Directional Control of π-Stacked Building Blocks for Crystal Engineering: the 1,8-Naphthalimide Synthon.

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General Considerations. All operations, unless otherwise specified, were carried out under a nitrogen atmosphere by using standard Schlenk techniques. Solvents for air-sensitive synthetic procedures were dried by conventional methods and distilled under a dry N_2 atmosphere immediately prior to use. All reagents are commercially available and were used without further purification. Robertson Microlit Laboratories performed all elemental analyses. Mass spectrometric measurements were obtained on a Micromass Q-Tof spectrometer. Clusters assigned to specific ions show appropriate isotopic patterns as calculated for the atoms present. In electrospray experiments, one generally observes peaks generated from neutral fragments from the sample interaction with either NH_4^+, Na^+ or K^+ present in the spectrometer. NMR spectra were recorded by using a Varian Gemini 300, and the PGSE-NMR experiments were performed using a Varian Inova 500.

N-[2,2-(dimethoxy)ethane]-1,8-napthalimide. 1,8-naphthalic anhydride (19.82 g, 0.10 mol) and 2,2-dimethoxyethaneamine (12.49 g, 0.12 mol) were refluxed in ethanol (500 mL) for 4h. The solution was allowed to cool to room temperature, whereupon the desired compound deposited as a crystalline solid which was filtered and air dried. A second crop was isolated by removing the solvent via rotary evaporation. The solid was air dried to yield a total of 27.75 g (0.097 mol, 97.3%) of a tan product. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.61 (d, J = 7.2 Hz, 2H, *napth.*), 8.22 (d, J = 8.7 Hz, 2H, *napth.*), 7.76 (dd, J = 8.7, 7.2 Hz, 2H, *napth.*), 4.92 (t, J = 7 Hz, 2H, C*H*(OMe)$_2$), 4.40 (d, J = 7 Hz, 4H, N-C*H*$_2$), 3.42 (s, 12H, OC*H*$_3$).

N-[2,2-bis(pyrazolyl)ethane]-1,8-naphthalimide (L1). A 500 mL round-bottom flask was charged with pyrazole (19.86 g, 0.292 mol), *N*-(2,2-dimethoxyethane)-1,8-naphthalimide (27.75 g, 0.097 mol) and toluenesulfonic acid (500 mg). A distillation

head equipped with a volumetric liquid trap was attached to the flask. The reaction apparatus was evacuated and backfilled with N_2 and heated neat to 220ºC. The mixture was kept at 220ºC until the theoretical amount of methanol was collected (ca. 4 hrs.). The molten product was added to 500 mL of boiling CH_2Cl_2 (*Caution: Very hot; addition of the molten product may cause product and solvent to splatter*). The solution was allowed to cool to room temperature, and the solvent was reduced by rotary evaporation. The concentrated organic solution was then shaken in a separatory funnel against a K_2CO_3(aq) solution to remove the unreacted pyrazole. The organic layer was separated, dried over $MgSO_4$, filtered, and the solvent removed by rotary evaporation yielding 31.35 g (90.5 %) of the desired solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.54 (d, J = 7.2 Hz, 2H *napth.*), 8.19 (d, J = 8.1 Hz, 2H, *napth.*), 7.83 (d, J = 2.1 Hz, 2H, H_5-pz), 7.72 (dd, J = 8.1, 7.2 Hz, 2H, *napth.*), 7.47 (d, J = 1.2 Hz, 2H, H_3-pz), 7.14 (t, J = 7.2 Hz, 1H, CH(pz)$_2$), 6.26 (dd, J = 2.1, 1.2 Hz, 2H, H_4-pz), 5.29 (d, J = 7.2 Hz, 2H, N-CH_2).

{*N*-[2,2-bis(pyrazolyl)ethane]-1,8-naphthalimide}Re(CO)$_3$Br (1). A 50 mL round-bottom flask was charged with 178 mg (0.50 mmol) of *N*-[2,2-bis(pyrazolyl)ethane]-1,8-naphthalimide and 203 mg of Re(CO)$_5$Br (0.50 mmol). Toluene (50 mL) was then added to the flask followed by the attachment of a reflux condenser. The reaction mixture was left to stir overnight, while heating at reflux, resulting in a white, powdery precipitate. The mixture was filtered, and the collected precipitate was left to air dry yielding 302 mg (85%) of product. ^{1}H-NMR (300 MHz, DMSO): δ 8.46 (m, 4H, *napht.*), 8.17 (d, J = 2.4 Hz, 2H, H_5-pz), 8.12 (d, J = 2.1 Hz, 2H, H_3-pz), 7.86 (t, J = 7.5 Hz, 2H, *napht.*), 7.53 (t, J = 5.7 Hz, 1H, CH(pz)$_2$), 6.58 (t, J = 2.4 Hz, 2H, H_4-pz), 4.78 (d, J = 5.7 Hz, 2H, N-CH_2); ES$^+$/MS calcd. for

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$\{C_{23}H_{15}N_5O_5BrRe+K\}^+$ = 743.9423, found 743.9457. Anal. calcd. for $C_{23}H_{15}BrN_5O_5Re$:

C = 39.05, H = 2.14, N = 9.90; found: C = 39.38, H = 2.34, N = 9.68.

N-[2,2-bis(3,5-dimethylpyrazolyl)ethane]-1,8-naphthalimide (L2). A 100 mL round-bottom flask was charged with 7.50 g (77.2 mmol) of 3,5-dimethylpyrazole, 10.01g (35.1 mmol) of N-(2,2-dimethoxyethane)-1,8-naphthalimide, and 0.15 g (1.5 mol %) of toluenesulfonic acid. A distillation head equipped with a volumetric liquid trap was attached to the flask. The reaction apparatus was evacuated and backfilled with N_2 and heated neat to 220ºC. The reaction was heated until the theoretical amount of methanol was collected (4 hrs.) and the molten product added to 500 mL of boiling CH_2Cl_2 (*Caution: Very hot; addition of the molten product may cause product and solvent to splatter*). The solution was allowed to cool to room temperature, and the solvent was reduced by rotary evaporation. The concentrated organic solution was then shaken in a separatory funnel against a K_2CO_3(aq) solution to remove the unreacted pyrazole. The organic layer was separated, dried over $MgSO_4$, filtered, and the solvent removed by rotary evaporation yielding 11.90 g (82%) of tannish-yellow solid. ^{1}H-NMR (300 MHz, acetone-d_6): δ 8.51 (dd, J = 1.2, 7.2 Hz, 2H, *napht*), 8.44 (dd, J = 1, 8.4 Hz, 2H, *napht*), 7.87 (t, J = 8 Hz, 2H, *napht*), 6.86 (t, J = 7.2 Hz, 1H, C*H*), 5.79 (s, 2H, H_4-pz)), 5.28 (d, J = 7.2 Hz, 2H, C*H*$_2$), 1.93, 2.09 (s, 12H, 3,5-C*H*$_3$),. ES$^+$/MS for $\{C_{24}H_{23}N_5O_2+H\}^+$ = 414.1930; Found = 414.1930. Anal. calcd for $C_{24}H_{23}N_5O_2$: C = 69.72, H = 5.61, N = 16.94; found: C = 67.27, H = 4.56, N = 16.21.

$\{N$-[2,2-bis(3,5-dimethylpyrazolyl)ethane]-1,8-naphthalimide$\}$Re(CO)$_3$Br (2). A 50 mL round-bottom flask was charged with 207 mg (0.50 mmol) of N-[2,2-bis(3,5-dimethylpyrazolyl)ethane]-1,8-naphthalimide and 203 mg of Re(CO)$_5$Br (0.50 mmol).

Toluene (30 mL) was then added to the flask followed by the attachment of a reflux condenser. The reaction mixture was left to stir while heating at reflux overnight, resulting in a white, powdery precipitate. The mixture was filtered, and the collected precipitate was left to air dry yielding 175 mg (45%) of product. ^{1}H-NMR (300 MHz, acetone-d_6): δ 8.60 (d, J = 8.4 Hz, 2H, *napht*), 8.52 (d, J = 8.4 Hz, 2H, *napht*), 7.93 (t, J = 7.6 Hz, 2H, *napht*), 6.87 (t, J = 6 Hz, 1H, CH), 6.22 (s, 2H, H_4-pz), 5.28 (d, J = 6 Hz, 2H, CH_2), 2.44, 2.69 (s, 12H, 3,5-CH_3),. ES[+]/MS calcd for $\{C_{27}H_{23}N_5O_5BrRe+K\}^+$ = 800.0049, found 800.0043. Anal. calcd for $C_{27}H_{23}N_5O_5BrRe$: C = 42.47, H = 3.04, N = 9.17; found: C = 42.51, H = 3.07, N = 8.64.

PGSE-NMR Data:

Our compounds are not spherical. Therefore, the calculated hydrodynamic radii were multiplied by a frictional coefficient (Perrin factor) of 1.11, which corresponds to a prolate elipsoid with a major axis to minor axis ratio of 3. Accordingly, the crystallographic radii were derived by dividing the longest intermolecular distance of the dimers (bromine to bromine) by 2. PGSE-NMR Data plots were derived based on the following equation:

$$\ln\left(I/I_o\right) = -\gamma \delta^2 G^2 (\Delta - \delta/3) D$$

Raw Data Plots of $ln(I/I_o)$ versus G^2.

Graph 1. $ln(I/I_o)$ versus G^2 for Complexes 1 and 2 in DMSO.
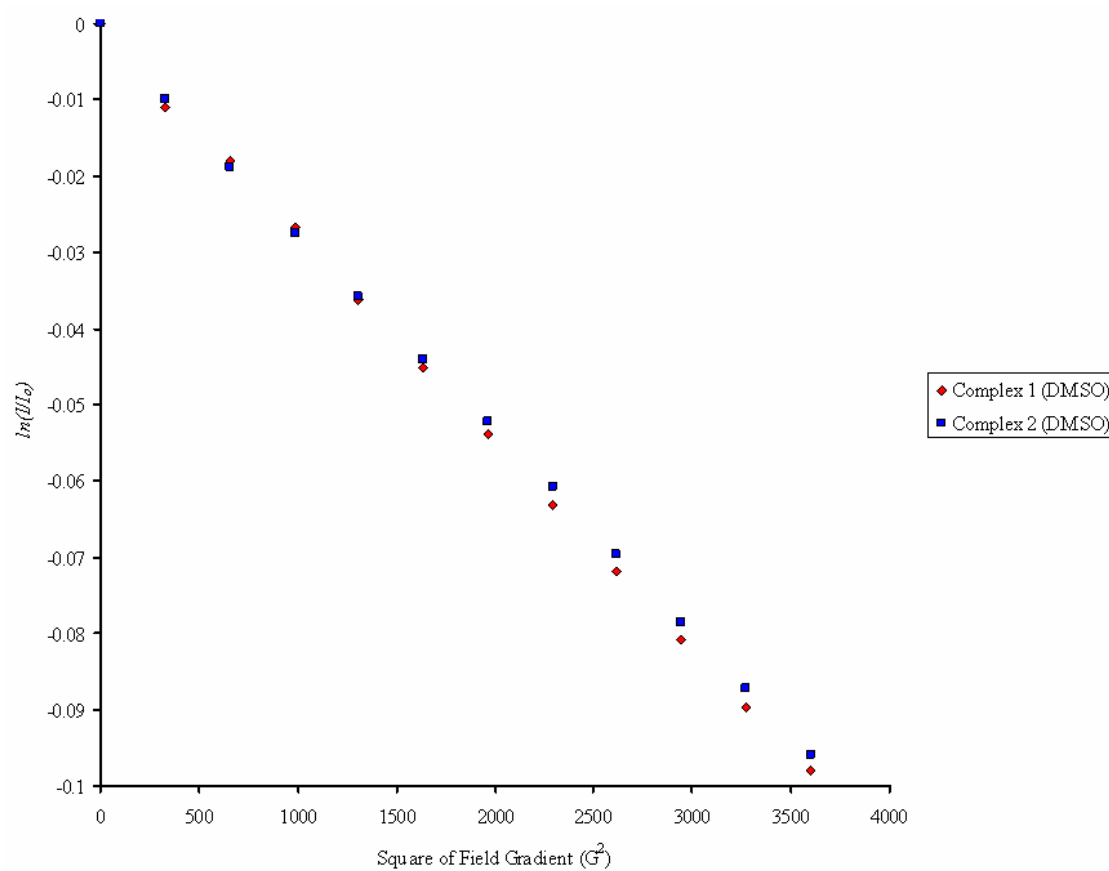
Graph 2. $ln(I/I_o)$ versus G^2 for L2 and Complex 2 in TCE.