

# Directional control of $\pi$ -stacked building blocks for crystal engineering: the 1,8-naphthalimide synthon†

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Incorporating the 1,8-naphthalimide group into bis(pyrazolyl)methane ligands triggers the association of their rhenium(I) complexes into directionally ordered dimers in both solution and solid state, as demonstrated by ES<sup>+</sup>/MS, PGSE-NMR and X-ray diffraction studies.

The understanding and control of intra- and intermolecular forces and of the supramolecular self-assembly process is a prerequisite for the progress of crystal engineering.<sup>1</sup> Hydrogen bonding is a widely used tool in crystal engineering because the directionality and robustness of its associative protocol enable facile and reliable transfer to other systems.<sup>2</sup> In contrast,  $\pi$ - $\pi$  stacking has a less predictable directional associative protocol, due to the fact that in the solid state, variable orientations of the moieties involved often occur in order to maximize the electrostatic attraction between the  $\sigma$  framework and the  $\pi$  electron density of the stacked groups.<sup>3</sup> Although association of several  $\pi$  species in solution was substantiated in some cases, little is known about their solution structure and their relative orientation.<sup>4</sup>

We wish to report here the design and syntheses of two new bis(pyrazolyl)methane ligands and their rhenium(I) complexes that incorporate a new supramolecular synthon, the 1,8-naphthalimide group. It has long been established that the order of stability in the interaction of two  $\pi$  systems is  $\pi$ -deficient- $\pi$ -deficient >  $\pi$ -deficient- $\pi$ -rich >  $\pi$ -rich- $\pi$ -rich.<sup>3</sup> We reasoned that since  $\pi$ - $\pi$  stacking interactions between  $\pi$ -deficient functionalities are the most favorable, incorporating such groups into our ligands will allow us to exploit their strong  $\pi$ - $\pi$  stacking interactions within metal complexes. While the photophysical properties of 1,8-naphthalimide derivatives were extensively utilized by incorporating this moiety into a large variety of chemosensors and other devices,<sup>5</sup> its  $\pi$ -deficiency was not exploited to the benefit of crystal engineering. A search of the CSD database (version 5.26, Nov. 2004) identified a surprisingly small number of crystal structures incorporating the 1,8-naphthalimide group, only 19, with 13 of them meeting the requirements for a  $\pi$ - $\pi$  stacking interaction. Out of these 13 structures, all but one had a common feature: a  $\pi$ - $\pi$  stacking interaction with the dipole vectors (which run from the center of the fused aromatic group through the nitrogen atom) of the 1,8-naphthalimide groups oriented at 180°.

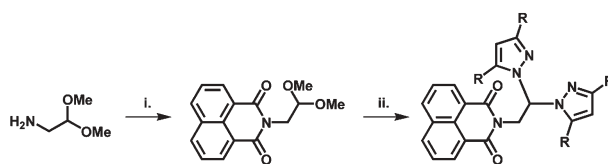
Based on these facts, we anticipated that a 1,8-naphthalimide group built into a bidentate, bis(pyrazolyl)methane ligand will let

us exploit the predetermined directional characteristics for intermolecular stacking of the 1,8-naphthalimide group. Furthermore, in our quest for the understanding and application of crystal engineering principles as related to metal complexes of poly-(pyrazolyl)methane ligands, we have recently described a cooperative  $\pi$ - $\pi$  stacking and C-H $\cdots$  $\pi$  interaction found between adjacent bis- or tris(pyrazolyl)methane units, a motif that we named the “quadruple pyrazolyl embrace”.<sup>6</sup> The ubiquitous nature of the quadruple pyrazolyl embrace makes coupling this supramolecular synthon with the  $\pi$ - $\pi$  stacking of the 1,8-naphthalimide group a potentially powerful combination in crystal engineering.

The new ligands, *N*-[2,2-bis-(3,5-*R*-pyrazolyl)ethane]-1,8-naphthalimide (*R* = H, **L1**; *R* = Me, **L2**), were synthesized by the toluenesulfonic acid-catalyzed reaction of the corresponding pyrazole with *N*-[2,2-(dimethoxy)ethane]-1,8-naphthalimide (Scheme 1), which is easily prepared starting from 1,8-naphthalic anhydride and 2,2-dimethoxyethaneamine. **L1** and **L2** both react with Re(CO)<sub>5</sub>Br to yield **L1**[Re(CO)<sub>3</sub>Br] (**1**) and **L2**[Re(CO)<sub>3</sub>Br] (**2**) as white solids.

The molecular structure of **1**† consists of an octahedral rhenium center (Fig. 1) formed by three facially positioned carbonyl moieties, two nitrogen atoms from the  $\kappa^2$ -bonded ligand **L1** and a bromide ligand. All bond lengths and angles are within normal parameters found in these types of complexes.

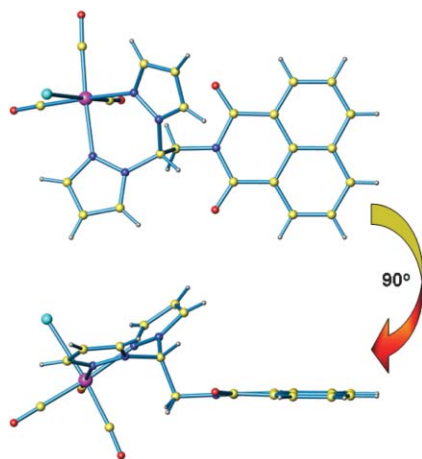
Compound **1** is associated into dimers by the anticipated  $\pi$ - $\pi$  stacking interaction of the 1,8-naphthalimide units, with a perpendicular distance of *ca.* 3.5 Å between the aromatic rings; see Fig. 2. The dipole vectors of the stacked 1,8-naphthalimide units are oriented at 180°, placing the bis(pyrazolyl)methane donor sets in opposite directions. The dimers are then organized into stair-like 1-D chains by the pyrazolyl embrace interaction (Fig. 3). Two pyrazolyl rings are involved in offset  $\pi$ - $\pi$  stacking with a perpendicular distance between the rings of 3.5 Å. The hydrogen atoms situated on the fourth position of the pyrazolyl rings involved in the  $\pi$ - $\pi$  stacking are pointed towards the other two pyrazolyl rings with the following geometrical details: H-centroid distance = 3.0 Å, C-centroid distance = 3.8 Å and the C-H-centroid angle = 142°.



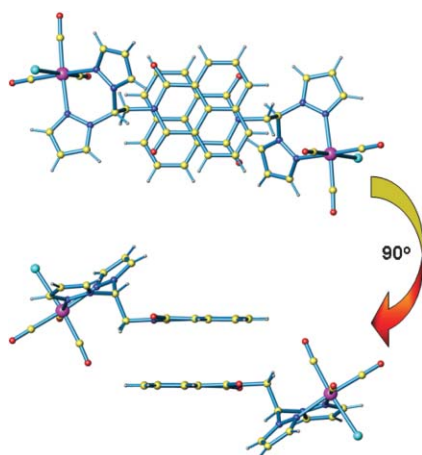
**Scheme 1** Synthetic route to **L1** and **L2**: i. 1,8-naphthalic anhydride, EtOH, reflux; ii. 3,5-*R*<sub>2</sub>-Hpz, (pz = pyrazolyl ring, *R* = H, **L1**; *R* = Me, **L2**), *p*-toluenesulfonic acid (cat.), neat, 220 °C.

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† Electronic supplementary information (ESI) available: synthetic details and PGSE-NMR data. See <http://dx.doi.org/10.1039/b504998a>



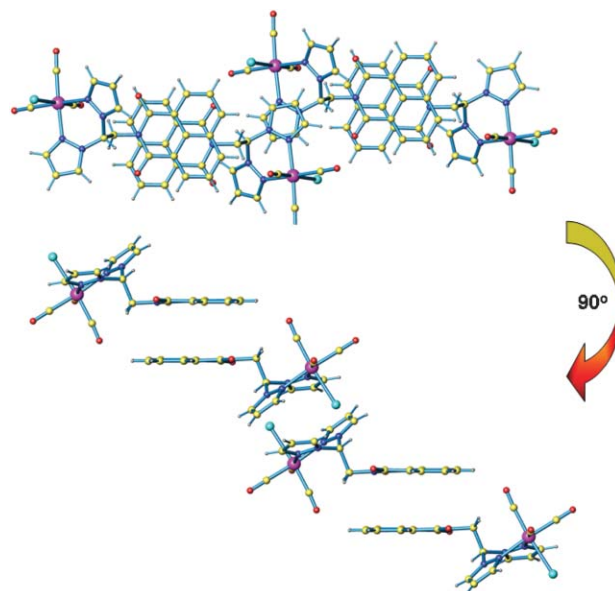
**Fig. 1** Molecular structure of **L1**[Re(CO)<sub>3</sub>Br] (**1**); color code: carbon, yellow; hydrogen, gray; oxygen, red; nitrogen, blue; bromine, light blue and rhenium, purple.



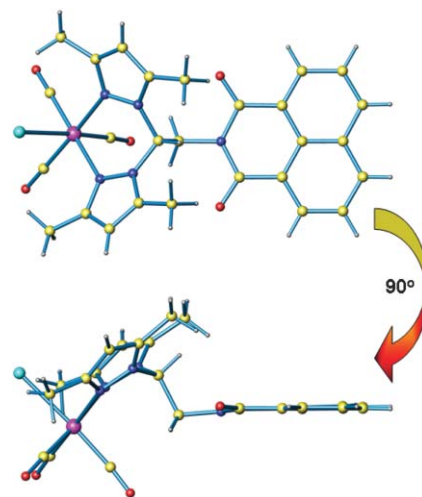
**Fig. 2** Dimeric association of **1** and the relative position of the individual units within the dimer.

The molecular structure of **2**<sup>‡</sup> (Fig. 4) is similar to that of **1** with only small differences in bond lengths and angles. The supramolecular association of **2** into dimers is maintained, as can be seen in Fig. 5 and is supported by a similar  $\pi$ - $\pi$  stacking of the 1,8-naphthalimide units as in **1**. The 180° orientation of the dipole vectors of the stacked 1,8-naphthalimide units and the subsequent opposing directional orientation of the bis(pyrazolyl)methane donor sets is maintained. However, the addition of 3- and 5-position methyl groups on the pyrazole rings decreases the dimensionality of the supramolecular structure of **2**, when compared to **1**, because the chain forming pyrazolyl embrace is disrupted by the substitution.<sup>7</sup>

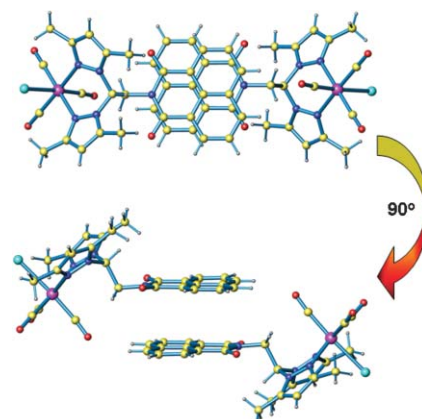
The solution-state supramolecular self-assembly of both **1** and **2** was studied by the means of ES<sup>+</sup>/MS and PGSE-NMR experiments. For **1**, the ES<sup>+</sup>/MS spectrum showed peaks that correspond to monomeric {**L1**[Re(CO)<sub>3</sub>]}<sup>+</sup>, {**L1**[Re(CO)<sub>3</sub>] + CH<sub>3</sub>CN}<sup>+</sup> and {**L1**[Re(CO)<sub>3</sub>Br] + NH<sub>4</sub>}<sup>+</sup> species at 628, 669 and 725 *m/z* respectively. Dimeric species such as {**L1**[Re(CO)<sub>3</sub>Br]·**L1**[Re(CO)<sub>3</sub>]}<sup>+</sup> and {2**L1**[Re(CO)<sub>3</sub>Br] + Na}<sup>+</sup> produced peaks at 1335 and 1437 *m/z*. A peak corresponding to the trimetallic {3**L1**[Re(CO)<sub>3</sub>Br] + Na}<sup>+</sup> species was also identified



**Fig. 3** 1-D chain of **1** formed by  $\pi$ - $\pi$  stacking and pyrazolyl embrace interactions; the  $\pi$ - $\pi$  stacking component of the pyrazolyl embrace is clearly shown in the middle of the top figure.



**Fig. 4** Molecular structure of **L2**[Re(CO)<sub>3</sub>Br] (**2**).



**Fig. 5** Dimers formed by  $\pi$ - $\pi$  stacking with **2**.

at 2144 *m/z*. In the case of **2**, only mono- and dimeric species were observed, in concordance with its solid state structure. Thus,  $\{\mathbf{L2}[\text{Re}(\text{CO})_3]\}^+$ ,  $\{\mathbf{L2}[\text{Re}(\text{CO})_3\text{Br}] + \text{NH}_4\}^+$ ,  $\{\mathbf{L2}[\text{Re}(\text{CO})_3\text{Br}]\cdot\mathbf{L2}[\text{Re}(\text{CO})_3]\}^+$ ,  $\{2\mathbf{L2}[\text{Re}(\text{CO})_3\text{Br}] + \text{Na}\}^+$  were identified at 684, 781, 1447 and 1544 *m/z* respectively.

In order to further test the solution associations of **1** and **2**, we performed the pulsed-field gradient spin-echo NMR experiment (PGSE-NMR). Described in detail elsewhere,<sup>8</sup> the PGSE-NMR technique provides an indirect measure of molecular size by allowing the determination of the diffusion coefficient of a given species in solution. Subsequent application of the Stokes–Einstein relation then yields the hydrodynamic radius, which typically falls within *ca.* 20% of the crystallographic radius. This technique has been used successfully in a number of different applications,<sup>9</sup> including establishing the presence or absence of dimeric species in solution.<sup>9c,d</sup> Table 1 shows the comparison of the experimentally calculated hydrodynamic radii of both complexes along with **L2**. For complexes **1** and **2**, the PGSE-NMR method radii are in accordance with those found from the X-ray data for the dimeric units, indicating that the 1,8-naphthalimide groups are associated in solution and that their dipole vectors are oriented approximately 180° apart, as any significant deviation from linearity would produce smaller radii values in the PGSE-NMR experiment. For comparison, similar experiments with  $\text{Re}(\text{CO})_3\text{Br}[(\text{pz}^{4\text{-pyrene}})]_2\text{-CH}(\text{Pr})$  (pz = pyrazolyl ring) that we have reported previously showed the complexes were monomeric in solution even though the solid state structure showed association by  $\pi$ - $\pi$  stacking of the pyrene groups.<sup>9c</sup> As expected, the free ligand **L2** is also dimeric in solution, with a reasonable difference in its radius due to the lack of a metallic center.

To date, the directionality in multimetallic structures has been mainly controlled by using multibranching ligands because of their increased preorganization.<sup>10</sup> In our earlier work, we used preorganized polytopic ligands such as  $\text{C}_6\text{H}_6\text{-}n[\text{CH}_2\text{OCH}_2\text{C}(\text{pz})_3]_n$  (*n* = 2, 3, 4 and 6) and  $(\text{CH}_2)_m[\text{CH}(\text{pz})_2]_2$  (*m* = 1–3) to control the outcome of solid state structures.<sup>6,11</sup> We show here that the strong, directionally oriented  $\pi$ -association of the 1,8-naphthalimide group is a valuable synthon in crystal engineering. The directionality is maintained in solution, even in a highly polar solvent like DMSO, as demonstrated by NMR experiments. The naphthalimide group can be easily incorporated into a large variety of compounds that can have other specially designed functionalities (with donor properties or not). From a crystal engineering point of view, the facile transfer of this directional associative protocol from one system to another (as demonstrated by our results and the CSD search), opens the door for the synthesis of new supramolecular (not covalently linked), discrete species or coordination polymers.

**Table 1** Comparison of radii from PGSE-NMR calculations and X-ray data<sup>a</sup>

Compound	Calculated radii/Å	
	PGSE	X-ray
<b>1</b>	8.28 <sup>b</sup>	9.70
<b>L2</b>	8.06 <sup>c</sup>	n/a
<b>2</b>	9.42 <sup>b</sup> , 9.50 <sup>c</sup>	9.96

<sup>a</sup> See ESI for details. <sup>b</sup> DMSO-*d*<sub>6</sub>. <sup>c</sup> Tetrachloroethane-*d*<sub>2</sub>.

In summary, we have successfully designed, synthesized, and implemented the use of *directional*  $\pi$ - $\pi$  stacking in crystal engineering, by building 1,8-naphthalimide moieties into a bis(pyrazolyl)methane ligand system. The 1,8-naphthalimide group leads to association into dimers of metal complexes of the ligands in both solution and solid state, as evidenced by electrospray and pulsed-field gradient spin echo NMR spectrometry techniques and X-ray diffraction experiments. We also demonstrated the use of the quadruple pyrazolyl embrace, an important interaction for bis(pyrazolyl)methane metal complexes, to organize the dimeric units into chains for **1** and these types of chains were intentionally disrupted in **2** by substitution of the pyrazolyl rings.

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## Notes and references

‡ Compound **1**·(CD<sub>3</sub>)<sub>2</sub>SO: C<sub>25</sub>H<sub>15</sub>BrD<sub>6</sub>N<sub>5</sub>O<sub>6</sub>ReS, *M* = 791.67, triclinic, *a* = 8.6135(5), *b* = 10.6869(6), *c* = 15.705(1) Å,  $\alpha$  = 73.925(1)°,  $\beta$  = 75.037(1)°,  $\gamma$  = 83.696(1)°, *U* = 1340.90(14) Å<sup>3</sup>, *T* = 150 K, space group *P*1̄ (no. 2), *Z* = 2,  $\mu(\text{Mo-K}\alpha)$  = 6.149 mm<sup>-1</sup>, 13416 reflections measured, 5462 unique (*R*<sub>int</sub> = 0.0234), 352 parameters refined, *R*1(*F*) = 0.0236, *wR*(*F*<sup>2</sup>) = 0.0559 (all data). CCDC 268888.

Compound **2**·C<sub>3</sub>H<sub>6</sub>O: C<sub>30</sub>H<sub>29</sub>BrN<sub>5</sub>O<sub>6</sub>Re, *M* = 821.69, triclinic, *a* = 8.8427(5), *b* = 13.4707(8), *c* = 13.9727(8) Å,  $\alpha$  = 67.162(1)°,  $\beta$  = 89.597(1)°,  $\gamma$  = 82.302(1)°, *U* = 1518.27(15) Å<sup>3</sup>, *T* = 150 K, space group *P*1̄ (no. 2), *Z* = 2,  $\mu(\text{Mo-K}\alpha)$  = 5.369 mm<sup>-1</sup>, 16466 reflections measured, 6199 unique (*R*<sub>int</sub> = 0.0263), 394 parameters refined, *R*1(*F*) = 0.0257, *wR*(*F*<sup>2</sup>) = 0.0612 (all data). CCDC 268889. See <http://dx.doi.org/10.1039/b504998a> for crystallographic data in CIF or other electronic format.

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