

organization of **1** into a liquid-crystalline phase is that it allows the unprecedented control of the molecular orientation of **1** in thin solid films. Induced orientation of the liquid-crystalline domains of **1** under a shearing force results in highly anisotropically ordered thin solid films that serve as dichroic polarizers of light at long wavelengths (greater than 600 nm). Future work will investigate the fluorescence, semiconducting, and photoconducting properties of **1**.

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Pentalene Bonding in Fullerenes

Sc₃N@C₆₈: Folded Pentalene Coordination in an Endohedral Fullerene that Does Not Obey the Isolated Pentagon Rule**

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- [1] M. C. Fyfe, J. F. Stoddart, *Acc. Chem. Res.* **1997**, *30*, 393–401.
- [2] J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, **1995**.
- [3] D. L. Gin, W. Gu, B. A. Pindzola, W.-J. Zhou, *Acc. Chem. Res.* **2001**, *34*, 973–980.
- [4] H. O. Jacobs, A. R. Tao, A. Schwartz, D. H. Gracias, G. M. Whitesides, *Science* **2002**, *296*, 323–325.
- [5] S. M. Kauzlarich, P. K. Dorhout, J. M. Honig, *J. Solid State Chem.* **2000**, *149*, 3–8.
- [6] G. Y. Liu, S. Xu, Y. Qian, *Acc. Chem. Res.* **2000**, *33*, 457–466.
- [7] M. D. Ward, A. M. Pivovar, *Curr. Opin. Solid State Mater. Sci.* **1999**, *4*, 581–586.
- [8] L. Schmidt-Mende, A. Fechtenkötter, K. Müllen, E. Moons, R. H. Friend, J. D. MacKenzie, *Science* **2001**, *293*, 1119–1122.
- [9] A. B. Gregg, R. A. Cormier, *J. Am. Chem. Soc.* **2001**, *123*, 7959–7960.
- [10] A. P. H. J. Schenning, J. V. Herrikhuyzen, P. Jonkheijm, Z. Chen, F. Würthner, E. W. Meijer, *J. Am. Chem. Soc.* **2002**, *124*, 10252–10253.
- [11] F. Würthner, C. Thalacker, S. Diele, C. Tschierske, *Chem. Eur. J.* **2001**, *7*, 2245–2253.
- [12] J. S. Moore, *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 777–788.
- [13] H. Quante, K. Müllen, *Angew. Chem.* **1995**, *107*, 1487–1489; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1323–1325.
- [14] Y. Geerts, H. Quante, H. Platz, R. Mahrt, M. Hopmeier, A. Böhm, K. Müllen, *J. Mater. Chem.* **1998**, *8*, 2357–2369.
- [15] K. Y. Law, *Chem. Rev.* **1993**, *93*, 449–486.
- [16] M. Emmelius, G. Pawlowski, H. W. Vollmann, *Angew. Chem.* **1989**, *101*, 1475–1502; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1445–1600.
- [17] K. Shirai, M. Sumitani, N. Takeda, M. Arai, US patent 5,278,853 **1994**.
- [18] P. J. Collings, J. S. Patel, *Handbook of Liquid Crystal Research*, Oxford University Press, New York, **1997**.
- [19] I. K. Iverson, S. M. Casey, W. Seo, S.-W. Tam-Chang, B. A. Pindzola, *Langmuir* **2002**, *18*, 3510–3516.
- [20] I. K. Iverson, S.-W. Tam-Chang, *J. Am. Chem. Soc.* **1999**, *121*, 5801–5802.
- [21] A manuscript that describes the detailed procedure for the synthesis of **1** is in preparation.
- [22] K. Saito, *J. Phys. Chem. B* **2001**, *105*, 4235–4238.
- [23] P. M. Kamaier, R. A. Hoffmann, *J. Am. Chem. Soc.* **1994**, *116*, 9684–9691.
- [24] Liquid crystals that result from the π -stacking interactions between aromatic molecules, in addition to hydrophobic interactions, are called lyotropic, chromonic liquid crystals as distinct from the lyotropic liquid crystals of aliphatic surfactants. See references [25] and [26].
- [25] J. Lydon in *Handbook of Liquid Crystals*, Vol. 2B (Eds.: D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, V. Vill), Wiley-VCH, Weinheim, **1998**, pp. 981–1007.
- [26] J. Lydon, *Curr. Opin. Colloid Interface Sci.* **1998**, *3*, 458–466.
- [27] T. K. Attwood, J. E. Lydon, C. Hall, G. J. T. Tiddy, *Liq. Cryst.* **1990**, *7*, 657–668.
- [28] C. D. West, R. C. Jones, *J. Opt. Soc. Am.* **1951**, *41*, 976–986.

The new family of endohedral metallofullerenes, Sc₃N@C₈₀, Sc₃N@C₇₈, and Sc₃N@C₆₈, has been prepared by the Krätschmer–Huffman arc fullerene preparation with graphite rods doped with Sc₂O₃ in a dynamic atmosphere of helium and dinitrogen.^[1–4] Crystallographic studies have shown that Sc₃N@C₈₀ contains a planar {Sc₃N} unit within a C₈₀ cage with I_h symmetry,^[1] while Sc₃N@C₇₈ consists of a similar {Sc₃N} unit contained within a fullerene cage of D_{3h} symmetry.^[3] These endohedral structures, as well as most known empty-cage fullerenes, obey the isolated pentagon rule (IPR) which requires that each of the twelve pentagons in the carbon cage be surrounded by five hexagons. However, theoretical studies have suggested that some endohedral fullerenes (for example, Ca@C₇₂ and La₂@C₇₄) may not obey the IPR.^[5] Additionally, two endohedral fullerenes, Sc₃N@C₆₈^[4] and Sc₂@C₆₆,^[6] and one empty-cage fullerene, C₆₂,^[7] have been recently reported, which cannot obey the IPR as no possible IPR cages exist for C₆₂, C₆₄, C₆₆, or C₆₈.^[8]

Here we report the detailed structural characterization of Sc₃N@C₆₈. For a C₆₈ cage whose surface consists solely of pentagons and hexagons, there are 6332 possible isomers, but the ¹³C NMR spectrum of Sc₃N@C₆₈ restricts these possibilities to only 11 isomers that have either D₃ or S₆ symmetry.^[4] On the basis of density functional calculations, two isomers (isomer 6140^[4] and isomer 6275;^[9] Figure 1) have emerged as the likely cage structures present in Sc₃N@C₆₈. As Figure 1 shows, these isomers have different shapes (6140 is rounded while 6275 is flattened), although both have D₃ symmetry.

Black crystals of Sc₃N@C₆₈·[Ni^{II}(OEP)]·2 C₆H₆ (OEP = 2,3,7,8,12,13,17,18-octaethylporphinate) were obtained by the gradual diffusion of a solution of Sc₃N@C₆₈ (prepared

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Figure 1. Idealized models of isomer 6140 (left, green pentagons) and isomer 6275 (right, blue pentagons) of C_{68} .

and purified as outlined previously^[4] in benzene into a solution of $[Ni^{II}(\text{OEP})]$ in benzene. This fullerene/porphyrin cocrystallization procedure has previously been demonstrated to form crystalline samples with sufficient order in the location of the fullerene cage to produce meaningful structural information.^[10]

The structure was solved by direct methods which yielded the entire porphyrin, two benzene molecules, and the major $\{\text{Sc}_3\text{N}\}$ unit (site **A**). Successive cycles of refinement, and the selection of atoms from difference maps produced one entire C_{68} molecule (site **A**) but with a fractional occupancy of only approximately 0.5, based on thermal parameters; at this stage the $R1$ value was 0.151. Refinement then took advantage of the D_3 symmetry to yield a set of 771 same-distance restraints that were used to preserve this symmetry. Further refinement resulted in the location of an additional 13 scandium sites with occupancies ranging from 0.25 to 0.04. By trial and error, a second orientation (site **B**) of the C_{68} cage was identified. This procedure used a rigid group constructed from the coordinates of the refined C_{68} cage (**A**) to fit peaks from the difference Fourier maps. This second orientation was the best fit when using the opposite enantiomer from that found in site **A**, and refined to a group occupancy of 0.29. Thus, another orientation of the cage needed to be located. Again, using the rigid group, and trial and error, the inclusion of a third cage (site **C**) with an occupancy of 0.21, which was also of the opposite hand to site **A**, brought the $R1$ value to 0.093.

Figure 2 shows a drawing of the orientations of the individual molecular components with only the major site **A** (with 0.50 site occupancy of the $\text{Sc}_3\text{N}@C_{68}$ molecule) shown. As usual in structures of this type, the $\text{Sc}_3\text{N}@C_{68}$ molecule is cupped in the cavity provided by the nickel porphyrin and its eight ethyl groups. There are no unusual aspects to the geometry of the nonfullerene components of this crystal.

Figure 3 shows diagrams of the major site **A**. The carbon cage is shown to be isomer 6140 with D_3 symmetry, as predicted by earlier theoretical work.^[4] In this cage structure, there are three equivalent sites where pairs of pentagons

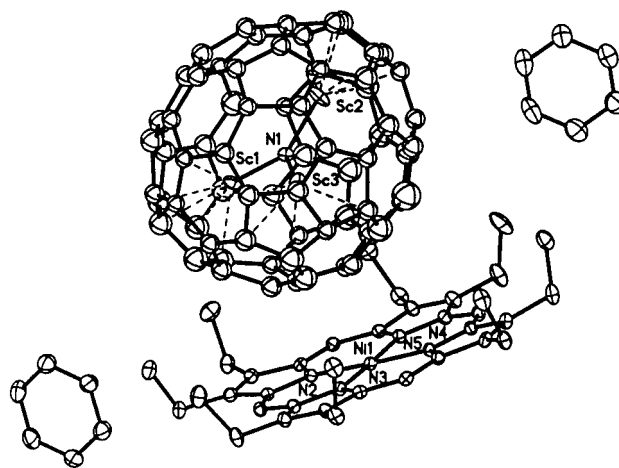


Figure 2. A drawing of the structure of $\text{Sc}_3\text{N}@C_{68}\cdot[\text{Ni}^{II}(\text{OEP})]\cdot 2\text{C}_6\text{H}_6$ that shows the relative orientation of all components. Only the major orientation (0.50 site occupancy) of the $\text{Sc}_3\text{N}@C_{68}$ molecule is shown.

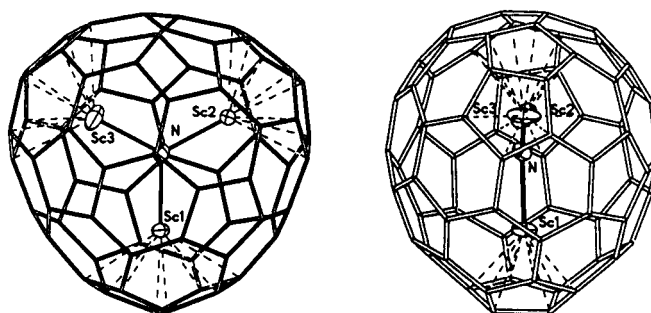


Figure 3. Two orthogonal views of the major form (0.50 site occupancy) of the $\text{Sc}_3\text{N}@C_{68}$ molecule in $\text{Sc}_3\text{N}@C_{68}\cdot[\text{Ni}^{II}(\text{OEP})]\cdot 2\text{C}_6\text{H}_6$.

share a side (pentalene units). The maximum degree of outward bulge in the cage occurs at these sites, and the principle scandium sites are located in these pockets. The $\{\text{Sc}_3\text{N}\}$ portion is planar, and the $\text{N1}-\text{Sc}$ bond lengths are

2.022(3), 1.974(4), and 1.961(4) Å for Sc1, Sc2, and Sc3, respectively. These separations are just slightly shorter than their counterparts in $\text{Sc}_3\text{N@C}_{78}$ (1.983(15)–2.125(5) Å)^[3] and in $\text{Sc}_3\text{N@C}_{80}$ (1.9931(14)–2.0526(14) Å).^[1] The Sc–N–Sc angles are Sc1–N–Sc2 130.3(5), Sc1–N–Sc3 113.8(5), and Sc2–N–Sc3 115.9(5)°.

As was previously pointed out, the scandium atoms are situated over the centers of pentalene portions of the fullerene cage. There is an extensive literature on the organometallic chemistry of pentalene ligands, which frequently bridge two metals.^[11] However, compounds containing a metal bonded at the center of a folded pentalene ligand have only recently been reported.^[12,13] Figure 4 presents a

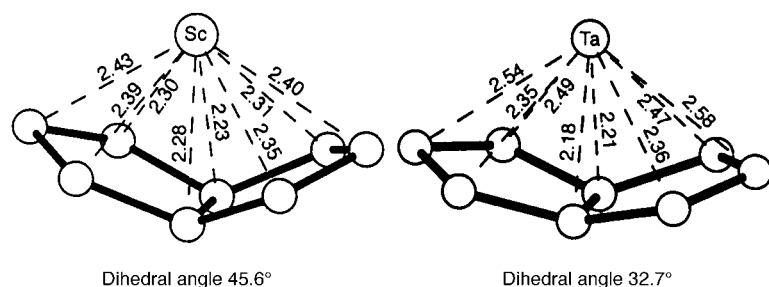


Figure 4. Comparison of the average pentalene coordination in $\text{Sc}_3\text{N@C}_{68}$ and in $[\eta^8\text{-C}_8\text{H}_4(\text{SiMe}_3)_2\text{-1,4}]\text{TaCl}_3$.

comparison of the Sc–pentalene coordination geometry in $\text{Sc}_3\text{N@C}_{68}$ with the Ta–pentalene coordination in a conventional organometallic complex, $[\eta^8\text{-C}_8\text{H}_4(\text{SiMe}_3)_2\text{-1,4}]\text{TaCl}_3$.^[12] The major differences all result from the fold angle of the pentalene unit, (45.6° in $\text{Sc}_3\text{N@C}_{68}$, 32.7° in $[\eta^8\text{-C}_8\text{H}_4(\text{SiMe}_3)_2\text{-1,4}]\text{TaCl}_3$) which is greater in the fullerene where the closed nature of the carbon cage more tightly constricts the geometry. As a consequence of this fold, the pyramidalization^[14] of the carbon atoms at the 5:5-ring junction is significantly higher (16.5°) than it is for the other carbon atoms of the cage (which range from 8.8 to 12.2°). In $\text{Sc}_3\text{N@C}_{68}$, the Sc–C bond lengths fall in a narrower range (2.225(5)–2.450(5) Å) than they do in $[\eta^8\text{-C}_8\text{H}_4(\text{SiMe}_3)_2\text{-1,4}]\text{TaCl}_3$ (2.182(13)–2.582(12) Å). In both cases, the shortest metal-to-carbon separations involve the carbon atoms at the 5:5-ring junctions.

Disorder in the positioning of the fullerene has been resolved with a model that includes two other orientations (**B** and **C**) for the C_{68} cage. A central nitrogen atom is common to all three cage orientations. Three scandium atoms (Sc4, Sc5, and Sc6), each with an occupancy of 0.21, fit into the three pentalene units within the C_{68} cage at site **C** to create a molecule analogous to that in the major site. One additional scandium atom with an occupancy of 0.25 is situated within a pentalene unit of the cage occupying site **B**. Nine other scandium-atom positions with site occupancies ranging from 0.10 to 0.04 have been identified. These appear to be associated with the C_{68} cage in site **B** but they are situated in various locations within the cage. Highly correlated overlap of multiple $\{\text{Sc}_3\text{N}\}$ units precluded accurate identification of distinct entities except for one triangular array comprised of

Sc7, Sc8, and Sc9, with an occupancy of 0.10. Thus, as is often the case with complex supramolecular structures, the model we have developed is the most plausible we could find, but is not without some ambiguities. Consequently, further structural work on non-IPR fullerene cages, particularly in endohedral complexes, is clearly warranted.

Coordination of the scandium atoms to the pentalene portion of a fullerene cage may provide a means of stabilizing this substructure. The computed non-IPR structures for Ca@C_{72} and Ca@C_{74} place the metals within the pentalene clefts.^[5] A similar arrangement, with metal atoms over pentalene units, has been proposed for $\text{Sc}_2\text{@C}_{66}$.^[6]

Experimental Section

Crystals of $\text{Sc}_3\text{N@C}_{68}[\text{Ni}^{\text{II}}(\text{OEP})]\cdot 2\text{C}_6\text{H}_6$ were obtained by layering a purple solution of $\text{Sc}_3\text{N@C}_{68}$ (approximately 0.5 mg) in benzene (0.5 mL) of over a red solution of $[\text{Ni}^{\text{II}}(\text{OEP})]$ (2.5 mg) in benzene (1.5 mL). The two solutions were allowed to diffuse together over five days, by which time, black crystals had formed.

Crystal data for $\text{Sc}_3\text{N@C}_{68}[\text{Ni}^{\text{II}}(\text{OEP})]\cdot 2\text{C}_6\text{H}_6$: black parallelepiped, $0.14 \times 0.10 \times 0.07$ mm, triclinic, space group $P\bar{1}$, $a = 14.362(2)$, $b = 14.3902(14)$, $c = 18.986(2)$ Å, $\alpha = 85.433(2)$, $\beta = 88.606(23)$, $\gamma = 61.786(3)^\circ$, $V = 3446.3(7)$ Å³, $\lambda = 0.71073$ Å, $Z = 2$, $\rho_{\text{calc}} = 1.651$ Mg m^{−3}; $\mu(\text{MoK}\alpha) = 0.622$ mm^{−1}; $T = 91(2)$ K; Bruker SMART 1000; ω scans, $2\theta_{\text{max}} = 60^\circ$; 49366 reflections collected; 19925 independent ($R_{\text{int}} = 0.079$) included in the refinement; min/max transmission = 0.92/0.96 (no absorption correction applied); Patterson and difference Fourier methods solution (SHELXS-97; Sheldrick, 1990); full-matrix least-squares based on F^2 (SHELXL-97; Sheldrick, 1998); $R = 0.150$, $wR = 0.302$ for all data; conventional $R_I = 0.093$ computed for 10967 observed data ($> 2\sigma(I)$) with 771 restraints and 1015 parameters.

CCDC-190814 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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- [1] S. Stevenson, G. Rice, T. Glass, K. Harich, F. Cromer, M. R. Jordan, J. Craft, E. Hadju, R. Bible, M. M. Olmstead, K. Maitra, A. J. Fisher, A. L. Balch, H. C. Dorn, *Nature* **1999**, *401*, 55.
- [2] "Electronic Properties of Novel Materials and Molecular Nanostructures": H. C. Dorn, S. Stevenson, J. Craft, F. Cromer, J. Duchamp, G. Rice, T. Glass, K. Harich, P. W. Fowler, T. Heine, E. Hajdu, R. Bible, M. M. Olmstead, K. Maitra, A. J. Fisher, A. L. Balch, Proceedings of the IWEPNM2000 Conference, Kirchberg/Tyrol (Austria), **2000**, p. 135 (American Institute of Physics).
- [3] M. M. Olmstead, A. de Bettencourt-Dias, J. C. Duchamp, S. Stevenson, D. Marciu, H. C. Dorn, A. L. Balch, *Angew. Chem.* **2001**, *113*, 1263; *Angew. Chem. Int. Ed.* **2001**, *40*, 1223.
- [4] S. Stevenson, P. W. Fowler, T. Heine, J. Duchamp, G. Rice, T. Glass, K. Harich, E. Hajdu, R. Bible, H. C. Dorn, *Nature* **2000**, *408*, 427.
- [5] K. Kobayashi, S. Nagase, M. Yoshida, E. Osawa, *J. Am. Chem. Soc.* **1997**, *119*, 12693.
- [6] C.-R. Wang, T. Kai, T. Tomiyama, T. Yoshida, Y. Kobayashi, E. Nishibori, M. Takata, M. Sakata, H. Shinohara, *Nature* **2000**, *408*, 426.

- [7] W. Qian, M. D. Bartberger, S. J. Pastor, K. N. Houk, C. L. Wilkins, Y. Rubin, *J. Am. Chem. Soc.* **2000**, 122, 8333.
 [8] P. W. Fowler, D. E. Manolopoulos, *An Atlas of Fullerenes*, Oxford University Press, Oxford, **1995**.
 [9] J. Aihara, *Chem. Phys. Lett.* **2001**, 343, 465.
 [10] M. M. Olmstead, D. A. Costa, K. Maitra, B. C. Noll, S. L. Phillips, P. M. Van Calcar, A. L. Balch, *J. Am. Chem. Soc.* **1999**, 121, 7090.
 [11] H. Butenschön, *Angew. Chem.* **1997**, 109, 1771; *Angew. Chem. Int. Ed. Engl.* **1997**, 36, 1695.
 [12] Q. A. Abbasali, F. G. N. Cloke, P. B. Hitchcock, S. C. P. Joseph, *Chem. Commun.* **1997**, 1541.
 [13] K. Jonas, B. Gabor, R. Mynott, K. Angermund, O. Heinemann, C. Krüger, *Angew. Chem.* **1997**, 109, 1790; *Angew. Chem. Int. Ed. Engl.* **1997**, 36, 1712.
 [14] R. C. Haddon, *Science* **1993**, 261, 1545.

Multiparallel Organic Synthesis

A Three-Dimensional Array for Multiparallel Synthesis**

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Multiparallel organic synthesis combined with high-content screening has emerged as a valuable approach for identification of new molecular function. Emulating basic principles of natural selection, this strategy has proven particularly successful for discovery and optimization of modulators of metabolic pathways,^[1] identification of novel catalysts,^[2] and development of unique functional materials.^[3] Solid-phase synthesis^[4] has provided a foundation for the development of several innovative methods for the synthesis of chemical libraries.^[5–11] Among these formats, light-directed synthesis^[8] and split synthesis are particularly noteworthy.^[9] While the former provides complete positional encoding of individual library members,^[8] the latter features high throughput and operational simplicity,^[9] although it requires additional split–pool steps and encoding–decoding operations.^[10,11]

We describe herein a conceptually novel format for the synthesis of chemical libraries based on three-dimensional arrays of interconnected reaction wells. This method is unique and differs significantly from the existing formats of generat-

ing chemical diversity,^[5–11] combining the high efficiency of the split synthesis with a spatially addressable format.

The strategy entails layer-selective functionalization of a three-dimensional matrix, consisting of interconnected reaction wells. Each well is designed to encapsulate an individual library member by attachment to a physically localized solid support. Figure 1 provides a conceptual representation of the synthesis of an ABC library randomized with two building

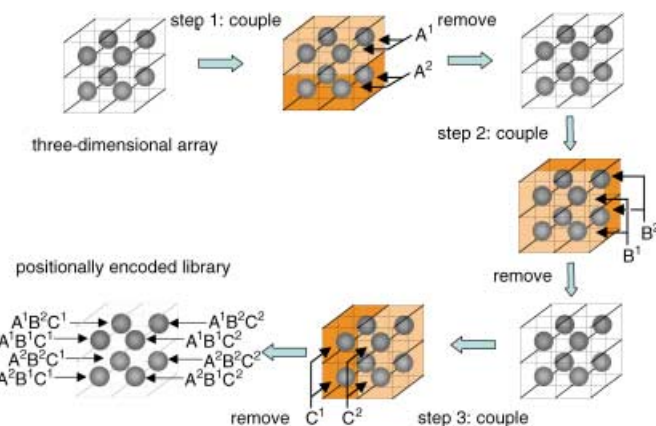


Figure 1. Conceptual representation of the synthesis of a chemical library in a three-dimensional array. The synthesis entails a layer-selective addition of reagents in each of the three dimensions. Three sets of building blocks (A^1 and A^2 , B^1 and B^2 , C^1 and C^2) are used sequentially. Each coupling step is followed by the appropriate washing and deprotection operations. The array is rotated by 90° prior to the addition of the next set of reagents. This process affords a positionally encoded library containing all the possible combinations.

blocks at each position (A^1 and A^2 , B^1 and B^2 , C^1 and C^2). The first functionalization step entails simultaneous addition of building blocks A^1 and A^2 to two parallel layers of the array. Following a washing cycle and a 90° rotation, the synthesis process is repeated with building blocks B^1 and B^2 . The third set of reactants— C^1 and C^2 —is introduced in a similar fashion following the final 90° rotation. This process affords a library of spatially separated compounds. The identity of each compound is established by its physical location within the array.

The design of an individual reactor is depicted in Figure 2 A. Encapsulating a suitable polymeric support, each microwell is equipped with four openings, connecting it to four adjacent wells. Insertion of the appropriate sealing elements (i.e. taper pins) seals the walls of the reactors. Removal of pins allows addition and withdrawal of reagents. This simple concept provides a general method for layer-selective multiparallel chemical synthesis in each of the three dimensions without cross-contamination. The synthesis cycle begins with removal of all the pins from one side of the cube, while the perpendicular pins remain inserted (Figure 2 B). The first set of reagents (A^1 and A^2) is added, allowing all the coupling steps to be performed simultaneously. Following the washing cycle, and rotation by 90° , the second coupling step is performed with B^1 and B^2 . The originally removed set of pins is reinserted, followed by withdrawal of the pins from the perpendicular side of the cube. The third coupling step is performed with C^1 and C^2 , as shown. A noteworthy feature of

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