

Inorganic 3-D photonic crystals with bicontinuous gyroid structure replicated from butterfly wing scales

Christian Mille,^{a,b} Eric C. Tyrode^c and Robert W. Corkery^{*a,b}

Electronic Supporting Information

Content	Page
SAXS data collection and analysis	S2
Methods	S3
Fig. S1	S4
Fig. S2	S5
Fig. S3	S6
Fig. S4	S7
Fig. S5	S8
Fig. S6	S9
References	S10

SAXS data collection and analysis

Synchrotron SAX experiments were performed at the MAX Lab I711 line¹. A two-slit transmission set up was used for the optics, with a samples mounted in a low background adhesive captar tape sandwich. Diffraction patterns were obtained with a 2D detector having 2048 x 2048 pixels (each 7.886 x 7.886 μm). Sampling time was a total of 600 seconds using two exposures. The x-ray wavelength was 1.095 Å, and the sample to detector distance was 2.428 meters. Diffraction patterns were processed using masking (beam stop) and radial integration routines using fit2d software to obtain 1D, I(q) vs q plots. The integrated 1D q vs I(q) curve was fitted with a power law through the region of interest (q=0.04-0.12). This fitted curve was used as a background and subsequently subtracted from the integrated data to obtain the curve shown above. The unit cell was refined with a non-linear least squares method using “Unit Cell” software.²

Observed and fitted results:

h	k	l	d(obs)	d(calc)
2	2	0	120*	
3	2	1	90.6	90.6
4	0	0	84.8	84.8
4	2	0	75.8	75.8
3	3	2	72.3	72.3
4	4	0	59.9	59.9

*Not used in the refinement due to its proximity to the central beam.

Materials and methods

Specimens of the butterfly were provided by the Swedish Museum of Natural History. To characterize the internal structure of the butterfly, wing scales were mounted on a silicon wafer and cross section polished with an argon beam (JEOL IB09010CP) perpendicular to the sample, followed by FE-SEM (JEOL 7000F). A sol-gel biotemplating method similar to Bartl et al. was used.³ The silica precursor was prepared by prehydrolyzing 2 ml tetra-ethyl orthosilicate (Aldrich) in hydrochloric acid at pH 2 for 20 minutes followed by addition of F-127 ($[(EO)_{106}(PO)_{70}(EO)_{106}]$ BASF) dissolved in ethanol in a F-127/Si molar ratio of 0.03. The solution was stirred at room temperature for 3 days. The wing scales were washed in ethanol and clamped between two silicon wafers followed by injection of the silica solution. The organic material was removed by soaking in chromosulfuric acid for 1 hour followed by extensive washing in water. Sample preparation for FE-SEM was done by mounting the replicated scales on a carbon tape or, for cross section polishing, by immersing them in an epoxy resin. Optical reflectance data were collected using a modified Zeiss Axio Scope upright light microscope with a 100x Nikon objective (N.A. 0.9) coupled to an Andor Shamrock spectograph and Andor Newton CCD camera. The illuminated area was reduced down to $\sim 20 \mu\text{m}$ in diameter adjusting the field diaphragm located in the conjugated plane of the image to isolate ~ 4 -8 domains. The reflectance from a mirror was used to normalize the spectra. For the dichroic measurements linearly polarized light was directed to the sample and a circular polarizer was used as analyzer.

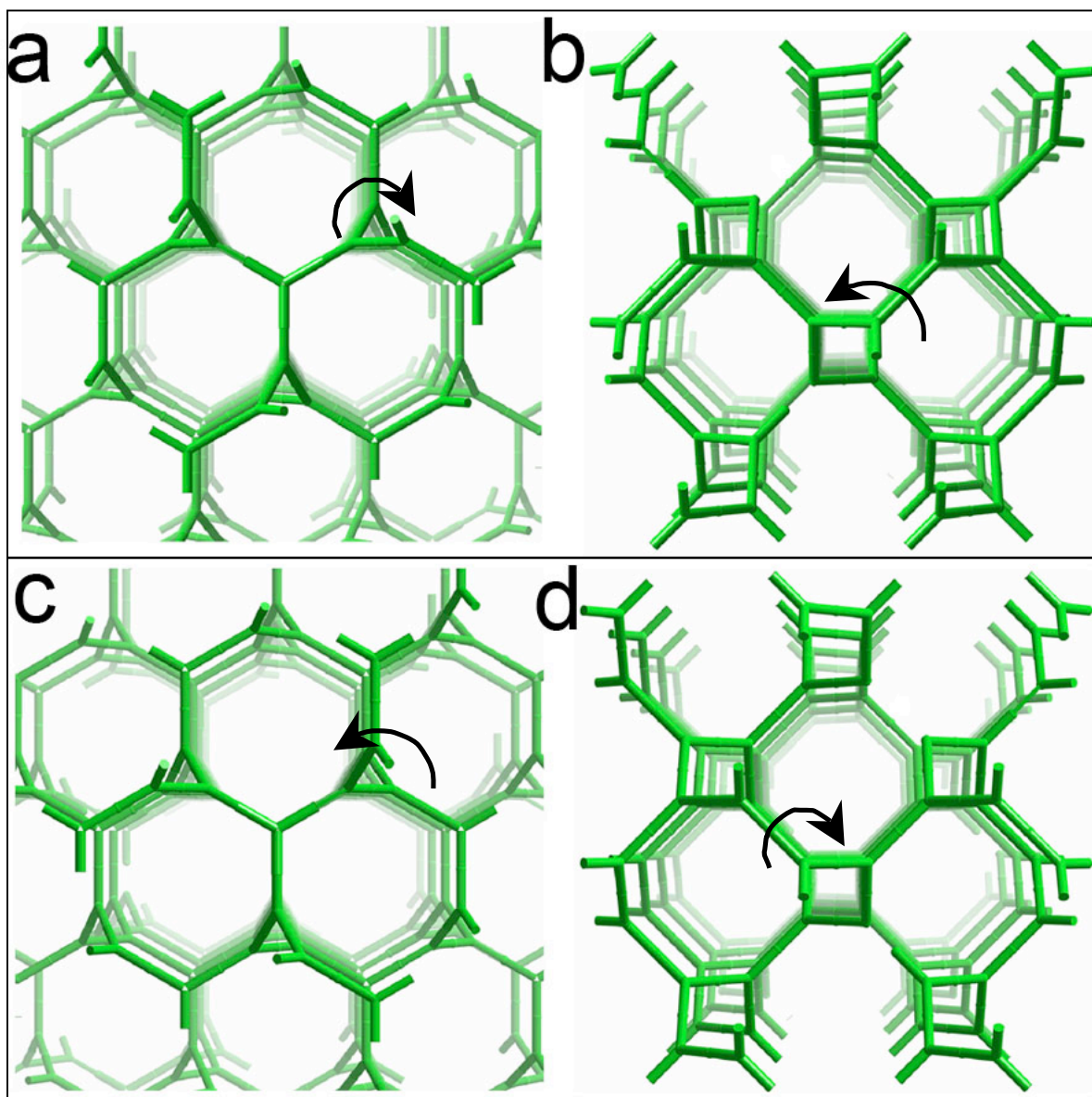


Figure S1. Different orientations of right handed (a-b) and left handed (c-d) **srs** nets. Each structure contains both left and right handed chiral elements in each net. The handedness of the entire net is named by convention according to the handedness of the chiral element oriented parallel to the $\langle 111 \rangle$ direction. (a-b) shows the right handed structure looking down the $\langle 111 \rangle$ axis (a) and the $\langle 100 \rangle$ axis (b). (c-d) shows the respective views for the left handed **srs** net. Thus each structure can give rise to both right and/or left handed optical activity, depending on the orientation of the crystallites to the optical axis. The chirality of the **srs** net and definitions of chiral space groups is discussed elsewhere^{4,5}.

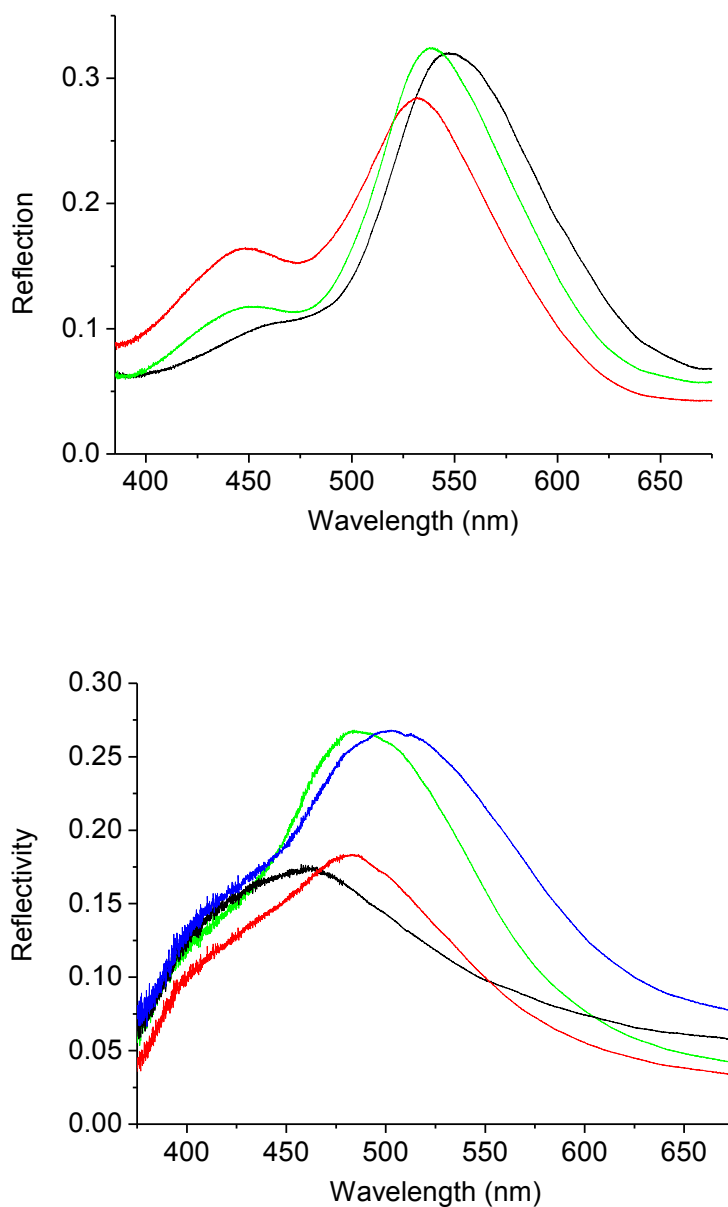


Figure S2. Representative reflectance spectra of (a) the butterfly and (b) the template, showing the variation in peak maxima depending on the position. Reflectance spectra collected with unpolarized light.

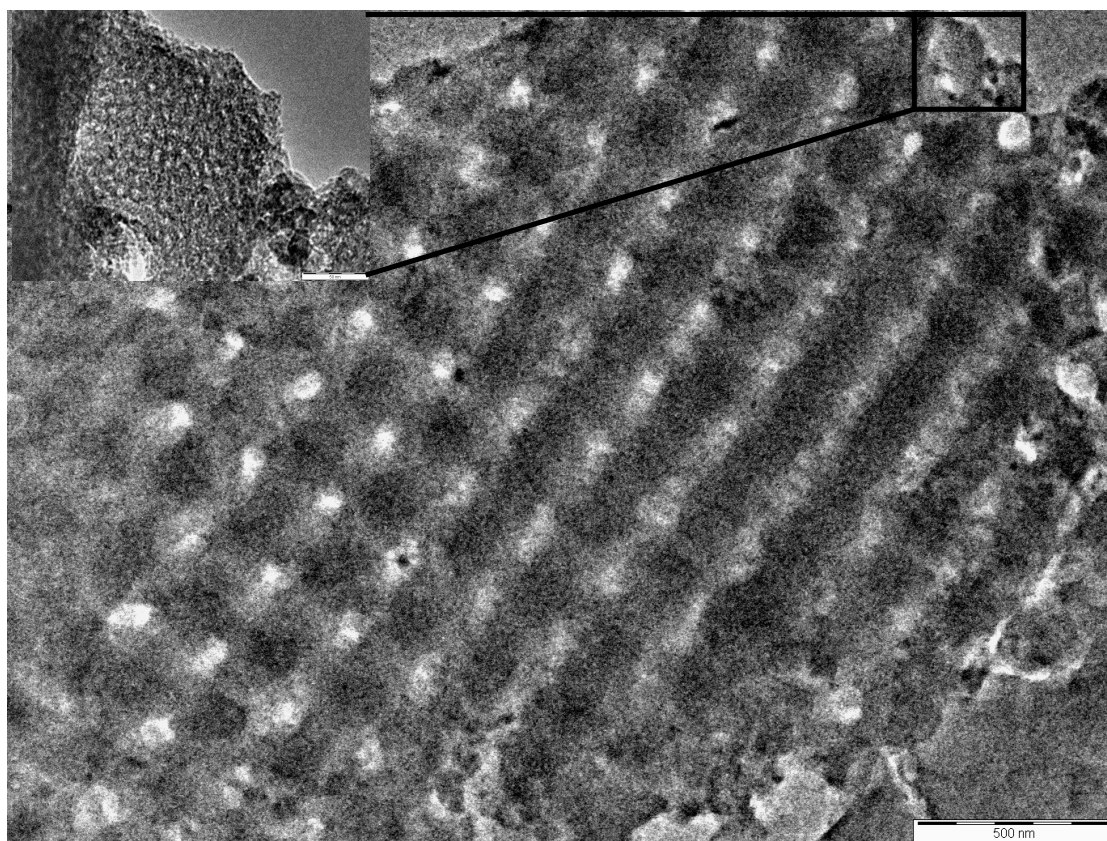


Figure S3. Transmission electron micrograph of a silica replica displaying the ordered macrostructure as well as the disordered mesostructure from the sol gel used to infiltrate the structure (insert). The porosity of the silica gives a refractive index of 1.23 ± 0.05^6 . Scale bar is $1 \mu\text{m}$ and 50 nm for the insert.



Figure S4. SEM of a cracked wing scale with the cubic structure visible. As seen here the replication of the internal structure occurs on a large scale. Not also the filling factor being higher than that of the butterfly (Fig. 2). Scale bar is 1 μm .

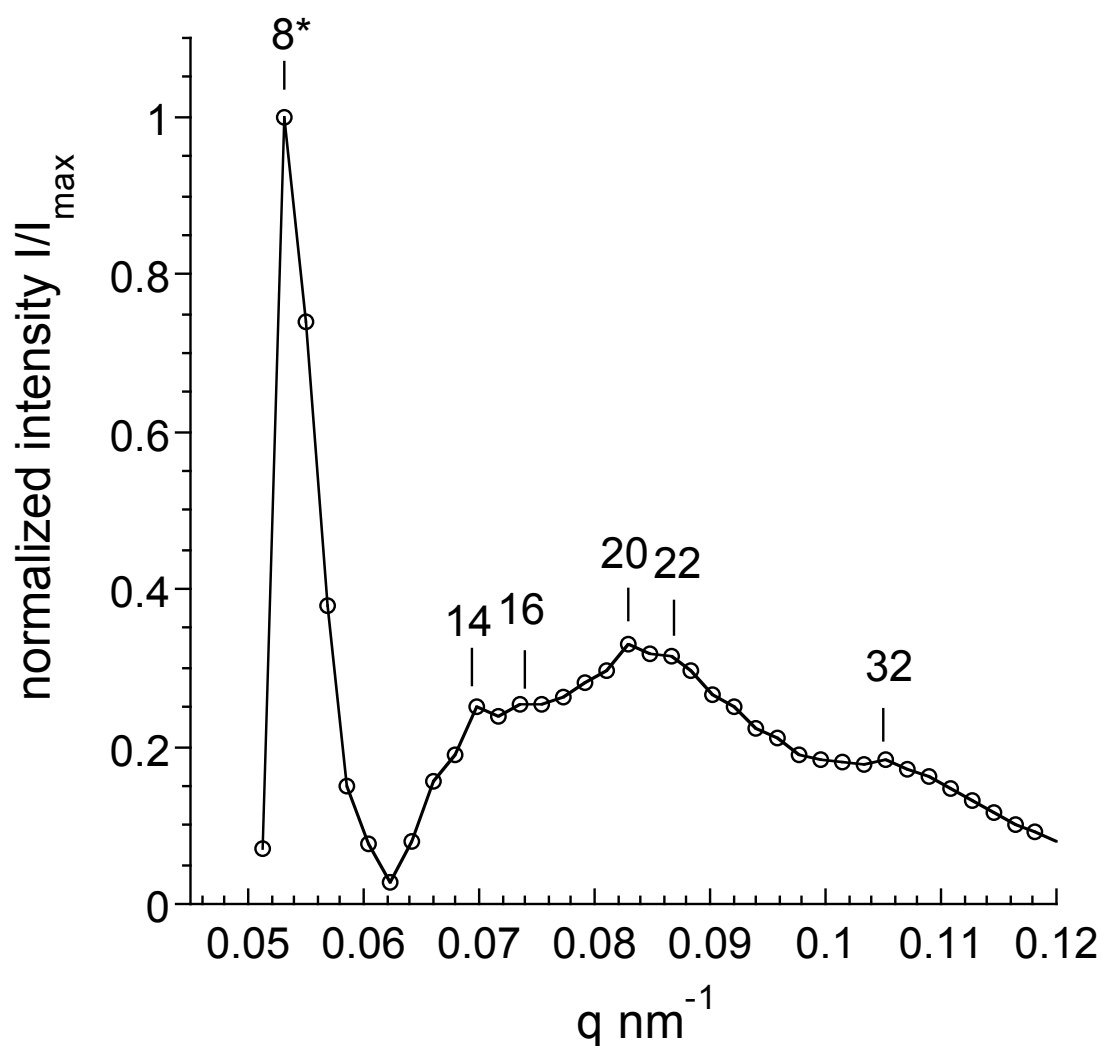


Figure S5. SAXS data from a piece of *C. rubi* wing oriented at right angles to the synchrotron beam. The indexing scheme here is in good agreement with the x-ray patterns of various Callophyrs species reported by Prum *et al*⁷. A refined unit cell of $a = 339 \pm 5$ nm was calculated here for *C. rubi*. This is in agreement with the unit cell calculated of FFT from SEM images (330 ± 10). The unit cell of the silica replica was 330 ± 15 nm as determined by FFT of SEM images.

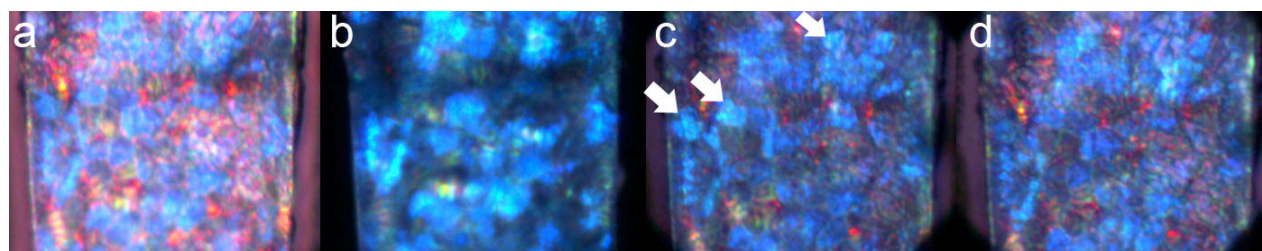


Figure S6. Silica replica imaged in unpolarized light (a), between cross linear polarizers (b), incident linearly polarized light with a left handed circular polarizer as analyzer (c) and incident linearly polarized light with a right handed circular polarizer (d). Note the difference between (c) and (d), how some domains (white arrows) light up more under one direction of the light. See also **Animation S1**.

References

1. Y. Cerenius, K. Stahl, L. A. Svensson, T. Ursby, Å. Oskarsson, J. Albertsson and A. Liljas, *Journal of synchrotron radiation*, 2000, **7**, 203-208.
2. T. J. B. Holland and S. A. T. Redfern, *Mineralogical Magazine*, 1997, **61**, 65.
3. J. W. Galusha, L. R. Richey, M. R. Jorgensen, J. S. Gardner and M. H. Bartl, *J. Mater. Chem.* , 2009, **20**, 1277-1284.
4. A. J. McCoy and R. J. Read, *Acta Crystallographica Section D: Biological Crystallography*, **66**, 458-469.
5. M. Saba, M. Thiel, M. D. Turner, S. T. Hyde, M. Gu, K. Grosse-Brauckmann, D. N. Neshev, K. Mecke and G. E. Schröder-Turk, *Physical Review Letters*, 2011, **106**, 103902.
6. D. Zhao, P. Yang, N. Melosh, J. Feng, B. F. Chmelka and G. D. Stucky, *Advanced Materials*, 1998, **10**, 1380-1385.
7. V. Saranathan, C. O. Osuji, S. G. J. Mochrie, H. Noh, S. Narayanan, A. Sandy, E. R. Dufresne and R. O. Prum, *Proc. Natl. Acad. Sci. U. S. A.* , 2010, **107**, 11676.