Supplementary information for

Cryptic iridescence in a fossil weevil generated by single diamond photonic crystals

Maria E. McNamara^{1,2}*, Vinod Saranathan³*, Emma Locatelli¹, Heeso Noh^{4,5}, Derek E.G. Briggs^{1,6}, Patrick J. Orr² and Hui Cao⁵

¹Dept. of Geology & Geophysics, Yale University, Kline Geology Laboratory, 210 Whitney Avenue, New Haven CT 06520, USA

²UCD School of Geological Sciences, University College Dublin, Belfield, Dublin 4, Ireland

³Edward Grey Institute, Dept. of Zoology, University of Oxford, Tinbergen Building, South Parks Road, Oxford OX1 3PS, UK

⁴Dept. of Nano and Electronic Physics, Kookmin University, 77 Jeong-neong Ro, Seongbuk-gu, Seoul, Korea

⁵Dept. of Applied Physics, Yale University, Becton Centre, 15 Prospect St., New Haven CT 06520, USA

⁶Yale Peabody Museum of Natural History, 170 Whitney Avenue, New Haven, CT 06520, USA

* Authors for correspondence (<u>maria.mcnamara@ucc.ie</u>, <u>vinodkumar.saranathan@aya.yale.edu</u>). Current address: MM: School of Biological, Earth and Environmental Sciences, University College Cork, Cork, Ireland; VS: Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore.

Supplementary Figures S1-S3

Supplementary Tables S1, S2

Supplementary references



Figure S1. Details of scales in fossil and extant *Hypera*. (a, b) Light (a) and scanning electron (b) micrographs of iridescent seta (arrow) in fossil *H. diversipunctata*. Note multiple domains in (a) and three-dimensional nanostructure in the seta lumen (b). (c, d) Light (c) and scanning electron (d) micrographs of poorly preserved scales in fossil *H. diversipunctata*. Note partially ordered to disordered nanostructure in (c). (e, f) Iridescent scales in extant *H. meles* and *H. nigrirostris* (images courtesy M. Morris). Scale bars: a, 25 µm; b, d, 2 µm; c, 10 µm; e, f, 100 µm.

Figure S2 (overleaf). 2D Small Angle X-ray Scattering (SAXS) analyses of *H. diversipunctata* scales. Left-hand column: SAXS patterns (unmasked; original images 1340 x 1300 pixels). The false colour scale corresponds to the logarithm of scattering intensity. The concentric white circles denote the expected locations of the scattering peaks for single diamond (Fd-3m) structures. Central column: Structural diagnoses of normalised, azimuthally-averaged SAXS profiles integrated from the 2D SAXS patterns. Vertical lines denote expected Bragg peak positional ratios for various cubic crystallographic space groups. Numbers above the vertical lines are squares of the moduli of the Miller indices (hkl) for the allowed reflections of the cubic space-groups. The normalised positional ratios of the scattering peaks are indexed to the predictions of specific crystallographic space groups or symmetries following IUCr conventions. Right-hand column: Indexing of the azimuthally averaged profiles of the respective 2D SAXS patterns of H. diversipunctata photonic scales, using the plot of the moduli of the hkl Miller indices of the Bragg peaks against the corresponding reciprocal lattice spacing, S. The observed peaks (solid black circles) are shown alongside the theoretically allowed reflections for the single diamond (Fd-3m) and face centred cubic (F4-3m) crystallographic space group symmetries. The linearity and zero intercepts of the plot confirm the cubic aspect of the nanostructures, and the slope gives an estimate of the lattice parameter, a.



(b) Hypera diversipunctata fossil







(c) Hypera diversipunctata fossil





(e) Hypera diversipunctata fossil



(f) Hypera diversipunctata fossil





(h) Hypera diversipunctata extant









(k) Hypera diversipunctata extant









(n) Hypera diversipunctata extant



(o) Hypera diversipunctata extant





(q) Hypera diversipunctata extant



(r) Hypera diversipunctata extant





Figure S3. Reflectance spectra from a 500 μ m spot from natural sediment samples from the Blackwater estuary, Co. Cork, Ireland (*a-c*) and from Fermoyle, Co. Kerry, Ireland (*d*, *e*).

Taxon	Тахопоту	Distribution	Biophotonic structure	Reference
Entimus imperialis	Curculinidae: Entiminae: Entimini	neotropical Brazil	diamond	1,2,3
Eudiagogus pulcher	Curculinidae: Entiminae: Eudiagogini	Brazil	diamond	4
Eupholus magnificus	Curculinidae: Entiminae: Eupholini	Papua New Guinea	inverse opal and quasi-ordered	5
Eupholus schoenherri	Curculinidae: Entiminae: Eupholini	Papua New Guinea	diamond	6
Platyomus cultricollis	Curculinidae: Entiminae: Naupactini	Brazil	opal?	7
Platyomus mutabilis	Curculinidae: Entiminae: Naupactini	Brazil	opal?	7
Lamprocyphus augustus	Curculinidae: Entiminae: Naupactini	Brazil, Argentina	diamond	8
Pachyrrhynchus argus (Metapocyrtus sp.)	Curculinidae: Entiminae: Pachyrrhynchini	Queensland, Australia, Philippines	opal	9
Pachyrrhynchus congestus	Curculinidae: Entiminae: Pachyrrhynchini	Philippines	opal	10
Pachyrrhynchus gemmatus	Curculinidae: Entiminae: Pachyrrhynchini	Philippines	not studied (opal)	11
Pachyrrhynchus moniliferus	Curculinidae: Entiminae: Pachyrrhynchini	Philippines	diamond	6
Phyllobius maculicornis, P. glaucus	Curculinidae: Entiminae: Phyllobini	Europe	not studied	7,12
Polydrusus sericeus	Curculinidae: Entiminae: Polydrusini	USA	not studied; opal	13
Anoplophora graafi	Cerambycidae: Lamiinae: Lamiini	Borneo, Indonesia, Malaysia	random close packing	14
Anoplophora elegans	Cerambycidae: Lamiinae: Lamiini	Borneo, Indonesia, Malaysia	opal	6
Pseudomyagrus waterhousei	Cerambycidae: Lamiinae: Lamiini	Malaysia, Java, Sumatra, Borneo	opal	15
Glenea celia	Cerambycidae: Lamiinae: Saperdini	Borneo, Indonesia, Malaysia	opal	6
Phosphorus virescens	Cerambycidae: Lamiinae: Tragocephalini	Nigeria	amorphous opal	16
Prosopocera lactator	Cerambycidae: Lamiinae: Prosopocerini	Equatorial Africa	face centred cubic	17
Sphingnotus mirabilis	Cerambycidae: Lamiinae: Tmesisternini	Papua New Guinea	disordered sponge	14
Calothyrza margaritifera	Cerambycidae: Lamiinae: Phrynetini	India, Nepal, Myanmar, Thailand	disordered sponge	18
Sternotomis virescens	Cerambycidae: Lamiinae: Sternotomini	Equatorial Africa	not studied	11

Table S1. Details of the taxonomy and geographic distribution of extant beetles known to possess threedimensional biophotonic nanostructures in their scales.

specimen	# of scales assayed (# of scales with >= 3 peaks)	SAXS structural correlation peak $q_{pk} (nm^{-1})$	peak width ∆q (nm ⁻¹)	lattice parameter a (nm)	bandwidth (∆q / q _{pk})	coherence length ξ≈2π/∆q (μm)	n _{avg} (chitin filling fraction)
fossil	8 (8)	0.02174 ± 0.00029	0.00197 ± 0.00022	500.68 ± 6.59	0.091	3.22 ± 0.38	1.25 (0.44)
extant	12 (9)	0.02083 ± 0.00057	0.00268 ± 0.00049	521.63 ± 14.48	0.128	2.42 ± 0.45	1.37 (0.65)

Table S2. Summary of the structural and optical properties of the single diamond photonic crystal in the cuticular scales of fossil and extant *Hypera diversipunctata*. Lattice parameters calculated from the slope of the plot of the moduli of assigned *hkl* inidces of SAXS peaks versus the respective reciprocal distance S (see figure S2). Coherence length calculated from the full widths at half- maximum (FWHM) of pseudo-Voigt fits to the first-order SAXS peaks.

Supplementary references

- Wilts B.D., Michielsen K., De Raedt H., Stavenga D.G. 2011 Hemispherical Brillouin zone imaging of a diamond-type biological photonic crystal. *J. R. Soc. Interface* 9, 1609-1614. (DOI 10.1098/rsif.2011.0730.)
- Deparis O. & Vigneron J.P. 2010 Modeling the photonic response of biological nanostructures using the concept of stratified medium: the case of a natural threedimensional photonic crystal. *Mat. Sci. Eng. B* 169, 12-15. (DOI 10.1016/j.mseb.2009.12.002.)
- Wilts B.D., Michielsen K., Kuipers J., De Raedt H., Stavenga D.G. 2012 Brilliant camouflage: photonic crystals in the diamond weevil, *Entimus imperialis*. J. R. Soc. *Interface* 279, 2524-2530. (DOI 10.1098/rspb.2011.2651.)
- Jorgensen M.R. & Bartl M.H. 2011 Biotemplating routes to three-dimensional photonic crystals. *J. Mater. Chem.* 21, 10583-10591. (DOI 10.1039/C1JM11037C.)
- Pouya, C., Stavenga D.G., Vukusic P. 2011. Discovery of ordered and quasiordered photonic crystal structures in the scales of the beetle *Eupholus magnificus*. *Opt. Express* 19, 11355-11364. (DOI 10.1364/OE.19.011355.)
- Galusha J.W., Richey L.R., Jorgensen M.R., Gardner J.S., Bartl M.H. 2010 Study of natural photonic crystals in beetle scales and their conversion into inorganic structures via a solgel bio-templating route. *J. Mater. Chem.* 20, 1277-1284. (DOI 10.1039/B913217A.)

- 7. Onslow H. 1923 On a periodic structure in many insect scales, and the cause of their iridescent colours. *Phil. Trans. R. Soc. Lond. B*, **211**, 1-74.
- Galusha J.W., Richey L.R., Gardner J.S., Cha J.N., Bartl M.H. 2008 Discovery of a diamond-based photonic crystal structure in beetle scales. *Phys. Rev. E* 77, 050904. (DOI 10.1103/PhysRevE.77.050904.)
- Parker A.R., Welch V.L., Driver D., Martini N. 2003 Structural colour: opal analogue discovered in a weevil. *Nature* 426, 786-787. (DOI 10.1038/426786a.)
- 10. Welch V., Lousse V., Deparis O., Parker A., Vigneron J.P. 2007 Orange reflection from a three dimensional photonic crystal in the scales of the weevil *Pachyrrhynchus congestus* pavonius (Curculionidae). *Phys. Rev. E* 75, 041919. (DOI 10.1103/PhysRevE.75.041919.)
- Seago A.E., Brady P., Vigneron J.-P., Schultz T.D. 2009 Gold bugs and beyond: a review of iridescence and structural colour mechanisms in beetles (Coleoptera). *J. R. Soc. Interface* 6, S165-S184. (DOI 10.1098/rsif.2008.0354.focus.)
- Gorb S. 2011 Insect-inspired technologies: insects as a source for biomimetics. In Insect Biotechnology (ed. A. Vilcinskas) pp. 241-264. Dordrecht: Springer.
- 13. Ghiradella H. 1984 Structure of iridescent lepidopteran scales variations on several themes. *Ann. Entomol. Soc. Am.* **77**, 637-645.
- 14. Dong B.Q., Zhan T.R., Liu X.H., Jiang L.P., Liu F., Hu X.H., Zi J. 2011 Optical response of a disordered bicontinuous macroporous structure in the longhorn beetle *Sphingnotus mirabilis*. *Phys. Rev. E* 84, 011915. (DOI 10.1103/PhysRevE.84.011915.)

- 15. Simonis P & Vigneron J.P. 2011 Structural color produced by a three-dimensional photonic polycrystal in the scales of a longhorn beetles: *Pseudomyagrus waterhousei* (Coleoptera: Cerambycidae). *Phys. Rev. E.* 2011 **83**, 011908. (DOI 10.1103/PhysRevE.83.011908.)
- 16. Van Hooijdonk E., Barthou C., Vigneron J.P., Berthier S. 2013 Yellow structurally modified fluorescence in the longhorn beetles *Celosterna pollinosa sulfurea* and *Phosphorus virescens* (Cerambycidae). *J. Luminescence* **136**, 313-321. (DOI 10.1016/j.jlumin.2012.12.022.)
- 17. Colomer J.-F., Simonis P., Bay A., Cloetens P., Suhonen H., Rassart M.,
 Vandenbem C., Vigneron J.P. 2012 Photonic polycrystal in the greenish-white scales of the African longhorn beetle *Prosopocera lactator* (Cerambycidae). *Phys. Rev. E* 85, 011907. (DOI 10.1103/PhysRevE.85.011907.)
- Lafait, J., Andraud, C., Berthier, S., Boulenguez, J., Callet, P., Dumazetb, S., Rassart, M. and Vigneron, J.-P. 2010 Modeling the vivid white color of the beetle *Calothyrza margaritifera. Mat. Sci. Eng. B* 169, 16-22. (DOI 10.1016/j.mseb.2009.12.026.)