

A flexible copper based microporous metal–organic framework displaying selective adsorption of hydrogen over nitrogen†

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A microporous metal–organic framework [Cu₃(ipO)₂(pyz)₂]_n, (ipO = 2-hydroxyisophthalic acid, pyz = pyrazine) was synthesized *via* an *in situ* ligand transformation reaction. The microporous framework displays helical arrays of ipO ligands holding the Cu atoms in 2D sheets, whilst the coordination of pyz molecules acts to arrange these sheets into a microporous 3D structure. Remarkable selective sorption behaviour (>5) for H₂ over N₂ is observed and explained with molecular dynamics simulations.

Metal–organic frameworks (MOFs) are novel porous crystalline materials consisting of metal ions or clusters interconnected by a variety of organic linkers and have attracted great attention because of their potential applications in gas separation,¹ gas storage,² ion exchange,³ catalysis,⁴ magnetism,⁵ and others. In addition to the above mentioned promising applications, their unique properties, such as their highly diversified structures, large range of pore sizes, very high surface areas, and even specific adsorption affinities, make MOFs excellent candidates for use in the construction of molecular sieve membranes of superior performance.⁶ The preparation of MOF membranes for gas separation is rapidly becoming a major research focus. Unlike traditional porous zeolite materials whose pores are confined by tetrahedral oxide skeletons and are thus difficult to tune, the pores within MOFs can be systematically adjusted by the judicious choice of metal-containing secondary building units and/or bridging organic linkers.⁷ This superior feature is very important for developing novel microporous materials with selective sorption behaviours or molecular sieving attributes.⁸ Despite their importance, MOFs showing selective gas adsorption behaviours are currently not so common. In particular, MOFs that can selectively absorb H₂ over N₂ are very important because they have the potential to be applied in the separation of H₂ enrichment from the N₂–H₂ exhaust in ammonia synthesis. To the best of our knowledge, preferential adsorption of H₂ over N₂ by a coordination solid Mn(HCO₂)₂, was first reported by

Dybtsev *et al.*, in 2004.⁹ In 2007, Chen *et al.*, reported a zinc based interpenetrated microporous MOF for selective adsorption of H₂ over N₂.¹⁰ In addition, a number of attempts have been made to prepare supported-MOF membranes.¹¹ Recently, supported MOFs were reported as molecular sieve membranes for high hydrogen selectivity over nitrogen.¹² However, progress is very limited and there is a need to focus on developing materials better tuned for this process. Further control may be obtained by utilizing short bridging ligands to target small pores,¹³ also flexibility in the structure may help in allowing the gas molecules to enter through the pores. We expect that introduction of short carboxylates and bidentate pillar linkers will lead to the formation of 3D frameworks having small pores suited to the selective uptake of small molecules like hydrogen. Herein, we report the discovery of preferential adsorption of H₂ over N₂ in just such a copper based microporous 3D metal–organic framework, [Cu₃(ipO)₂(pyz)₂]_n (**1**).

1 was synthesized by the *in situ* ligand transformation in a hydrothermal approach. A mixture of Cu(NO₃)₂·2.5H₂O (242 mg, 1 mmol), 1,2,3-benzene tricarboxylic acid (H₃btc; 123 mg, 0.5 mmol), pyrazine (pyz, 40 mg, 0.5 mmol), KOH (112 mg, 2 mmol) and H₂O (10 mL) was stirred for 10 min and sealed in a 23 mL Teflon lined stainless steel autoclave, which was heated to 220 °C and held at that temperature for 3 days. After cooling to room temperature, green hexagonal plates of **1** were recovered by filtration, washed, dried and picked out manually for further analysis. (yield: 32% based on Cu). The complex has previously been reported and our structural data is in close accord with Zheng *et al.* in 2009.¹⁴

The microporous framework **1** consists of two crystallographically different types of copper centers (Cu1 and Cu2). The Cu1 centre is in a distorted square pyramidal geometry and is bridged to another Cu1 atom *via* the central oxygen atom of the hydroxyl group of the ipO ligand, to form a dimer. Each Cu2 is in a distorted octahedral geometry, coordinated with the four oxygen atoms from two ipO ligands in the equatorial plane and with two nitrogen atoms of pyz at the axial positions. The compound displays helical arrays of ipO ligands, which hold the Cu atoms in 2D sheets, whilst

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the coordination of pyz molecules acts to arrange these sheets into a microporous 3D structure, Fig. 1. The phase purity of the bulk sample was independently confirmed by powder X-ray diffraction (PXRD), Fig S1.†

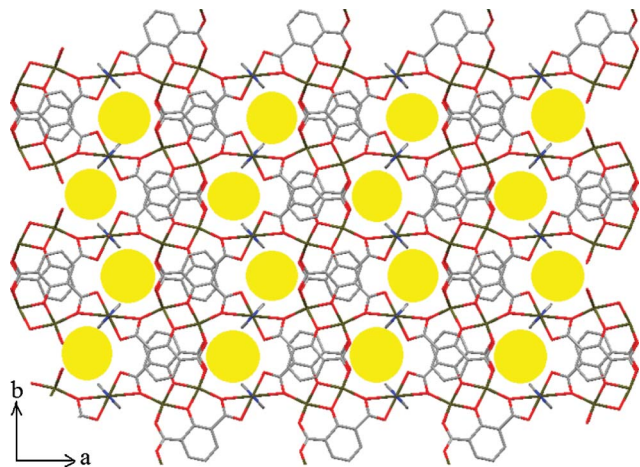


Fig. 1 A view of the microporous framework **1** showing pores along the *c*-axis.

The microporous framework **1** shows remarkable preferential adsorption of H₂ over N₂. Given the lower adsorption enthalpies typically associated with hydrogen in comparison to nitrogen, this is all the more exceptional. Molecular dynamics simulations indicate that **1** has a flexible structure that is able to accommodate H₂ 15.8% of the time, but N₂ only on a sporadic basis <1.5% of the time.

The structure of the microporous framework **1** reveals a topology that includes small, microporous channels aligned to the *c*-axis (Fig. 1). Blue and grey channels in Fig. 4 indicate the accessible surface areas available within the structure. These channels are too small to include solvent from the synthesis, which were absent during both crystallographic investigations and thermal analysis (Fig. S3†). Gas adsorption was conducted on the material at 77 K with H₂ and N₂ adsorbents. The gas adsorption/desorption data is given in Table S1 of the ESI.†

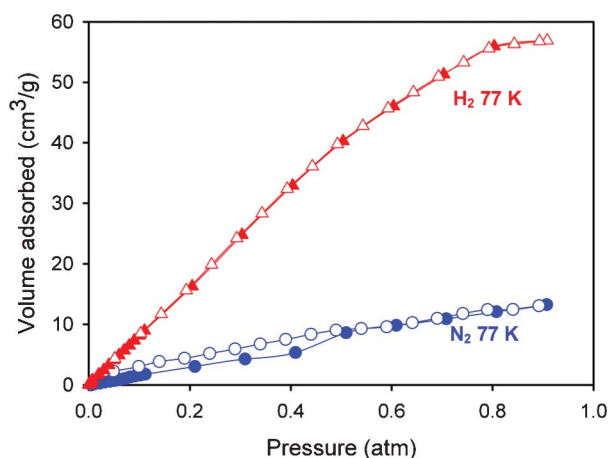


Fig. 2 Plot of N₂ and H₂ adsorption/desorption isotherms at 77 K.

The selectivity for this adsorption process was calculated by fitting the Toth isotherm model¹⁵ to each adsorption branch, as

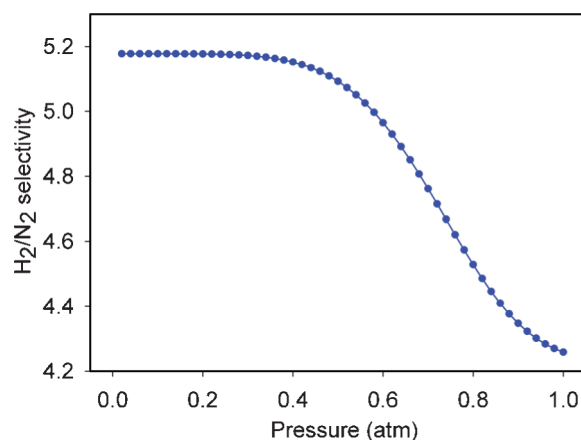


Fig. 3 H₂/N₂ selectivity as a function of pressure. In order to match equivalent pressures, raw data has been fitted to the Toth isotherm model.

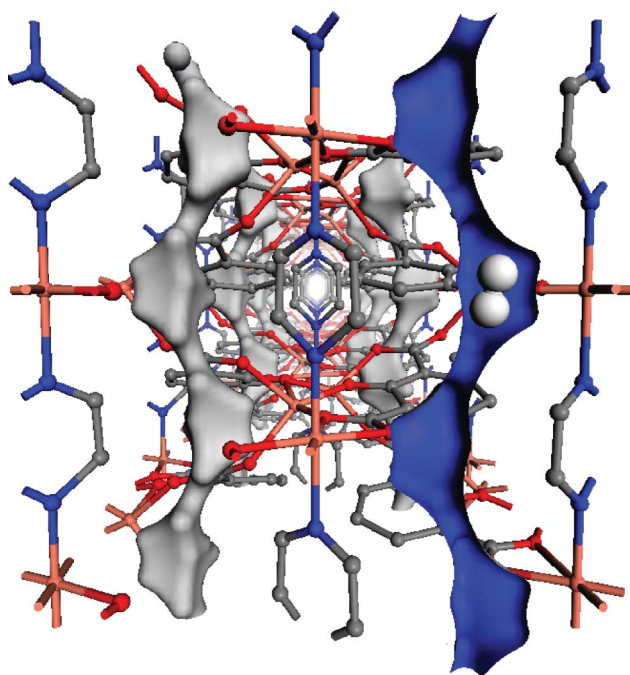


Fig. 4 Perspective view down the *a*-axis of microporous framework **1**. Blue and grey channels indicate the accessible surface areas available within the structure.

shown in Fig. 3. At low pressures H₂ adsorbs in preference to N₂ at a selectivity of greater than 5, a value which decays at higher partial pressures. The nitrogen isotherm does not exhibit the type I behaviour expected of a microporous material, and shows very low adsorption levels. Whilst the measurement was performed at the longest possible equilibration times, there may be large timescale diffusion effects that inhibit the adsorption curve. These effects are likely due to the flexibility observed within the structure (*vide infra*), and there may also be a small contribution from surface adsorption. Nevertheless, the uptake is extremely low; the material is essentially non-porous to nitrogen. Analysis with other gaseous probes at higher temperatures did not reveal sufficient uptake for a reliable interpretation.

Further investigations were undertaken to determine the cause of the remarkable preferential adsorption of H₂ over N₂. The

accessible free volume has been outlined in Fig. 4 for a probe radius of 1 Å, using a commercial package, Materials Studio.¹⁶

The narrow pore channels oriented in 1-dimension are likely to be responsible for the limited storage capacity of small molecules over larger molecules, for example H₂ over N₂. As shown in Fig. 5, the pore size distribution, calculated geometrically with the open source package RASPA 1.0,¹⁷ indicates a channel size of 1.75 Å in diameter. Though this is smaller than the estimated kinetic diameter of hydrogen (2.89 Å, assuming single spherical entity),¹⁸ by considering structural flexibility the axially orientated gas molecules and the known axial acceptance diameter for H₂ into a pore of 2.27 Å and N₂ 2.92 Å,¹⁹ it is reasonable that these channels are capable of gas storage. Molecular dynamics of the unit-cell has been performed with Materials Studio using the Universal Forcefield²⁰ and a microcanonical (NVE) ensemble over 1000 ps simulation time. Other simulation details include use of the Forcite module after an initial geometry optimization with an energy tolerance of 2×10^{-5} kcal mol⁻¹. Molecular dynamics was then performed in a NVT ensemble with a time step of 0.5 fs. Total simulation time was 2.1 ps with 2×10^5 equilibration steps and 4×10^6 simulation steps. The temperature was held constant at 77 K using a Nose–Hoover thermostat.

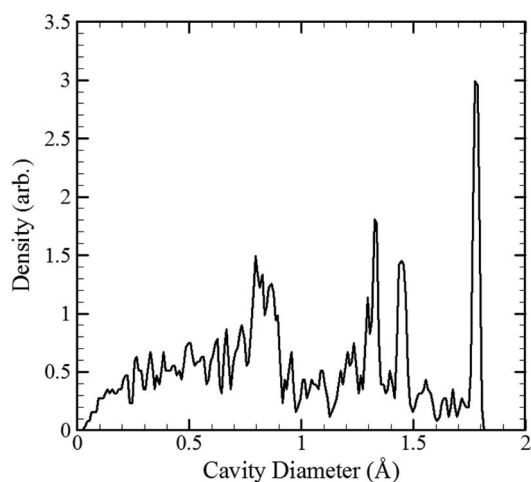


Fig. 5 Calculated cavity diameter distribution within the microporous framework **1** using RASPA 1.0.¹⁷

During the course of the simulation of **1**, an average measure of pore size fluctuation was determined, resulting in a standard deviation of 0.51 Å about the mean pore size of 1.75 Å. This means that the pore channel will expand to a size larger than 2.27 Å about 15.8% of the time and 2.92 Å < 1.5% of the time and as such, the structural flexibility of **1** is enough to allow hydrogen to penetrate the crystal at a higher rate than nitrogen. Additionally, the measured uptake at 0.9 atm. translates to 3 hydrogen molecules and 0.6 nitrogen molecules per unit cell, respectively. A video file demonstrating this flexibility is included with the ESI.†

In conclusion, we have reported a microporous framework, [Cu₃(ipO)₂(pyz)₂]_n (**1**), that exhibits a remarkable preferential adsorption for H₂ over N₂, with selectivity above 5 at sub-ambient pressures. This result has important implications for the isolation of H₂ from N₂ in ammonia synthesis waste streams, where energy expensive pressure-swing adsorption is typically required,

and N₂ is the typical adsorbent. The microporous framework **1** delivers the opportunity to conduct this separation in low H₂ streams by preferentially adsorbing it, and without the need for energy-expensive pressurisation. Molecular dynamics simulations revealed that although the channels of **1** are too small for inclusion of hydrogen, the structure is flexible, and adopts more open topologies that account for the preferential adsorption. Such flexibility was also observed in the hysteretic nitrogen adsorption isotherm.

Thermo-gravimetric analyses were performed under nitrogen using a Mettler Toledo TGA/DSC 1 at a heating rate of 10 °C min⁻¹. PXRD data were recorded on a Philips X'Pert Multipurpose X-ray Diffractometer (Cu_{Kα}, λ = 1.54056 Å). Gas adsorption experiments were performed on a Micromeritics ASAP 2420 equipped with a micropore pressure transducer. Data points were regarded to be measured after less than 2% variance in pressure was recorded over 1200 s intervals (typical conditions: 5 s intervals with 5% variance).

Notes and references

- (a) S. Ma, X.-S. Wang, D. Yuan and H.-C. Zhou, *Angew. Chem., Int. Ed.*, 2008, **47**, 4130; (b) S. Ma, D. Yuan, X.-S. Wang and H.-C. Zhou, *Inorg. Chem.*, 2009, **48**, 2072; (c) S. Ma, D. Sun, X.-S. Wang and H.-C. Zhou, *Angew. Chem., Int. Ed.*, 2007, **46**, 2458; (d) J.-R. Li, Y. Tao, Q. Yu, X.-H. Bu, H. Sakamoto and S. Kitagawa, *Chem.–Eur. J.*, 2008, **14**, 2771; (e) S. Ma, X.-S. Wang, E. S. Manis, C. D. Collier and H.-C. Zhou, *Inorg. Chem.*, 2007, **46**, 3432; (f) Y. E. Cheon and M. P. Suh, *Chem. Commun.*, 2009, 2296; (g) S. Ma, X.-S. Wang, C. D. Collier, E. S. Manis and H.-C. Zhou, *Inorg. Chem.*, 2007, **46**, 8499; (h) M. Dinca and J. R. Long, *J. Am. Chem. Soc.*, 2005, **127**, 9376; (i) P. L. Llewellyn, S. Bourrelly, C. Serre, Y. Filinchuk and G. Férey, *Angew. Chem., Int. Ed.*, 2006, **45**, 7751.
- (a) M. Dinca and J. R. Long, *Angew. Chem., Int. Ed.*, 2008, **47**, 6766; (b) A. G. Wong-Foy, A. J. Matzger and O. M. Yaghi, *J. Am. Chem. Soc.*, 2006, **128**, 3494; (c) H. J. Park and M. P. Suh, *Chem.–Eur. J.*, 2008, **14**, 8812; (d) Y.-G. Lee, H. R. Moon, Y. E. Cheon and M. P. Suh, *Angew. Chem., Int. Ed.*, 2008, **47**, 7741; (e) A. W. Thornton, K. M. Nairn, J. M. Hill, A. J. Hill and M. R. Hill, *J. Am. Chem. Soc.*, 2009, **131**, 10662; (f) A. W. Thornton, K. M. Nairn, D. Buso, M. R. Hill and M. R., *Gas Adsorp. Mater.*, 2009, PCT/AU2010/000004; (g) K. Sumida, M. R. Hill, S. Horike, A. Dailly and J. R. Long, *J. Am. Chem. Soc.*, 2009, **131**, 15120.
- (a) K. S. Min and M. P. Suh, *J. Am. Chem. Soc.*, 2000, **122**, 6834; (b) H. J. Choi and M. P. Suh, *Inorg. Chem.*, 2003, **42**, 1151; (c) F. Nouar, J. Eckert, J. F. Eubank, P. Forster and M. Eddaoudi, *J. Am. Chem. Soc.*, 2009, **131**, 2864; (d) S. Yang, X. Lin, A. J. Blake, K. M. Thomas, P. Hubberstey, N. R. Champness and M. Schröder, *Chem. Commun.*, 2008, 6108; (e) M. Dinca and J. R. Long, *J. Am. Chem. Soc.*, 2007, **129**, 11172.
- J. Y. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450.
- (a) M. A. Nadeem, D. Craig, R. Bircher and J. A. Stride, *Dalton Trans.*, 2010, **39**, 4358; (b) L. Arai, M. A. Nadeem, M. Bhadhbade and J. A. Stride, *Dalton Trans.*, 2010, **39**, 3372; (c) M. Kurmoo, *Chem. Soc. Rev.*, 2009, **38**, 1353.
- (a) J.-R. Li, R. J. Kuppler and H.-C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477; (b) D. Zacher, O. Shekhah, C. Woll and R. A. Fischer, *Chem. Soc. Rev.*, 2009, **38**, 1418.
- (a) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319; (b) S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334; (c) C. Janiak, *Dalton Trans.*, 2003, 2781; (d) B. Kesanli and W. Lin, *Coord. Chem. Rev.*, 2003, **246**, 305; (e) G. Férey, C. Mellot-Draznieks, C. Serre and F. Millange, *Acc. Chem. Res.*, 2005, **38**, 217; (f) D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Prior and M. J. Rosseinsky, *Acc. Chem. Res.*, 2005, **38**, 273; (g) W. B. Lin, *J. Solid State Chem.*, 2005, **178**, 2486; (h) J. L. C. Rowsell and O. M. Yaghi, *Angew. Chem., Int. Ed.*, 2005, **44**, 4670.

- 8 (a) R. Kitaura, K. Seki, G. Akiyama and S. Kitagawa, *Angew. Chem., Int. Ed.*, 2003, **42**, 428; (b) L. Pan, K. M. Adams, H. E. Hernandez, X. Wang, C. Zheng, Y. Hattori and K. Kaneko, *J. Am. Chem. Soc.*, 2003, **125**, 3062; (c) T. K. Maji, K. Uemura, H.-C. Chang, R. Matsuda and S. Kitagawa, *Angew. Chem., Int. Ed.*, 2004, **43**, 3269; (d) S. Bourrelly, P. L. Llewellyn, C. Serre, F. Millange, T. Loiseau and G. Férey, *J. Am. Chem. Soc.*, 2005, **127**, 13519; (e) R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, R. V. Belosludov, R. C. Kobayashi, H. Sakamoto, T. Chiba, M. Takata, Y. Kawazoe and Y. Mita, *Nature*, 2005, **436**, 238; (f) D. G. Samsonenko, H. Kim, Y. Sun, G.-H. Kim, H.-S. Lee and K. Kim, *Chem.–Asian J.*, 2007, **1**, 484; (g) J. A. R. Navarro, E. Barea, J. M. Salas, N. Masciocchi, S. Galli, A. Sironi, C. O. Ania and J. B. Parra, *Inorg. Chem.*, 2006, **45**, 2397; (h) L. Pan, D. H. Olson, L. R. Ciemnomolonski, R. Heddy and J. Li, *Angew. Chem., Int. Ed.*, 2006, **45**, 616; (i) T. J. Taylor, V. I. Bakhmutov and F. P. Gabbai, *Angew. Chem., Int. Ed.*, 2006, **45**, 7030; (j) T. K. Maji, R. Matsuda and S. Kitagawa, *Nat. Mater.*, 2007, **6**, 142; (k) S. M. Humphrey, J.-S. Chang, S. H. Jhung, J. W. Yoon and P. T. Wood, *Angew. Chem., Int. Ed.*, 2007, **47**, 272.
- 9 D. N. Dybtsev, H. Chun, S. H. Yoon, D. Kim and K. Kim, *J. Am. Chem. Soc.*, 2004, **126**, 32.
- 10 B. Chen, S. Ma, E. J. Hurtado, E. B. Lobkovsky and H.-C. Zhou, *Inorg. Chem.*, 2007, **46**, 8490.
- 11 (a) M. Arnold, P. Kortunov, D. J. Jones, Y. Nedellec, J. Karger and J. Caro, *Eur. J. Inorg. Chem.*, 2007, 60; (b) Y. Yoo and H. K. Jeong, *Chem. Commun.*, 2008, 2441; (c) J. Gascon, S. Aguado and F. Kapteijn, *Microporous Mesoporous Mater.*, 2008, **113**, 132; (d) Y. Liu, Z. Ng, E. A. Khan, H. K. Jeong, C. Ching and Z. P. Lai, *Microporous Mesoporous Mater.*, 2009, **118**, 296; (e) Y. Yoo, Z.-P. Lai and H. K. Jeong, *Microporous Mesoporous Mater.*, 2009, **123**, 100.
- 12 (a) Y.-S. Li, F.-Y. Liang, H. Bux, A. Feldhoff, W.-S. Yang and J. Caro, *Angew. Chem., Int. Ed.*, 2010, **49**, 548; (b) H. Guo, G. Zhu, I. J. Hewitt and S. Qiu, *J. Am. Chem. Soc.*, 2009, **131**, 1646.
- 13 B. Chen, S. Ma, F. Zapata, F. R. Fronczek, E. B. Lobkovsky and H.-C. Zhou, *Inorg. Chem.*, 2007, **46**, 1233.
- 14 Y.-Z. Zheng, Y.-B. Zhang, M.-L. Tong, W. Xue and X.-M. Chen, *Dalton Trans.*, 2009, 1396.
- 15 D. D. Do, *Adsorption Analysis: Equilibria and Kinetics*, Imperial College Press, London, 1998.
- 16 Materials Studio v5.0 Accelrys, Inc. San Diego, CA, USA, 2009.
- 17 (a) D. Dubbeldam, S. Calero, D. E. Ellis, R. Q. Snurr, *RASPA 1.0*, Northwestern University: Evanston, 2008; (b) L. D. Gelb and K. E. Gubbins, *Langmuir*, 1999, **15**, 305.
- 18 D. W. Breck, *Zeolite Molecular Sieves: Structure, Chemistry, and Use.*, John Wiley & Sons: New York, 1973.
- 19 A. W. Thornton, T. Hilder, A. J. Hill and J. M. Hill, *J. Membr. Sci.*, 2009, **336**, 101.
- 20 A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard and W. M. Skiff, *J. Am. Chem. Soc.*, 1992, **114**, 10024.