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Palaeontology

First Devonian tetrapod from Asia

The earliest tetrapods (vertebrates with limbs rather than paired fins) date from the Late Devonian Period (370–354 million years ago)[1,2]— nine genera have been described, all of which are from the Euramerican supercontinent that comprises Europe, north America and Greenland, apart from a single Gondwanan genus, *Metaxygnathus*, from Australia[3–5]. Here we report the discovery of the first Devonian tetrapod from Asia, a finding that substantially extends the geographical range of these animals and raises new questions about their dispersal. These forms seem to have achieved worldwide distribution and great taxonomic diversity within a relatively short time.

The new fossil, an incomplete left mandible (Fig. 1a; Box 1), was collected by us from the Late Devonian (about 355 million years BP) non-marine Zhongning Formation of the Ningxia Hui autonomous region, northwestern China, in July 2002. Associated fossils include the plants *Leptophloeum rhombicum* and *Sublepidodendron mirabile*, land plant spores, the antiarch fishes *Remigolepis* and *Sinolepis*[6], and undescribed lobe-finned fish remains. The specimen is exposed in mesial view and comprises most of the prearticular, together with the angular and postsplenial (exposed along the ventral jaw margin). The dentary and coronoids are missing.

Mandibles of early tetrapods differ substantially from those of lobe-finned fish[4], allowing this specimen to be identified with confidence as a tetrapod. The main diagnostic characters are the appearance of the prearticular, which carries a well-defined dorsal band of denticles but is otherwise smooth apart from a faint radial striation, and the absence of Meckelian ossification between the prearticular and infradentaries. Lobe-finned fish have denticles that extend across most or all of the prearticular, and a well-ossified Meckelian element that binds the prearticular and infradentaries together. The absence of the dentary is also significant: this bone is loosely attached in many Devonian tetrapods[4] and is often lost from isolated jaws[5], but in lobe-finned fish it is firmly sutured to the jaw and does not detach.

Box 1 Taxonomic description

Tetrapoda (Goodrich, 1930)
Sinostega pani Zhu and Ahlberg gen. et sp. nov.
Provisional diagnosis. A stem-group tetrapod lacking Meckelian ossification between the prearticular and infradentaries (angular and postsplenial) in the middle part of the lower jaw. The denticulated field on the prearticular does not reach as far anteriorly as in *Acanthostega*.
Etymology. Generic name from Latin *Sino-* (pertaining to China) and Greek *stega* (roof, now a conventional ending for Devonian tetrapod names, cf. *Ichthyostega*, *Ventastega*). Specific name in honour of Pan Jiang as contributor to the study of the Ningxia Devonian biota[6].
Holotype. V13576, an incomplete lower-jaw ramus. IVPP, Beijing.
Locality and horizon. Ningxia Hui autonomous region, China (see Fig. 1c). Zhongning Formation (late Famennian, Late Devonian).
Remarks. The absence of Meckelian ossification in the middle part of the jaw distinguishes *Sinostega* from all known Devonian tetrapods except *Acanthostega* and possibly *Tulerpeton*. It most closely resembles *Acanthostega*[4], but differs from that genus in having a smaller denticulated field on the prearticular.

During the Late Devonian, northern China lay in tropical latitudes adjacent to northeastern Gondwana (Fig. 1b)[7]. It is therefore interesting that *Sinostega* resembles the Euramerican genus *Acanthostega* more closely than it does the Australian *Metaxygnathus*. Tetrapods probably originated in Euramerica during the Frasnian Age[4,8,9]. We consider that tetrapods had achieved an essentially global distribution in tropical to subtropical latitudes by the end of the Famennian, some 5–10 million years later (supporting the idea that the earliest tetrapods might have been littoral[10]), and that their apparent scarcity in northern Gondwana and China is a sampling artefact that will be remedied by future discoveries.

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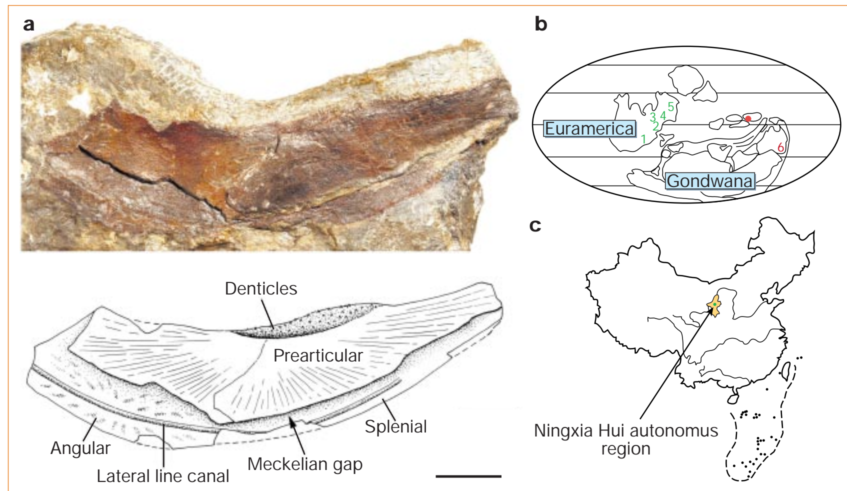

Figure 1 A new Devonian tetrapod from China. **a,** Photograph (top) and interpretative drawing (bottom) of IVPP V13576, a lower-jaw ramus from the Ningxia Hui autonomous region, China. Note the absence of Meckelian ossification (Meckelian gap) between the prearticular and infradentaries (splenial and angular), and the narrow denticulated band along the top of the prearticular, both of which are diagnostic tetrapod features. Scale bar, 10 mm. **b,** Late Devonian palaeogeographical map (modified from ref. 7) showing the location of the new Devonian tetrapod (red dot) in relation to previously discovered specimens. Green numbering, Euramerican taxa; red, non-Euramerican: 1, Pennsylvania (*Hynerpeton, Densignathus*); 2, Scotland (*Elginerpeton*); 3, Greenland (*Ichthyostega, Acanthostega*); 4, Latvia (*Obruchevichthys, Ventastega*); 5, Russia (*Tulerpeton*); 6, New South Wales (*Metaxygnathus*). **c,** Map of modern-day China, showing the Ningxia Hui autonomous region in orange; green dot indicates the fossil site, close to the Yellow River.

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Nanotechnology

Carbon nanotubes with DNA recognition

Since the discovery of their one-dimensional electronic band structure[1], the leading candidate that has emerged for nanodevice applications is single-walled carbon nanotubes (SWNTs) . Here we unite their unique properties with the specific molecular-recognition features of DNA by coupling SWNTs to peptide nucleic acid (PNA, an uncharged DNA analogue[2]) and hybridizing these macromolecular wires with complementary DNA. Our findings provide a new, versatile means of incorporating SWNTs into larger electronic devices by recognition-based assembly, and of using SWNTs as probes in biological systems by sequence-specific attachment.

At present, SWNT-based devices such as field-effect transistors[3], logic circuits[4,5] and single-electron transistors[6] are fabricated by 'top-down' lithographic methods. The construction of more complex architectures with high device density requires the development of a 'bottom-up', massively parallel strategy that exploits the molecular properties of SWNTs.

We have therefore developed a technique to couple SWNTs covalently to PNA. Our process begins by ultrasonically shortening SWNT ropes (Tubes@Rice) for 1 hour in a 3:1 mixture of concentrated H_2SO_4 and HNO_3. Subsequent exposure to 1 M HCl produces abundant carboxyl end-groups[7]. This material is dispersed in dimethylformamide (DMF, 99.5%) and incubated for 30 min in 2 mM 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride and 5 mM *N*-hydroxysuccinimide (NHS) to form SWNT-bearing NHS esters[8] (Fig. 1a).

PNA adducts are formed (Fig. 1b) by reacting this material in DMF for 1 hour with excess PNA (sequence: NH_2-Glu–GTGCTCATGGTG–$CONH_2$, where Glu is a glutamate amino-acid residue and the central block represents nucleic-acid bases; Fig. 1b). The PNA-derivatized SWNTs are transferred to water and dispersed in 0.5% aqueous sodium dodecyl sulphate, which stabilizes the individual SWNTs[9].

To investigate whether DNA would hybridize to PNA–SWNTs, we prepared fragments of double-stranded DNA with 12-base-pair, single-stranded 'sticky' ends that were complementary to the PNA sequence. These fragments were produced by cutting double-stranded DNA with the restriction enzyme *Hin*dIII and ligating the products to single-stranded oligonucleotides. This sticky DNA was hybridized to the PNA–SWNTs (Fig. 1c) in water, deposited on freshly cleaved mica with 5 mM $MgCl_2$, and the surface was rinsed and dried after 30 s. Atomic-force micrographs (Fig. 1d, e) of the DNA/PNA–SWNT hybrids were recorded under ambient conditions.

From our observations of several samples, we conclude that DNA attachment occurs predominantly at or near the nanotube ends. Because the derivatization chemistry is done on SWNT 'ropes', we contend that individual SWNTs are largely shielded, resulting in a low density of defects in their side walls. The rare attachment of DNA to other regions of SWNTs also indicates that this is the result of sequence-specific PNA–DNA base-pairing, rather than of nonspecific interaction.

We chose to couple PNA, rather than DNA, directly with SWNTs for several reasons[10]. First, PNA is compatible with the most convenient solvents (DMF, for example); second, PNA is not susceptible to enzymatic degradation; and third, the uncharged PNA backbone gives rise to PNA–DNA duplexes that are more thermally stable than their DNA–DNA counterparts because there is no electrostatic repulsion. Besides reducing the length of the sticky ends required for room-temperature hybridization, this last property should reduce nonspecific electrostatic interactions with metallic electrodes or with surfaces, such as silicon oxide, that are convenient for lithography.

The recognition properties imparted to SWNTs by oligonucleotide adducts could be used to programme the attachment of SWNTs to each other and to substrate features, such as electrodes, on which monolayers of complementary sequences are self-assembled. The antisense properties of PNA–SWNTs might also be exploited in a biological context, for example in biosensors. Our results represent a step towards full compatibility of SWNTs with enzymes and proteins[11,12] — a powerful approach for organizing complex devices at the sublithographic scale.

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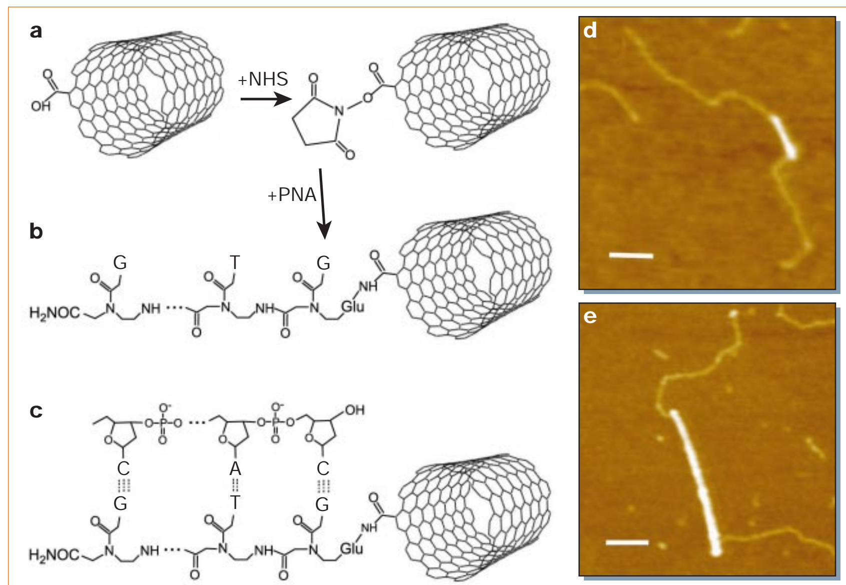

Figure 1 Attachment of DNA to carbon nanotubes. **a, b,** *N*-hydroxysuccinimide (NHS) esters formed on carboxylated, single-walled carbon nanotubes (SWNTs) are displaced by peptide nucleic acid (PNA), forming an amide linkage. **c,** A DNA fragment with a single-stranded, 'sticky' end hybridizes by Watson–Crick base-pairing to the PNA–SWNT. **d, e,** Atomic-force microscope (TappingMode) images of PNA–SWNTs. SWNTs appear as bright lines; the paler strands represent bound DNA. Scale bars: 100 nm; nanotube diameters: **d**, 0.9 nm; **e**, 1.6 nm.

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