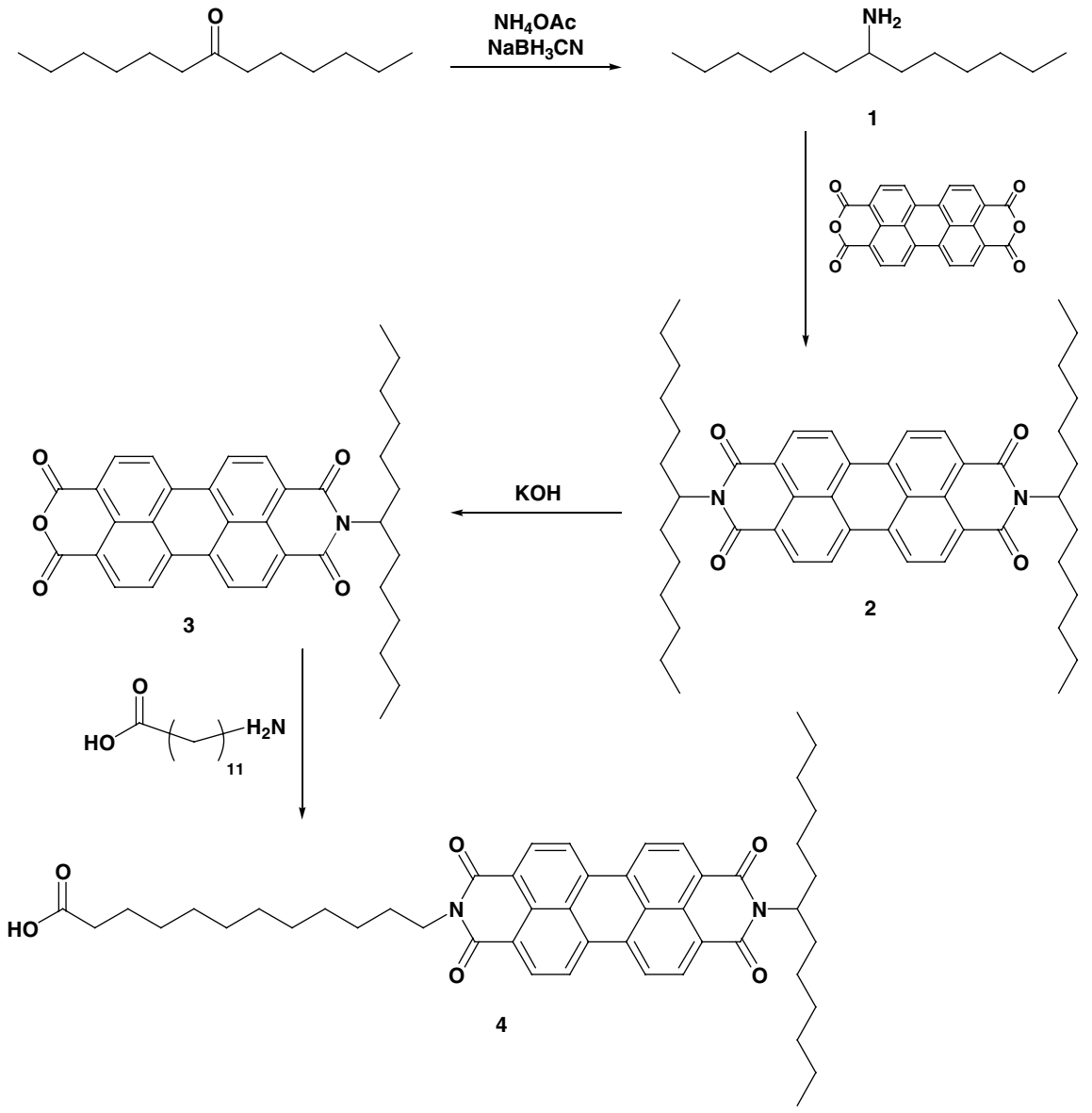
Supporting Information for "Single-Molecule Spectroscopy of Interfacial Electron Transfer" – ja0343104

Synthesis and charaterization of molecules used in this study



Scheme 1. Synthesis of HCP

1-hexylheptylamine[1] **(1)**

In a 250 mL RB flask, 5.05 g (25.5 mmol) 7-tridecanone, 19.7 g (255 mmol) NH_4OAc, and 1.12 g (17.8 mmol) $NaBH_3CN$ were dissolved in 75 mL absolute MeOH and stirred at r.t. for 48h, until starting material was gone by TLC (R_f = 0.8 in $CHCl_3$, dark blue with *p*-anisaldehyde). The mixture was quenched by added conc. HCl dropwise (~3 mL), then concentrated in vacuo. The resulting white solid was taken up in 500 mL H_2O, taken to pH~10 with solid KOH, and extracted with 400 mL and then 200 mL of $CHCl_3$. The $CHCl_3$ fractions were combined and concentrated to give 4.57g (90%) of pale yellow oil. ^{1}H-NMR (D_2O, 300 MHz): δ = 0.75 (t, 6H, CH_3), 1.17-1.22 (m, 16H, 8 CH_2), 1.53 (m, 4H, 2 CH_2CHNH_2), 3.15 (quint, 1H, $CHNH_2$).

N,N'-bis(1-hexylheptyl)perylene-3,4,9,10-tetracarboxylbisimide[2] (2)

In a 500 mL RBF, 3.7 g (9.4 mmol) perylene-3,4,9,10-tetracarboxylicdianhydride (Aldrich) and 4.5 g (23 mmol) **1** in 15 g imidazole were stirred 5h at 180° C. The reaction mixture was cooled to r.t., taken up in 100 mL ethanol, treated with 400 mL 2N HCl, and stirred overnight. The dark red precipitate was filtered and rinsed thoroughly with water, and dried at 130°C to give 7.1g (100%) of red solid. ^{1}H-NMR ($CHCl_3$, 300 MHz): d= 0.83 (t, 12H, CH_3), 1.18-1.30 (m, 32H, 16 CH_2), 1.84 (m, 4H, 2 C*H*$_2$CHN,), 2.25 (m, 4H, 2 C*H*$_2$CHN-), 5.19 (m, 2H, 2 CH_2C*H*N) , 8.67 (m, 8H, perylene)

N-(1-hexylheptyl)perylene-3,4,9,10-tetracarboxyl-3,4-anhydride-9,10-imide[3] (3)

In a 250 mL RBF, 3.45g (4.57 mmol) **2** was suspended in 85 mL *t*-BuOH and treated with 860 mg (15.3 mmol) solid 85% KOH. The reaction mixture was heated with vigorous stirring to reflux until the solution turned dark purple, ~30 min. The mixture was cooled to r.t., treated with 80 mL acetic acid and 40 mL 2N HCl, and stirred overnight. The dark red precipitate was filtered, washed with distilled water, and dried at 130°C. This solid was suspended in 150 mL 10% K_2CO_3 solution and heated to reflux ~30 minutes (whereupon the side product perylene-3,4,9,10-tetracarboxylicdianhydride went into solution as the bright green tetrapotassium tetracarboxylate). The mixture is cooled and filtered; the filter cake was rinsed with warm 10% K_2CO_3 until the filtrate was clear, rinsed twice with ~100 mL 2N HCl, then rinsed thoroughly with water and dried at 130°C. This solid was then suspended in 100 mL boiling water, and triethylamine (TEA) was added until a dark purple solution of the desired product formed. Remaining starting material was filtered off and the dark purple filtrate was acidified with 3 volumes 2N HCl, and stirred overnight. The resulting dark red precipitate was filtered, rinsed thoroughly with water, and dried at 130°C. This material was similarly treated once more with water/TEA to remove remaining traces of starting material, and upon precipitation and drying yielded 1.05g (40%) of red solid. ^{1}H-NMR ($CHCl_3$, 400 MHz): δ= 0.73 (t, 6H, CH_3), 1.11-1.20 (m, 16H, 8 CH_2), 1.75 (m, 2H, -C*H*$_2$CHN-), 2.15 (m, 2H, -C*H*$_2$CHN-), 5.18 (m, 1H, $(CH_2)_2$C*H*N) , 8.61 (dd, 8H, perylene)

N-(1-hexylheptyl)-N'-(12-carboxylicdodecyl)perylene-3,4,9,10-tetracarboxylbisimide (4)

In a 50 mL RBF, 47 mg (0.082 mmol) **3** and 21 mg (0.098 mmol, 1.2 eq), 12-aminododecanoic acid were dissolved in 250 mg imidazole and stirred 4h at 160º C, until the reaction was complete by TLC (95/5 $CHCl_3$/MeOH; starting material R_f = 0.6, product R_f = 0.3). The reaction mixture is cooled to r.t., suspended in 5 mL EtOH, then treated with 40 mL 2N HCl and stirred overnight. The dark red precipitate was filtered and dried at 130º C to give 49 mg (78%) of dark red solid. ^{1}H-NMR ($CHCl_3$, 400 MHz): δ= 0.82 (t, 6H, 2 CH_3), 1.29 (m, 32H, 16 CH_2's), 1.64 (quint, 2H, -NCH$_2$CH$_2$C*H*$_2$-), 1.77 (quint, 2H, -NCH$_2$C*H*$_2$-), 1.88 (m, 2H, -C*H*$_2$CHN-), 2.27 (m, 2H, -C*H*$_2$CHN-), 2.36 (t, 2H, CH$_2$C*H*$_2$COOH), 4.20 (t, 2H, -NC*H*$_2$CH$_2$-), 5.18 (m, 1H, -NC*H*$(C_6H_{13})_2$), 8.68 (dd, 8H, perylene).

1) Borch, R. F.; Bernstein, M. D.; Durst, H. D. *J. Am. Chem. Soc.* **1971**, *93*, 2897-2904.
2) Demming, S.; Langhals, H. *Chem. Ber.* **1988**, *121*, 225-230.
3) Kaiser, H.; Lindner, J.; Langhals, H. *Chem. Ber.* **1991**, *124*, 529-535.