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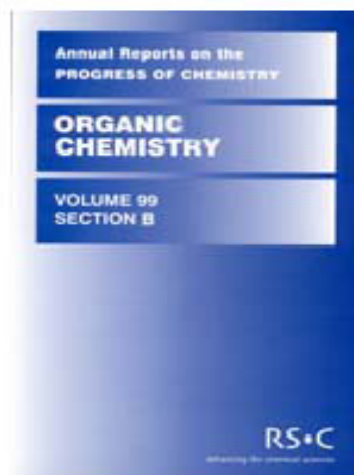
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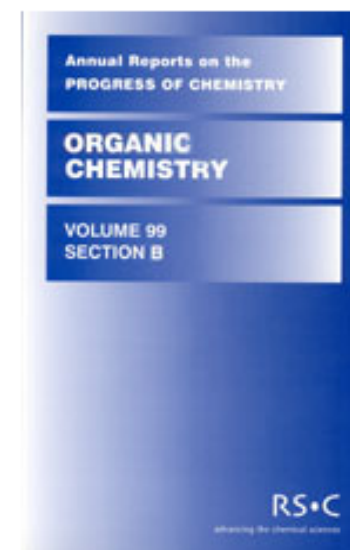
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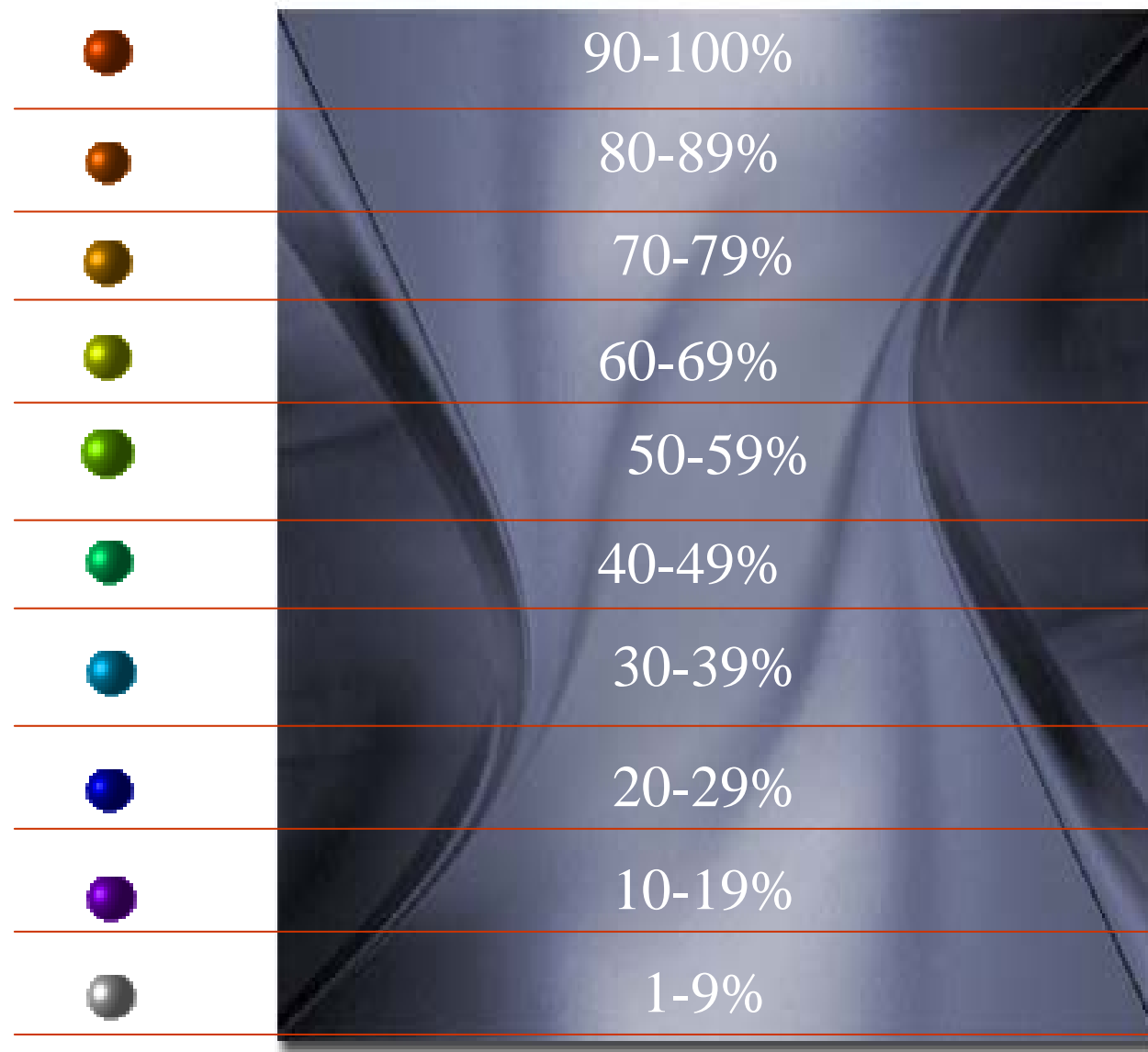
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Selective formation of rectangular grid coordination polymers with grid dimensions 10×15 , 10×20 and 15×20 Å Paper

Kumar Biradha and Makoto Fujita

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Using four linear bifunctional ligands of different lengths and $\text{Ni}(\text{NO}_3)_2$, three coordination polymers containing big rectangular cavities were shown to form selectively, despite the fact that all the four ligands are known to form square grid coordination polymers when they are reacted independently with $\text{M}(\text{NO}_3)_2$.

Chem. Commun., 2001, (1), 15 - 16

DOI: 10.1039/b007014i

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**Selective formation of rectangular grid coordination
polymers with grid dimensions 10×15 , 10×20 and 15×20**

Communication

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Kumar Biradha^{*} and Makoto Fujita^{*}

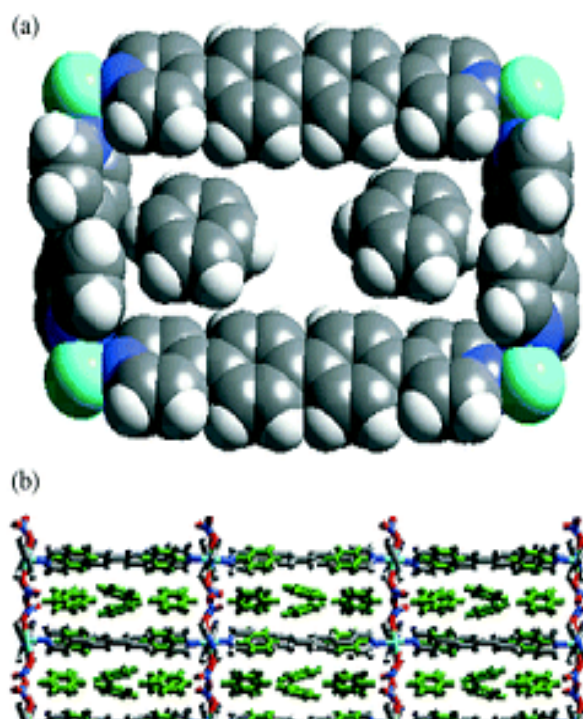
*Department of Applied Chemistry, Graduate School of Engineering, Nagoya University and CREST, Japan
Science and Technology Corporation (JST), Chikusaku, Nagoya, 464-8603, Japan. E-mail:
kbiradha@org.mol.nagoya-u.ac.jp E-mail: mfujita@apchem.nagoya-u.ac.jp*

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Using four linear bifunctional ligands of different lengths and $\text{Ni}(\text{NO}_3)_2$, three coordination polymers containing big rectangular cavities were shown to form selectively, despite the fact that all the four ligands are known to form square grid coordination polymers when they are reacted independently with $\text{M}(\text{NO}_3)_2$.

Complex **5** also formed 2D-network containing rectangular grids of dimension $19.9 \times 11.3 \text{ \AA}$ and enclosed eight benzene molecules per metal. Similarly to **4**, only two benzene molecules were encapsulated in the cavities while the remaining six exist between the layers ([Fig. 2](#)). Ligands **1** and **3** bridge metal atoms in (001) and (100) directions, respectively, and the grid planes pack in the (010) direction. The packing of the grids is similar to that of **4** but now there are three layers of benzene molecules accommodated in each compartment as the width of the compartment is increased from 15.6 to 19.9 \AA [[Fig. 2\(b\)](#)]. In this triple layer the outer layers have the same topology as shown in [Fig. 1](#) (b) and are linked together by a middle layer, (6,3) net, that is generated by two disordered benzene molecules. In effect each moiety of **3** is surrounded by 18 benzene molecules *via* edge-to-face aromatic interactions.



Selective formation of rectangular grid coordination polymers with grid dimensions 10×15 , 10×20 and 15×20 Å

Kumar Biradha* and Makoto Fujita*

Department of Applied Chemistry, Graduate School of Engineering, Nagoya University and CREST, Japan Science and Technology Corporation (JST), Chikusa-ku, Nagoya 464-8603, Japan. E-mail: kbiradha@org.mol.nagoya-u.ac.jp; mfujita@apchem.nagoya-u.ac.jp

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Using four linear bifunctional ligands of different lengths and $\text{Ni}(\text{NO}_3)_2$, three coordination polymers containing big rectangular cavities were shown to form selectively, despite the fact that all the four ligands are known to form square grid coordination polymers when they are reacted independently with $\text{M}(\text{NO}_3)_2$.

The utility of linear bifunctional ligand such as 4,4'-bipyridine **1** has been well explored in the studies of crystal engineering of coordination polymers.¹⁻⁴ Although there are a considerable number of reports dealing with designing square grid coordination polymers, their rectangular counterparts are not explored to that extent. The synthesis of rectangular grids at will allows the modulation of size and function of the cavity. Only few rectangular grid polymers have been designed either using two charged ligands or using charged and neutral ligands.⁶⁻⁹ However using two neutral ligands to date only one rectangular grid coordination polymer has been reported.¹⁰ In this structure the rectangular cavities are too small to encapsulate guest molecules. Recently we have shown that the higher analogues of **1**, 1,4-bis(4-pyridyl)benzene **2** and 4,4'-bis(4-pyridyl)biphenyl **3**, can also be used in designing open square grid polymers with dimensions of 15×15 and 20×20 Å.^{11,12} Herein we show that one can employ these longer ligands to design their rectangular counterparts.

accommodates two benzene layers which interpenetrates through the moieties of **2** such that each molecule of **2** interacts with 12 benzene molecules *via* edge-to-face aromatic interactions.

Complex **5** also formed 2D-network containing rectangular grids of dimension 19.9×11.3 Å and enclosed eight benzene molecules per metal. Similarly to **4**, only two benzene molecules were encapsulated in the cavities while the remaining six exist between the layers (Fig. 2). Ligands **1** and **3** bridge

