 H, xy), 7.19 (s, 1 H, xy), 7.24 (s, 2 H, xy), 7.29 (s, 1 H, xy), 7.36 (s, 1 H, xy) ppm.

Molecule **39** (PTZ-xy_2-tmb-xy_2-TMS). Iodo-compound **36** (300 mg, 0.36 mmol), boronic acid **8** (80 mg, 0.36 mmol) and sodium carbonate (115 mg, 1.1 mmol) were suspended in a mixture of toluene, ethanol and water (85:10:5). After addition of the tetrakistriphenylphosphinepalladium(0) catalyst, the reaction mixture was deoxygenated by bubbling nitrogen gas, and then it was heated to reflux under nitrogen atmosphere over night. Subsequent cooling to room temperature was followed by extraction with dichloromethane and purification of the crude product by column chromatography on silica gel with a pentane-dichloromethane (98:2) eluent mixture. This gave the coupling product **39** as a pale yellow solid in 63% yield (200 mg). ^{1}H NMR ($CDCl_3$): δ = 0.40 (s, 9 H, $Si(CH_3)_3$), 2.13 (s, 3 H, CH_3), 2.17 (s, 3 H, CH_3), 2.19 (s, 3 H, CH_3), 2.21 (s, 3 H, CH_3), 2.23 (s, 3 H, CH_3), 2.26 (s, 3 H, CH_3), 2.49 (s, 3 H, CH_3), 3.61 (s, 3 H, OCH_3), 3.62 (s, 3 H, OCH_3), 3.68 (s, 3 H, OCH_3), 3.70 (s, 3 H, OCH_3), 6.16 (dd, *J* = 8.0, 1.2 Hz, 2 H, PTZ), 6.82 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.88 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.96 (dd, *J* = 7.6, 1.6 Hz, 2 H, PTZ), 7.05 (s, 1 H, xy), 7.08 (s, 1 H, xy), 7.17 (m, 1 H, xy), 7.20 (m, 1 H, xy), 7.25 (m, 2 H, xy), 7.33 (s, 1 H, xy), 7.33 (s, 1 H, xy) ppm.

Molecule **40** (PTZ-xy_5-I). To a suspension of trimethylsilyl-protected compound **37** (660 mg, 0.83 mmol) in a mixture of dichloromethane (2 ml) and acetonitrile (6 ml) at 0 °C was added slowly a solution of iodine monochloride (270 mg, 1.67 mmol) in dichloromethane (2 ml). This reaction mixture was stirred at room temperature for 20 hours. Then, it was hydrolyzed by addition of aqueous $Na_2S_2O_3$ solution, and the product was extracted with dichloromethane. Purification occurred by column chromatography on a silica gel stationary phase with a pentane-dichloromethane mixture (98:2) as an eluent. This gave pure **40** as a yellow solid in 85% yield (600 mg). ^{1}H NMR ($CDCl_3$): δ = 2.06-2.20 (m, 27 H, CH_3), 2.44 (s, 3 H, CH_3), 6.13 (dd, *J* = 8.0, 1.2 Hz, 2 H, PTZ), 6.79 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.86 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.98 (m, 3 H), 7.08-7.12 (m, 6 H, xy), 7.24 (s, 1 H, xy), 7.28 (s, 1 H, xy), 7.75 (s, 1 H, xy) ppm.

Molecule **41** (PTZ-xy_2-dmb-xy_2-I). To a suspension of molecule **38** (720 mg, 0.87 mmol) in a mixture of dichloromethane (2 ml) and acetonitrile (6 ml) at 0 °C was added slowly a solution of iodine monochloride (284 mg, 1.7 mmol) in dichloromethane (2 ml). This mixture was reacted at room temperature during 20 hours before hydrolyzing with aqueous $Na_2S_2O_3$ solution. After extraction with dichloromethane, the crude product was purified by column chromatography on silica gel using a pentane-dichloromethane mixture (98:2) as an eluent. This gave the pure product in essentially quantitative yield (757 mg). ^{1}H NMR ($CDCl_3$): δ = 2.08 (s, 6 H, CH_3), 2.17 (s, 6 H, CH_3), 2.20 (s, 3 H, CH_3), 2.21 (s, 3 H, CH_3), 2.24 (s, 3 H, CH_3), 2.43 (s, 3 H, CH_3), 3.80 (s, 6 H, OCH_3), 6.13 (dd, *J* = 8.0, 1.2 Hz, 2 H, PTZ), 6.78 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.86 (m, 4 H), 6.95 (s, 1 H), 6.98 (dd, *J* = 7.6, 1.6 Hz, 2 H, PTZ), 7.08 (s, 1 H), 7.12 (s, 1 H), 7.18 (s, 1 H), 7.23 (s, 2 H), 7.28 (s, 1 H), 7.75 (s, 1 H) ppm.

Molecule **42** (PTZ-xy_2-tmb-xy_2-I). A solution of iodine monochloride (73 mg, 0.45 mmol) in dichloromethane (2 ml) was added to a suspension of molecule **39** (200 mg, 0.23 mmol) in a mixture of dichloromethane (2 ml) and acetonitrile (8 ml) at 0 °C. The dark orange mixture was stirred at room temperature during 20 hours. After hydrolysis with aqueous $Na_2S_2O_3$ solution and subsequent extraction with dichloromethane, the crude product was subjected to column chromatography on silica gel. A pentane-dichloromethane mixture (98:2) was used as a mobile phase. This procedure gave pure iodo-compound **42** in 95% yield (202 mg). ^{1}H NMR ($CDCl_3$): δ = 2.00 (s, 6 H, CH_3), 2.06 (s, 3 H, CH_3), 2.08 (s, 3 H, CH_3), 2.15-2.20 (m, 6 H, CH_3), 2.17 (s, 3 H, CH_3), 2.44 (s, 3 H, CH_3), 3.58 (s, 3 H, OCH_3), 3.60 (s, 3 H, OCH_3), 3.66 (s, 3 H, OCH_3), 3.67 (s, 3 H, OCH_3), 6.14 (dd, *J* = 8.0, 1.2 Hz, 2 H, PTZ), 6.79 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.86 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.95 (dd, *J* = 7.6, 1.6 Hz, 2 H, PTZ), 7.02 (s, 1 H, xy), 7.10 (s, 1 H, xy), 7.15 (m, 1 H, xy), 7.21 (m, 2 H, xy), 7.24 (s, 1 H, xy), 7.31 (s, 1 H, xy), 7.75 (s, 1 H, xy) ppm.

Molecule **43** (PTZ-xy_5-py). Iodo compound **40** (300 mg, 0.36 mmol), 3-pyridineboronic acid **20** (50 mg, 0.39 mmol) and sodium carbonate (113 mg, 1.1 mmol) were suspended in a mixture of toluene, ethanol and water (85:10:5). Following addition of tetrakistriphenylphosphinepalladium(0) catalyst (8 mg, 0.007 mmol), the yellow suspension was deoxygenated thoroughly by bubbling nitrogen gas before heating it to reflux under nitrogen atmosphere over night.

After cooling to room temperature, the mixture was extracted with dichloromethane, and the combined organic phases were evaporated to dryness. The remaining dark brown solid was purified by column chromatography on silica gel using a dichloromethane-methanol mixture (98:2) as an eluent. This gave the product as a pale yellow solid in 55% yield (155 mg). ^{1}H NMR ($CDCl_3$): δ = 2.08-2.30 (m, 27 H, CH_3), 2.36 (s, 3 H, CH_3), 6.13 (d, *J* = 7.6 Hz, 2 H, PTZ), 6.78 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ, 6.86 (ddd, *J* = 7.6, 7.6, 1.6 Hz, 2 H, PTZ, 6.96 (dd, *J* = 7.6, 1.6 Hz, 2 H, PTZ), 7.06-7.21 (m, 9 H, xy), 7.28 (s, 1 H, xy), 7.41 (dd, *J* = 7.6, 4.8 Hz, 1 H, py), 7.77 (d, *J* = 8.0 Hz, 1 H, py), 8.61 (d, *J* = 4.8 Hz, 1 H, py), 8.70 (s, 1 H, py) ppm.

Molecule **44** (PTZ-xy_2-dmb-xy_2-py). To a suspension of iodo compound **41** (300 mg, 0.34 mmol), 3-pyridineboronic acid **20** (55 mg, 0.44 mmol) and sodium carbonate (109 mg, 1.0 mmol) in a mixture of toluene, ethanol and water (85:10:5) was added tetrakistriphenylphosphinepalladium(0) catalyst (20 mg, 0.017 mmol). This mixture was deoxygenated thoroughly by bubbling nitrogen gas. After refluxing under nitrogen atmosphere over night, the reaction mixture was cooled to room temperature and extracted with dichloromethane. The combined organic phases were evaporated to dryness, and the remaining dark brown solid was subjected to column chromatography on a silica gel stationary phase. A dichloromethane-methanol mixture (98:2) was used as a mobile phase. This gave the coupling product as a pale yellow solid in 66% yield (183 mg). ^{1}H NMR ($CDCl_3$): δ = 2.16 (s, 6 H, CH_3), 2.18 (s, 6 H, CH_3), 2.20 (s, 3 H, CH_3), 2.24 (s, 3 H, CH_3), 2.26 (s, 3 H, CH_3), 2.30 (s, 3 H, CH_3), 3.81 (s, 6 H, OCH_3), 6.13 (dd, *J* = 8.0, 1.2 Hz, 2 H, PTZ), 6.78 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.86 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.88 (s, 2 H), 6.95 (s, 1 H), 6.97 (dd, *J* = 7.6, 1.6 Hz, 2 H, PTZ), 7.08 (s, 1 H), 7.13 (s, 1 H), 7.16 (s, 1 H), 7.23 (s, 1 H), 7.24 (s, 2 H), 7.29 (s, 1 H), 7.38 (dd, *J* = 7.6, 4.8 Hz, 1 H, py), 7.74 (ddd, *J* = 7.6, 1.6, 1.6 Hz, 2 H, py), 8.61 (dd, *J* = 4.8, 1.6 Hz, 1 H, py); 8.70 (d, *J* = 2.8 Hz, 1 H, py) ppm. MS (ESI): calcd. for $C_{51}H_{52}N_2O_2S+H^+$ 829.1; found 829.5.

Molecule **45** (PTZ-xy_2-tmb-xy_2-py). To a stirred and deoxygenated suspension of iodo compound **42** (16 mg, 0.13 mmol), 3-pyridineboronic acid **20** and sodium carbonate (34 mg, 0.32 mmol) in a mixture of toluene, ethanol and water (85:10:5) was added tetrakistriphenylphosphinepalladium(0) (6 mg, 0.005 mmol). The yellow suspension was degassed additionally by bubbling nitrogen gas during 10 minutes prior to heating to reflux under nitrogen over night. After cooling to room temperature, the mixture was extracted with dichloromethane. Subsequent solvent evaporation of the combined organic phases gave a dark brown solid, which was purified by chromatography on a silica gel column. A dichloromethane-methanol (98:2) mixture was used to elude the product as a pale yellow solid in 54% yield (51 mg). ^{1}H NMR ($CDCl_3$): δ = 2.14-2.44 (m, 21 H, CH_3), 2.30 (s, 3 H, CH_3); 3.59 (s, 3 H, OCH_3), 3.60 (s, 3 H, OCH_3), 3.67 (s, 6 H, OCH_3), 6.13 (dd, *J* = 7.6, 1.2 Hz, 2 H, PTZ), 6.79 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.87 (ddd, 7.6, 7.6, 1.2 Hz, 2 H, PTZ), 6.95 (ddd, *J* = 7.6, 1,2 Hz, 2 H, PTZ), 7.10 (s, 1 H, xy), 7.15 (m, 2 H, xy), 7.17 (s, 1 H, xy), 7.21-7.24 (m, 3 H, xy), 7.31 (s, 1 H, xy), 7.38 (dd, *J* = 7.6, 4.4 Hz, py), 7.75 (dd, *J* = 7.6, 2.0 Hz, 1 H, py), 8.61 (dd, *J* = 4.4 Hz, 1.6 Hz, 1 H, py), 8.69 (d, *J* = 2.0 Hz, 1 H, py) ppm. MS (ESI): calcd. for $C_{53}H_{56}N_2O_4S+H^+$ 889.2; found 889.5.

Scientific instrumentation used for experimental investigations

A Bruker Avance 400 MHz spectrometer was used for all ^{1}H-NMR experiments. All chemical shifts are reported relative to the signal of tetramethylsilane. Electrospray mass spectrometry was performed on Finnigan MAT SSQ 7000 and QSTAR XL (AB/MDS Sciex) instruments. Elemental analyses were conducted by Dr. Hansjörg Eder from the School of Pharmaceutical Sciences at the University of Geneva. Optical absorption spectroscopy was performed using a Cary 5000 UV-Vis-NIR spectrophotometer from Varian, and steady-state luminescence spectra were measured on a Horiba Fluorolog-3 instrument from Jobin-Yvon.

Transient absorption spectroscopy was performed on an experimental set-up comprised of a Quantel Brilliant Nd:YAG laser with an integrated Magic Prism OPO as an excitation source and a probe consisting of a 900-W tungsten lamp. The detection system was comprised of a Spex 270M monochromator, a Hamamatsu photomultiplier, and a Tektronix TDS 540B oscilloscope.

For all luminescence and transient absorption experiments, samples were deoxygenated in three subsequent freeze-pump-thaw cycles in home-built quartz cuvettes. Solvents of spectrophotometric grade from the Fluka chemical company were used for all optical-spectroscopic experiments.

Cyclic voltammetry experiments were performed using a Versastat3-100 potentiostat from Princeton Applied Research equipped with the K0264 Micro-Cell kit. A silver wire served as a quasi-reference electrode. The supporting electrolyte was a 0.1 M solution of tetrabutylammonium hexafluorophosphate in dry acetonitrile. Prior to voltage sweeps, the solution was deoxygenated by bubbling nitrogen gas. The potential scan rate was 200 mV/s.

Optical absorption data

Figure S3 shows the optical absorption spectra of molecules **1** – **5** in dichloromethane solution at room temperature.

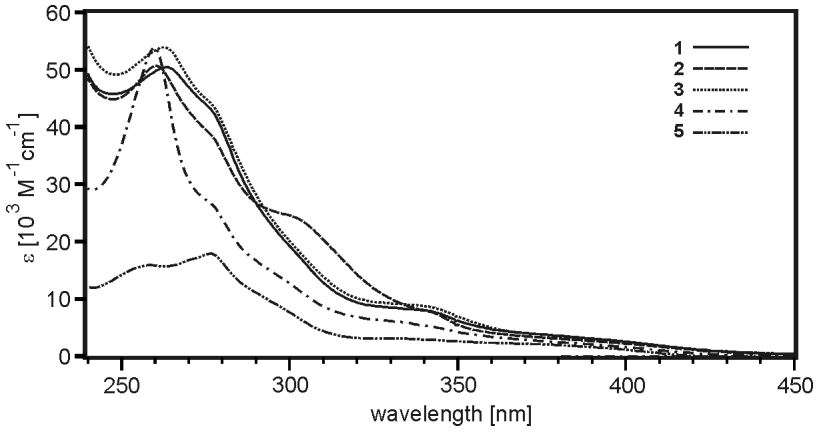

Figure S3.Optical absorption of molecules **1** – **5** in CH_2Cl_2.

The origin of the shoulder at 305 nm in the spectrum of dyad **2** is unclear.

Cyclic voltammetry data

Figure S4 shows cyclic voltammetry sweeps in the oxidative region for molecules **1** – **5** and free 1,2,4,5-tetramethoxybenzene molecule **16**.

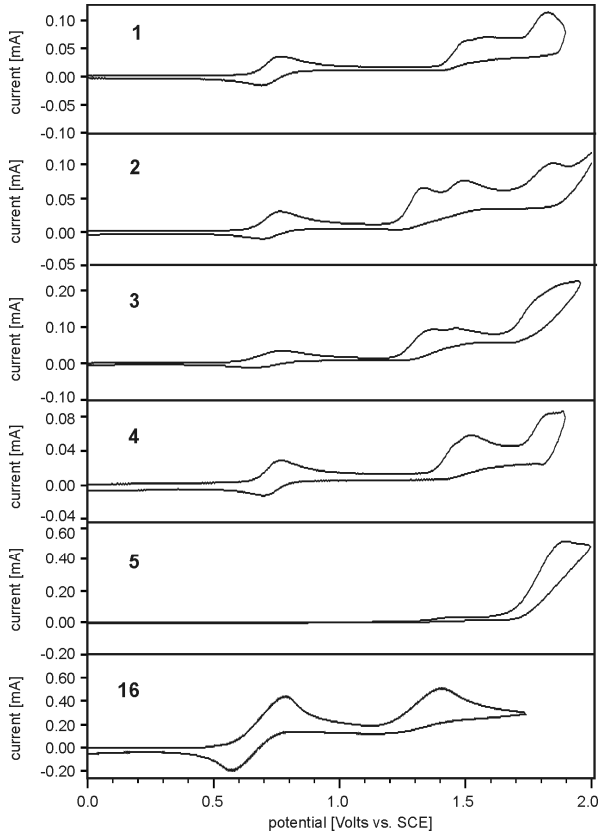

Figure S4. Cyclic voltammograms for molecules **1** – **5** and **16**.

The voltammograms of molecules **1** – **4** all exhibit a reversible wave around 0.8 V vs. SCE that can be attributed to oxidation and reduction of the phenothiazine moiety. Inspection of the voltammogram for molecule **16** (lowest panel) indicates that for free tmb there is a redox wave at nearly identical potential. Thus, in molecule **3** the phenothiazine wave is likely to be overlapped by the tmb wave. The first oxidation of rhenium complex **5** is seen as a weak irreversible wave around 1.45 V vs. SCE. The dyads **1** – **4** exhibit irreversible waves at nearly identical potentials, and therefore they are attributed to oxidation of the photosensitizer unit. In dyads **2** and **3** there are additional oxidative waves at 1.33 V vs. SCE which we attribute to the first oxidation of the dmb central unit in the case of dyad **2** and to the second oxidation of tmb in the case of dyad **3**. This assignment is based on literature data for the redox potentials of free dmb and tmb,[7] and on the comparison to the voltammogram for molecule **16** shown in the bottom panel of Figure S4. Oxidation of the *p*-xylene units does not appear to be observable in these experimental data. Yet, the data in Figure S4 provide clear evidence for the lowering of the electrochemical potentials that are required for oxidation of the central dmb and tmb units of dyads **2** and **3** with respect to the central xy unit in dyad **1**.

Additional time-resolved luminescence data

Figure S5 shows the decay of the emission of dyad **4** on an expanded time scale along with an emission decay that is limited by the instrument response. The oscillations around t = -20 ns and t = +40 ns are due to an electronic noise.

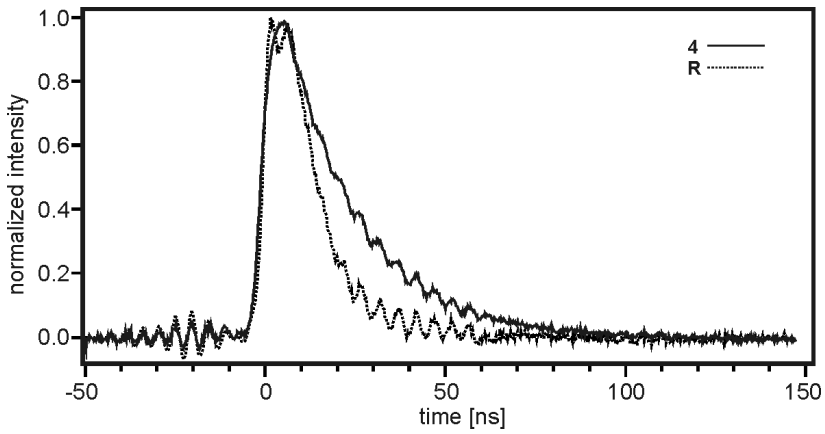

Figure S5. Luminescence decay of dyad **4** in deoxygenated CH_2Cl_2 solution and instrument response function (R).

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