

Supplementary Information

for

COMPETITION BETWEEN CONFORMATIONAL RELAXATION AND
INTRAMOLECULAR ELECTRON TRANSFER WITHIN
PHENOTHIAZINE - PYRENE DYADS

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Synthesis of compounds 1 - 6

10-(1-Pyrenyl)-10H-phenothiazine **3**: 266 mg (0.81 mmol) of 1-iodopyrene **8a**, 162 mg
(0.81 mmol) of phenothiazine **7**, 30 mg activated copper powder, 455 mg (3.29 mmol)
of potassium carbonate and 20 mg dibenzo-18-crown-6 in 4 ml decaline were heated to
160°C for 6 h. After cooling to room temperature the product was suspended in 50 ml
methylene chloride and filtrated. The filtrate was evaporated and the residue was
chromatographed on silica gel with methylene chloride/ligroin 1:3. Recrystallization
from methylene chloride/hexane yielded 177 mg (0.44 mmol, 55%) **3** of yellow
crystals, mp 283-288°C. IR (KBr): 1465, 845. ¹H NMR (250 MHz, CDCl₃): 8.39-8.05
(m, 9H, pyrene), 7.06-5.95 (m, 8H, phenothiazine). MS (EI, 70eV): 399 (100%, M⁺),
201 (24%, [pyrene-H]⁺), 198 (34%, [phenothiazine-H]⁺). Calculated for C₂₈H₁₇NS: C
84.18, H 4.29, N 3.51. Found: C 83.35, H 4.66, N 3.37.

10-(3-(1-Pyrenyl)phenyl)-10H-phenothiazine **4**: 2.63 g (7.42 mmol) of 10-(3-bromophenyl)-10H-phenothiazine were dissolved in 80 ml THF and cooled to -78°C. 5.4 ml (8.60 mmol) of n-BuLi solution in hexane (1.6 M) were added and stirred for 20 min. A solution of 3.0 ml (2.57 g, 11.2 mmol) of tributyl borate in 4.5 ml THF were added and the mixture was allowed to thaw. THF was evaporated and the green-blue residue was emulsified in 20 ml 2 N HCl. After 1 h a white solid precipitated. The precipitate was sucked off, was washed with water, and was dried under vacuum. The boronic acid **14** is pure enough for further reactions. 1.13 g (4.02 mmol) of 1-bromopyrene **8b** and 130 mg (0.11 mmol) of tetrakis(triphenylphosphine)palladium(0) were dissolved in 35 ml 1,2-dimethoxyethane and stirred for 5 min. 1.04 g (3.26 mmol) of 3-(10-phenothiazinyl)phenylboronic acid **14** and 60 ml 1 M NaHCO₃ solution were added. The mixture was stirred under reflux conditions for 5 h. The raw material was extracted with methylene chloride and purified by column chromatography on silica gel with methylene chloride/ligroin 1:3. Recrystallization from methylene chloride/hexane yielded 980 mg (2.06 mmol, 63%) **6** as pale green yellow crystals, mp 176-180°C. IR (KBr): 1460, 1240, 845, 745. ¹H NMR (250 MHz, CDCl₃): 8.25-7.99 (m, 9H, pyrene), 7.79-7.49 (m, 4H, phenyl), 7.05-6.48 (m, 8H, phenothiazine). MS (EI, 70eV): 475 (100%, M⁺), 276 (40%, [phenylpyrene-H]⁺), 198 (29%, [phenothiazine-H]⁺). Calculated for C₃₄H₂₁NS: C 85.86, H 4.45, N 2.95. Found: C 85.39, H 4.57, N 2.92.

3-(4-(1-Pyrenyl)phenyl)-10-methyl-10H-phenothiazine **6**: 1.00 g (3.42 mmol) of 3-bromo-10-methyl-10H-phenothiazine **9** were dissolved in 20 ml THF and cooled to -78°C. 2.5 ml of n-BuLi solution in hexane (1.6 M) were added and the mixture was stirred for 20 min. 1.0 ml (1.21 g, 3.72 mmol) of tributyltin chloride was dropped to the solution and the mixture was allowed to reach room temperature. 50 ml water were added and the product was extracted with methylene chloride. After washing the organic solution with saturated NaHCO₃-solution evaporation of the solvent yielded a yellowish oil of 3-tributylstannyl-10-methyl-10H-phenothiazine **10** which was pure enough for further reactions. 930 mg (1.80 mmol) of 3-tributylstannyl-10-methyl-10H-

phenothiazine **10**, 395 mg (1.11 mmol) of 1-(4-bromophenyl)pyrene **13** and 63 mg (0.05 mmol) of tetrakis(triphenylphosphine)palladium(0) were dissolved in 25 ml DMF and heated at 90°C for 20 h. The solvent was evaporated and the residue was chromatographed on silica gel with methylene chloride. Recrystallization from methylene chloride/hexane yielded 230 mg (0.47 mmol, 42%) **6** as yellow crystals, mp 250-255°C. IR (KBr): 1465, 845, 745. ¹H NMR (250 MHz, CDCl₃): 8.27-7.99 (m, 9H, pyrene), 7.76-7.67 (m, 4H, phenyl), 7.55-6.84 (m, 7H, phenothiazine), 3.45 (s, 3H, -CH₃). MS (EI, 70eV): 489 (100%, M⁺), 474 (46%, [M-CH₃]⁺). Calculated for C₃₅H₂₃NS: C 85.86, H 4.21, N 2.86. Found: C 85.35, H 5.09, N 2.55.

10-(4-(1-Pyrenyl)phenyl)-10H-phenothiazine **5**: 170 mg (0.48 mmol) of 1-(4-bromophenyl)pyrene **13**, 86 mg (0.43 mmol) of phenothiazine **7**, 22 mg (0.02 mmol) of tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct, 52 mg (0.17 mmol) of tri-*o*-tolylphosphine and 41 mg (0.43 mmol) of sodium *tert*-butoxide were dissolved in 20 ml toluene and heated at 90°C for 3 h. After addition of 50 ml water the product was extracted with methylene chloride. The raw material is purified by chromatography on silica gel with methylene chloride/ligroin 1:3. Recrystallization from methylene chloride/hexane yielded 136 mg (0.29 mmol, 66%) **5** as pale yellow crystals, mp 188-189°C. IR (KBr): 1460, 1260, 845. ¹H NMR (250 MHz, CDCl₃): 8.30-8.04 (m, 9H, pyrene), 7.86 (m, 2H, phenyl), 7.58 (m, 2H, phenyl), 7.09-6.49 (m, 8H, phenothiazine). MS (EI, 70eV): 475 (100%, M⁺), 276 (22%, [phenylpyrene-H]⁺), 198 (16%, [phenothiazine-H]⁺). Calculated for C₃₄H₂₁NS: C 85.86, H 4.45, N 2.95. Found: C 85.86, H 4.86, N 2.79.