

# Supporting information for: Competing Interactions in Surface Reticulation with a Prochiral Dicarbonitrile Linker

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## Collection of all possible 2D Co-*p*NC-*p*Ph<sub>3</sub>-*m*CN coordination motifs

The molecule *p*NC-*p*Ph<sub>3</sub>-*m*CN comprises a directionality concerning the functional CN moieties substituted in *para* (p) and *meta* (m) position. Hence in order to provide a full overview on the nodal motifs we have to distinguish between *para* CN group and *meta* CN group coordinated to the Co center.

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## 1. Threefold coordination motifs:

Redundant motifs are omitted.

{ppp}: 4

p<sub>D</sub>p<sub>D</sub>p<sub>D</sub>      p<sub>D</sub>p<sub>D</sub>p<sub>L</sub>

p<sub>D</sub>p<sub>L</sub>p<sub>L</sub>      p<sub>L</sub>p<sub>L</sub>p<sub>L</sub>

{mmm}: 4

p<sub>D</sub>m<sub>D</sub>p<sub>D</sub>      p<sub>D</sub>m<sub>D</sub>p<sub>L</sub>

p<sub>D</sub>m<sub>L</sub>p<sub>L</sub>      p<sub>L</sub>m<sub>L</sub>p<sub>L</sub>

{ppm}: 8

p<sub>D</sub>p<sub>D</sub>m<sub>D</sub>      p<sub>D</sub>p<sub>D</sub>m<sub>L</sub>

p<sub>D</sub>p<sub>L</sub>m<sub>L</sub>      p<sub>L</sub>p<sub>L</sub>m<sub>L</sub>

p<sub>L</sub>p<sub>L</sub>m<sub>D</sub>      p<sub>L</sub>p<sub>D</sub>m<sub>D</sub>

p<sub>D</sub>p<sub>L</sub>m<sub>D</sub>      p<sub>L</sub>p<sub>D</sub>m<sub>L</sub>

{pmm}: 8

p<sub>D</sub>m<sub>D</sub>m<sub>D</sub>      p<sub>D</sub>m<sub>D</sub>m<sub>L</sub>

p<sub>D</sub>m<sub>L</sub>m<sub>L</sub>      p<sub>L</sub>m<sub>L</sub>m<sub>L</sub>

p<sub>L</sub>m<sub>L</sub>m<sub>D</sub>      p<sub>L</sub>m<sub>D</sub>m<sub>D</sub>

p<sub>D</sub>m<sub>L</sub>m<sub>D</sub>      p<sub>L</sub>m<sub>D</sub>m<sub>L</sub>

$$\Sigma_{3-fold} = 24$$

## 2. Fourfold coordination motifs:

{pppp}: 6

p<sub>D</sub>p<sub>D</sub>p<sub>D</sub>p<sub>D</sub>      p<sub>D</sub>p<sub>D</sub>p<sub>D</sub>p<sub>L</sub>      p<sub>D</sub>p<sub>D</sub>p<sub>L</sub>p<sub>L</sub>

p<sub>D</sub>p<sub>L</sub>p<sub>L</sub>p<sub>L</sub>      p<sub>L</sub>p<sub>L</sub>p<sub>L</sub>p<sub>L</sub>      p<sub>L</sub>p<sub>D</sub>p<sub>L</sub>p<sub>D</sub>

{mmmm}: 6

$m_D m_D m_D m_D$	$m_D m_D m_D m_L$	$m_D m_D m_L m_L$
$m_D m_L m_L m_L$	$m_L m_L m_L m_L$	$m_L m_D m_L m_D$

{pppm}: 16

$p_D p_D p_D m_D$	$p_L p_D p_D m_D$	$p_D p_L p_D m_D$	$p_D p_D p_L m_D$
$p_L p_D p_L m_D$	$p_D p_L p_L m_D$	$p_L p_L p_D m_D$	$p_L p_L p_L m_D$
$p_D p_D p_D m_L$	$p_L p_D p_D m_L$	$p_D p_L p_D m_L$	$p_D p_D p_L m_L$
$p_L p_D p_L m_L$	$p_D p_L p_L m_L$	$p_L p_L p_D m_L$	$p_L p_L p_L m_L$

{ppmm}: 16

$p_D p_D m_D m_D$	$p_L p_D m_D m_D$	$p_D p_L m_D m_D$	$p_D p_D m_L m_D$
$p_L p_D m_L m_D$	$p_D p_L m_L m_D$	$p_L p_L m_D m_D$	$p_L p_L m_L m_D$
$p_D p_D m_D m_L$	$p_L p_D m_D m_L$	$p_D p_L m_D m_L$	$p_D p_D m_L m_L$
$p_L p_D m_L m_L$	$p_D p_L m_L m_L$	$p_L p_L m_D m_L$	$p_L p_L m_L m_L$

{pmpm}: 12

$p_D m_D p_D m_D$	$p_L m_D p_D m_D$	$p_D m_L p_D m_D$	$p_D m_D p_L m_D$
$p_L m_D p_L m_D$	$p_D m_L p_L m_D$	$p_L m_L p_D m_D$	$p_L m_L p_L m_D$
$p_D m_L p_D m_L$	$p_D m_L p_L m_L$	$p_L m_L p_D m_L$	$p_L m_L p_L m_L$

{pmmm}: 16

$p_D m_D m_D m_D$	$p_L m_D m_D m_D$	$p_D m_L m_D m_D$	$p_D m_D m_L m_D$
$p_L m_D m_L m_D$	$p_D m_L m_L m_D$	$p_L m_L m_D m_D$	$p_L m_L m_L m_D$
$p_D m_D m_D m_L$	$p_L m_D m_D m_L$	$p_D m_L m_D m_L$	$p_D m_D m_L m_L$
$p_L m_D m_L m_L$	$p_D m_L m_L m_L$	$p_L m_L m_D m_L$	$p_L m_L m_L m_L$

$$\Sigma_{4-fold} = 70$$

$$\implies \Sigma_{3+4-fold} = 94$$

### 3. Geometrical representation of three- and fourfold coordination nodes classified as above

Threefold coordination nodes:

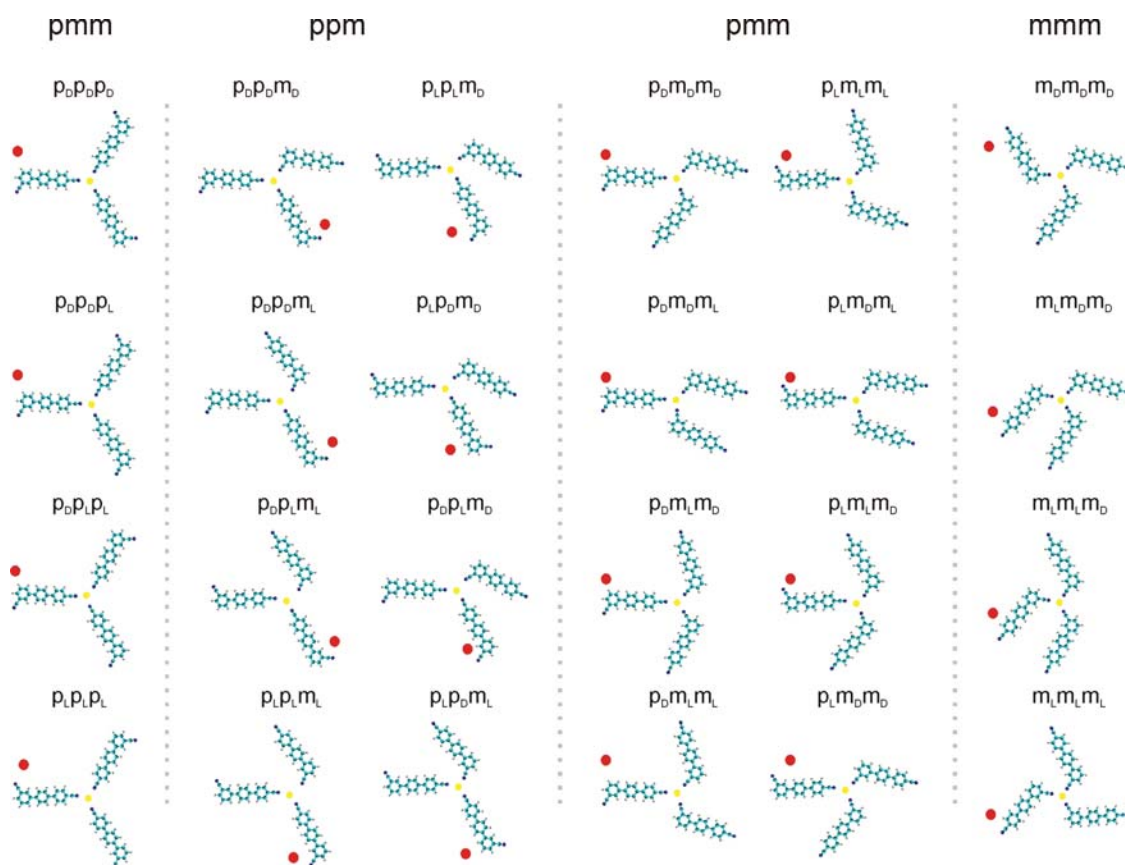


Figure 1: Atomistic models of threefold metal-organic nodal motifs. The metal center is marked yellow, the carbon atoms in the molecule cyan, nitrogen blue and hydrogen white. The red dot aside of every nodal motif highlights the starting point for the nomenclature.

Fourfold coordination nodes:

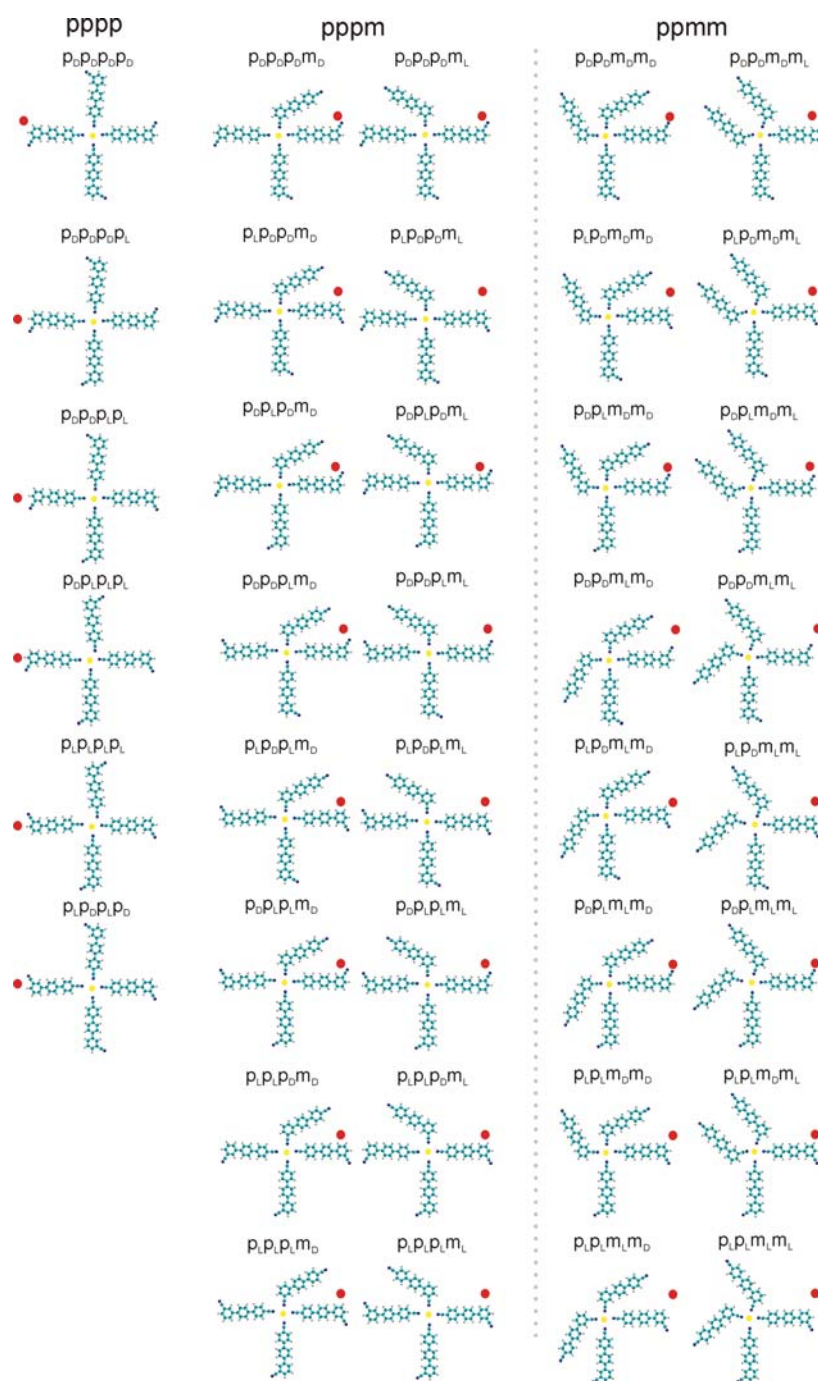


Figure 2: Atomistic models of fourfold metal-organic nodal motifs. The metal center is marked yellow, the carbon atoms in the molecule cyan, nitrogen blue and hydrogen white. The red dot aside of every nodal motif highlights the starting point for the nomenclature.

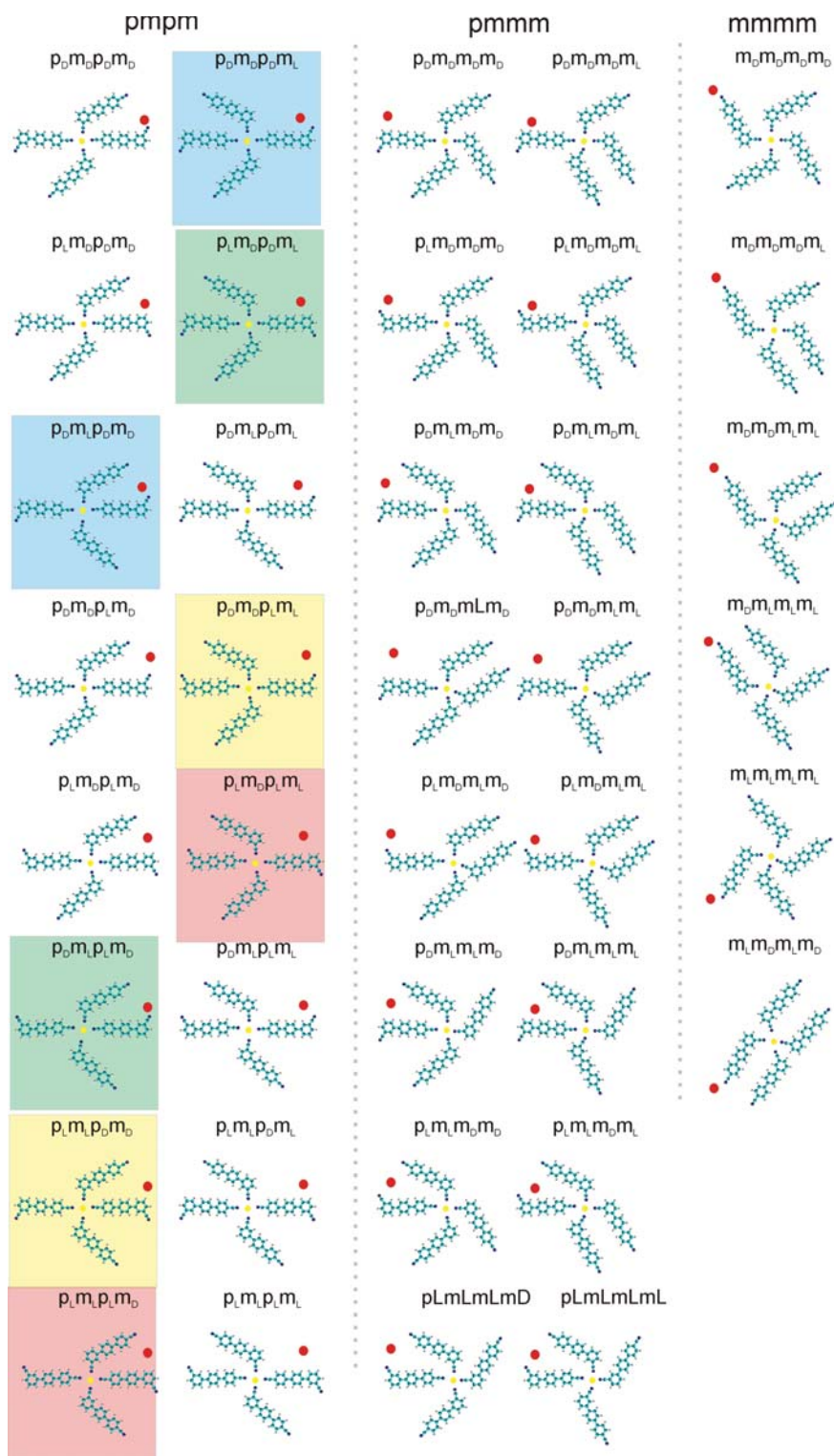


Figure 3: Continuation of Figure 2: Atomistic models of fourfold metal-organic nodal motifs. The color code of the highlighted motifs marks redundant nodal motifs. The metal center is marked yellow, the carbon atoms in the molecule cyan, nitrogen blue and hydrogen white. The red dot aside of every nodal motif highlights the starting point for the nomenclature.

## Procedures

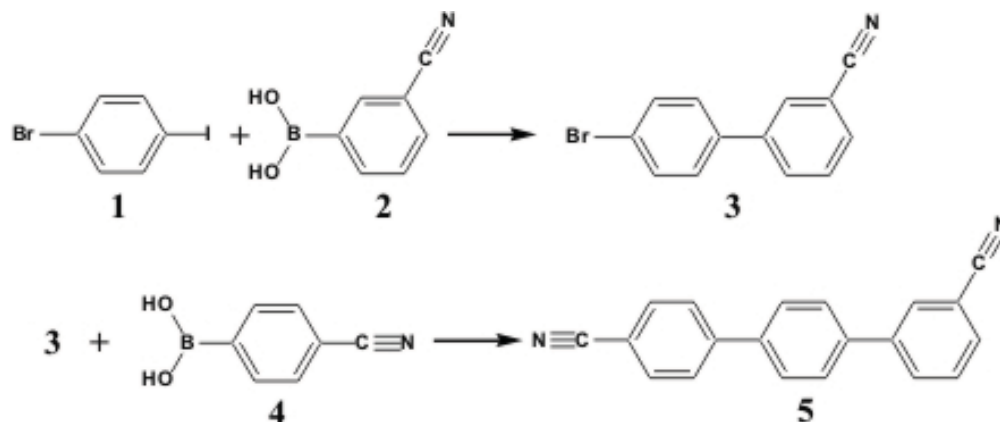


Figure 4: Synthesis of [1,1';4',1'']-terphenyl-3,4''-dicarbonitrile.

### Synthesis

1-Bromo-4-iodo-benzene (**1**), boronic acids (**2** and **4**) were purchased from commercial sources and used as received. FT-IR spectra were recorded on a Perkin Elmer Spectrum GX spectrometer in KBr pellets, Maldi-Tof spectra were recorded on Perseptive Biosystems Voyager-DePro, NMR spectra were recorded at room temperature on Bruker 300 Ultrashield series, elemental analyses was performed by using a ThermoQuest Flash 1112 Series EA apparatus, and melting point was measured on Büchi B-545 using open-ended glass capillaries. The compound [1,1';4',1'']-terphenyl-3,4''-dicarbonitrile (**5**) is known in literature but has been synthesized in a different stepwise way, according to the procedure reported therein.

#### 1. 4'-Bromo-biphenyl-3-carbonitrile (**3**)

Under an inert atmosphere in a round bottomed two-neck flask 1,4-bis-iodo-benzene (**1**, 0.55 g, 2.0 mmol) and 3-cyanophenyl-boronic acid (**2**, 0.3 g, 2.05 mmol) were dissolved in 25 ml of 1,4-dioxane. Excess of base (2 M solution of  $K_2CO_3$ , 10 ml) was added to the solution of reactants. The so obtained mixture was initially warmed to 40°C for 20 min, and then was added by using a syringe under argon  $Pd(II)(PPh_3)_2$  (70 mg, 0.1 mmol) and  $PPh_3$  (50 mg, 0.2 mmol), both dissolved previously in 5 ml of EtOH saturated in argon. The solution was heated to 55°C for 1 h. The

mixture from bright yellow turned very dark. Upon cooling to r.t. a precipitate formed. The organic/water phase was evaporated under reduced pressure, leaving a brownish-yellow solid, which was solubilised completely in warm (40°C) CH<sub>2</sub>Cl<sub>2</sub> (200 ml) and the organic phase was treated with NH<sub>4</sub>Cl/H<sub>2</sub>O saturated solution (30 ml). The organic phase was collected, dried over MgSO<sub>4</sub> and purified by flash-chromatography on SiO<sub>2</sub> column using Hexane/CH<sub>2</sub>Cl<sub>2</sub> mixture as an eluent ( $R_f$  = 0.69) affording 0.39 g (yield 79%) of **3** as soft white solid. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 7.82 (t, 1H, 2-H,  $J$  = 1.8 Hz), 7.79 (dt, 1H, 4-H,  $^3J$  = 7.9 Hz,  $^4J$  = 1.4 Hz), 7.76-7.59 (m, 3H, 6-H, 2', 6'-H), 7.52 (t, 1H, 5-H,  $J$  = 7.9 Hz), 7.44 (dt, 4H, 3', 5'-H,  $^3J$  = 8 Hz,  $^4J$  = 1.6 Hz). Maldi-*Tof* (Matrix ferulic acid)  $m/z$ : found 256.29 (MH<sup>+</sup>, 100%), calculated for C<sub>13</sub>H<sub>8</sub>BrN (MH<sup>+</sup>) to 256.98.

## 2. [1,1';4',1'']-Terphenyl-4,3''-dicarbonitril (**5**)

As described above. 86 mg (**3**, 3.3 mmol) and 59 mg (3.9 mmol) **4** in 25 ml 1,4-dioxane/10 ml ethanol/10 ml 2 M aqueous sodium carbonate; 3 h reflux; yield: 70 mg (75%) colorless crystals from benzene/hexane; mp 202-203 °C (lit. 201-202 °C). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 7.69 (t, 1H, 5''-H), 7.85 (dt, 1H, 4''-H,  $^3J$  = 7.9 Hz,  $^4J$  = 1.4 Hz), 7.87-7.97 (m, 8H, 2-H, 3-H, 5-H, 6-H, 2'-H, 3'-H, 5'-H, 6'-H, 2 AA'BB'), 8.06-8.12 (m, 1H, 6''-H), 8.23 (t, 1H, 2''-H, 4J = 1.5 Hz). Maldi-*Tof* (Matrix ferulic acid)  $m/z$ : found 279.67 (MH<sup>+</sup>, 100%), calculated for C<sub>20</sub>H<sub>12</sub>N<sub>2</sub> (MH<sup>+</sup>) to 280.09.