Supporting Information

Wolkenstein 10.1073/pnas.1417262112

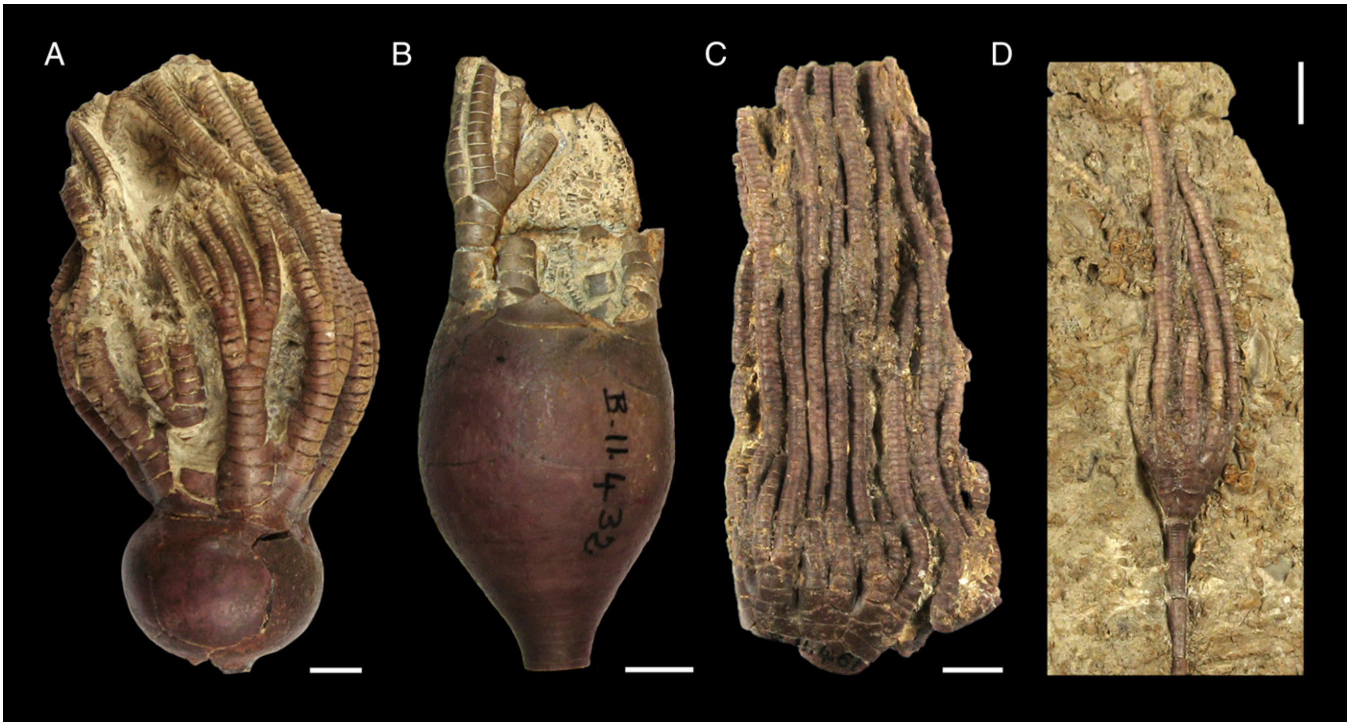

Fig. S1. Examples of millericrinids from the Lower Kimmeridgian of the La Rochelle area (western France) with distinct purple to violet coloration. (*A*) *Pomatocrinus magnificus* (lectotype, MNHN B11439). (*B*) *Apiocrinites roissyanus* (lectotype, MNHN B11432). (*C*) *Liliocrinus polydactylus* (syntype, MNHN B11461). (*D*) *Angulocrinus gracilis* (lectotype, MNHN B11447). (*A*) La Jarrie near La Rochelle; (*B–D*) Angoulins near La Rochelle. (Scale bar, 1 cm.) In addition to the shown species, purple to violet coloration was observed in the millericrinids *Guettardicrinus dilatatus* (syntype, MNHN A25646), *Pomatocrinus fleuriausianus* (holotype, MNHN B11453), *Pomatocrinus insignis* (lectotype, MNHN B11442), *Liliocrinus murchisonianus* (holotype, MNHN B11441), *Angulocrinus angulatus* (lectotype, MNHN B11459), *Angulocrinus brevis* (holotype, MNHN B11462), *Angulocrinus inaequalis* (paralectotype, MNHN A09212), *Angulocrinus orbignyi* (holotype, MNHN B11457), and *Angulocrinus simplex* (lectotype, MNHN B11444).

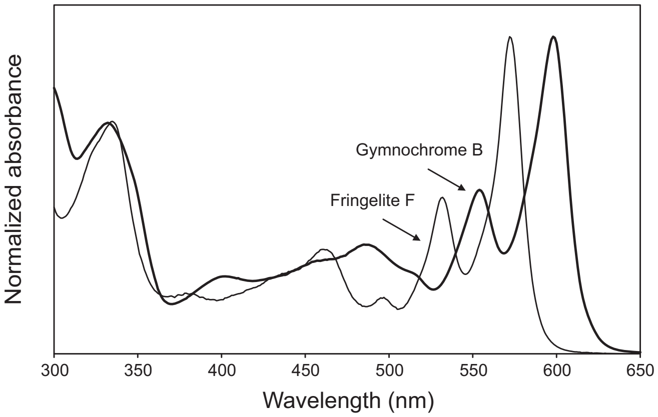

Fig. S2. UV-visible spectra of hypericinoid pigments from fossil and extant isocrinids (fringelite F from *Pentacrinites* and gymnochrome B from *Saracrinus*, Fig. 2).

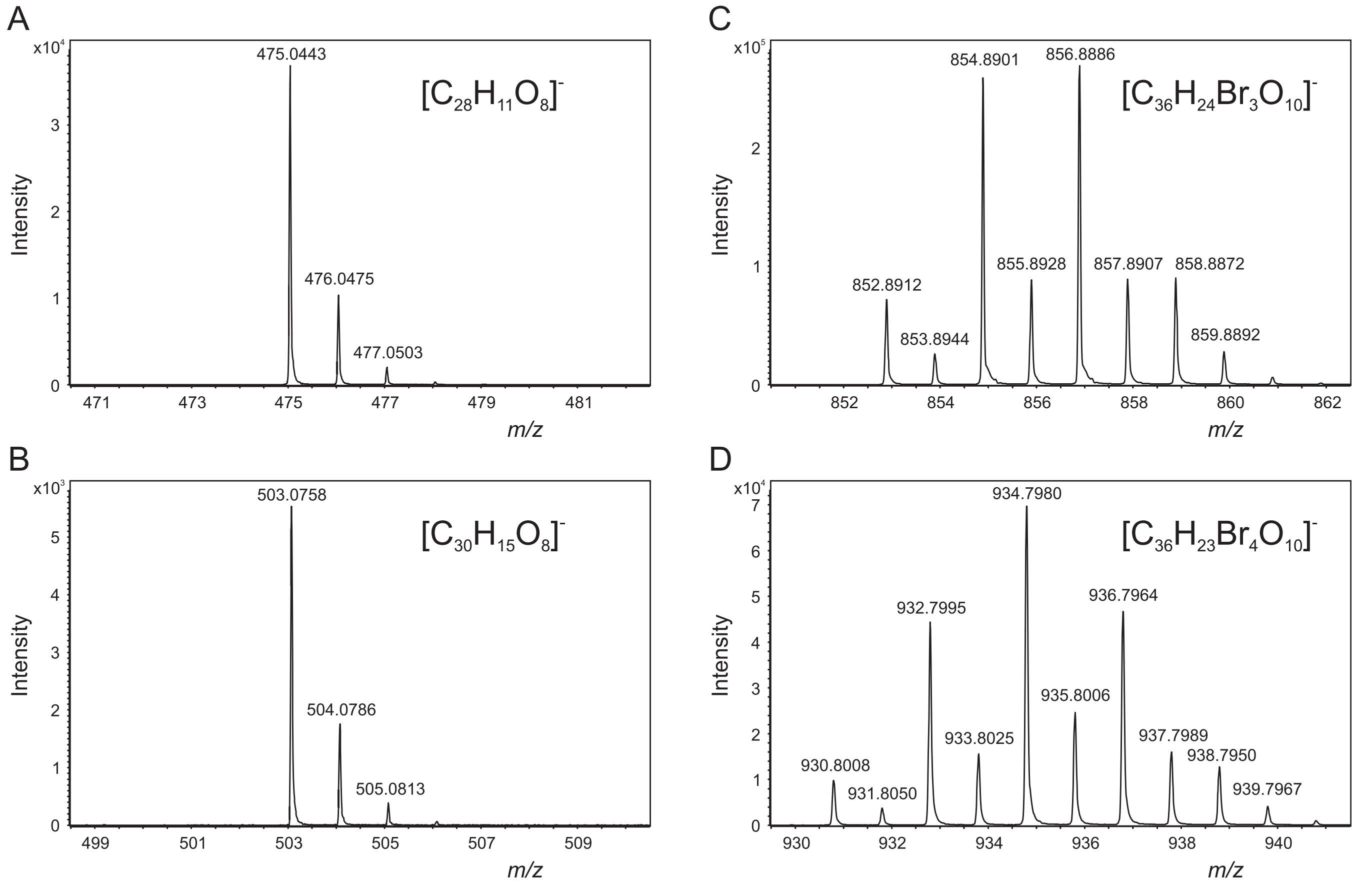

Fig. S3. Negative-ion electrospray ionization (ESI) mass spectra of hypericinoid pigments from fossil and extant isocrinids showing isotopic patterns that are characteristic for the number of bromine atoms in the molecules. (*A*) Fringelite F from *Pentacrinites* (Fig. 2*A*). (*B*) Hypericin from *Pentacrinites* (Fig. 2*A*). (*C*) Gymnochrome B from *Saracrinus* (Fig. 2*B*). (*D*) Gymnochrome A from *Saracrinus* (Fig. 2*B*).

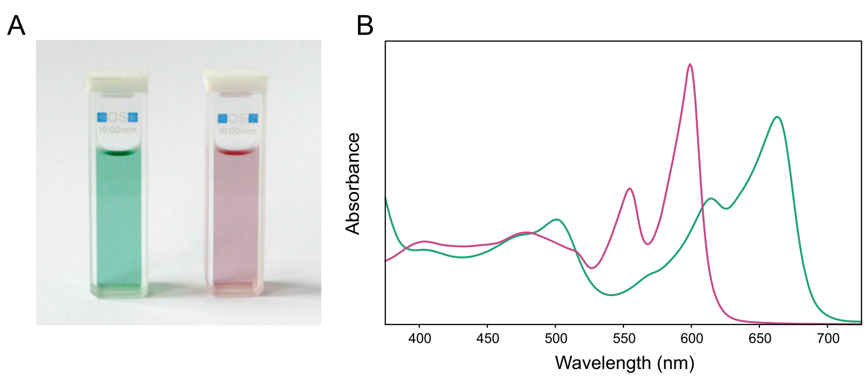

Fig. S4. pH-dependent absorption behavior of hypericinoid pigments (crude pigment isolate) of the extant isocrinid *Saracrinus*. (*A*) Pigments dissolved in ethanol (left cuvette) and pigments dissolved in ethanol containing 1% 1 M HCl (right cuvette). (*B*) UV-visible spectra of pigments dissolved in ethanol (green line) and pigments dissolved in ethanol containing 1% 1 M HCl (violet line).

Table S1. Hypericinoid pigment occurrence in colored fossil crinoids

Species	Description	Stratigraphy	Locality	Collection no.	Sediment (ref.)	Coloration of fossil	Sample amount, g	Hypericinoids*	Hypericinoid concentrations, ppm of fossil: Fringelite F	Hypericinoid concentrations, ppm of fossil: Hypericin
Millericrinida										
Millericrinid	Holdfast	Upper Jurassic, Lower Tithonian, Solnhofen/ Mörnsheim Formation	Langenaltheimer Haardt near Solnhofen, Bavaria, Germany	GZG. INV.79153	Gray limestone (hardground) (1)	Gray	2.1	8, 10	n.d.	<0.1
Millericrinid	Holdfast	Upper Jurassic, Upper Kimmeridgian–Lower Tithonian, Tendaguru Formation, *Indotrigonia africana* Member	Tendaguru, Tanzania	MB.E.6246	Sandstone succession (2)	Black	3.2	1, 2, 3, 4, 5, 6, 7, 8, 9, 10	7.4	4.7
Millericrinus lusitanicus	Stalk fragment	Upper Jurassic, Middle Kimmeridgian, Alcobaça Formation	Vestiaria, Portugal	BSPG 1984 XXII 363	Gray marl (3)	Gray	2.9	5, 8, 9, 10	0.2	<0.1
Liliocrinus polydactylus	Cup	Upper Jurassic, Lower Kimmeridgian	Angoulins, Charente-Maritime, France	SMNS 70207	Buff-colored marl, flank of coral-microbialite patch reef (4)	Violet	0.2	5, 7, 8, 9, 10	41.6	<0.9
Apiocrinites roissyanus	Stalk fragment	Upper Jurassic, Lower Kimmeridgian	Tonnerre, Yonne, France	MNHN A09153	White chalky limestone (5)	Violet	1.1	1, 3, 4, 5, 6, 7, 8, 9, 10	77.1	5.2
Millericrinid	Holdfast	Upper Jurassic, Upper Oxfordian–Lower Kimmeridgian, Korallenoolith	Hannover (Lindener Berg), Lower Saxony, Germany	NHMW 1858/ XVI/50	Light-brown bioclastic limestone	Violet	2.2	1, 3, 4, 5, 6, 7, 8, 9, 10	66.9	1.8
Liliocrinus munsterianus	Holdfast	Upper Jurassic, Oxfordian	L'Isle-sur-le-Doubs, Doubs, France	NHMW 1847/ 0051/0277a	Buff-colored oolite	Violet	1.2	1, 3, 4, 5, 6, 7, 8, 9, 10	129.5	4.3
Apiocrinites roissyanus	Cup	Upper Jurassic, Upper Oxfordian, Vellerat Formation	Boncourt (Queue au Loup), Canton Jura, Switzerland	MJSN QLP005-884	Buff-colored marl associated with oyster reef (6)	Violet	1.8	1, 3, 4, 5, 6, 7, 8, 9, 10	85.1	0.4
Angulocrinus echinatus	Stalk fragment	Upper Jurassic, Middle Oxfordian	Malton, Yorkshire, United Kingdom	NHMUK E5817	Light-brown oolitic limestone	Violet	1.0	1, 3, 4, 5, 6, 7, 8, 9, 10	38.6	0.2
Millericrinid	Holdfast	Upper Jurassic, Oxfordian	Villers-sur-Mer, Calvados, France	SMNS 70208	Gray micritic limestone	Black	1.1	3, 5, 6, 8, 10	<4.3	1,747.0
Apiocrinites negevensis	Partial cup	Middle Jurassic, Callovian, Matmor Formation	Hamakhtesh Hagadol, Israel	HUJ.PAL 100.32	Buff-colored marl between calcareous sponge and coral patch reefs (7)	Gray	2.7	5, 8, 9, 10	<0.2	<0.1
Apiocrinites parkinsoni	Holdfast	Middle Jurassic, Upper Bathonian, Forest Marble Formation	Bradford-on-Avon, Wiltshire, United Kingdom	NHMUK E5810	Hardground on top of a light-brown, cross-bedded bio-oosparite overlain by clay (8)	Violet	1.6	1, 3, 4, 5, 6, 7, 8, 9, 10	137.5	6.8
Ailsacrinus abbreviatus	Arm fragments	Middle Jurassic, Lower–Middle Bathonian, ?Sharps Hill Formation	Eastington, Gloucestershire, United Kingdom	NHMUK E67860	Sandy bio-oosparite (9)	Violet	1.1	5, 7, 8, 9, 10	0.5	<0.2

Table S1. Cont.

Species	Description	Stratigraphy	Locality	Collection no.	Sediment (ref.)	Coloration of fossil	Sample amount, g	Hypericinoids*	Hypericinoid concentrations, ppm of fossil: Fringelite F	Hypericinoid concentrations, ppm of fossil: Hypericin
Comatulida										
Solanocrinites sp.	Partial specimen	Upper Jurassic, Upper Kimmeridgian–Lower Tithonian, Tendaguru Formation	Tendaguru, Tanzania	NHMUK E25454	Light-brown sandstone (2)	Violet	0.2	5, 7, 8, 9, 10	113.6	<1.0
Solanocrinites beltremieuxi	Several specimens on slab	Upper Jurassic, Lower Kimmeridgian	Saint-Clément-des-Baleines, Île de Ré, Charente-Maritime, France	SMNS 67702	Buff-colored limestone	Violet	0.1	5, 8, 9, 10	28.2	9.5
Isocrinida										
Pentacrinites dargniesi	Crown fragment	Middle Jurassic, Upper Bathonian, Forest Marble Formation	Malmesbury, Wiltshire, United Kingdom	NHMUK E60	Crinoid lens, embedding sediment not documented	Violet	1.4	5, 7, 8, 9, 10	13.7	0.2
Hispidocrinus leuthardti	Crown fragment	Middle Jurassic, Lower Bathonian, Varians Beds	Liestal (Sichtern), Canton Basel-Landschaft, Switzerland	NMB M 11146	Crinoid lens within marlstone succession (10)	Violet	2.3	5, 7, 8, 9, 10	23.7	<0.1
Pentacrinites dargniesi	Crown fragment	Middle Jurassic, Upper Bajocian, Hauptrogenstein Formation	Develier, Canton Jura, Switzerland	NMB M 6093	Crinoid lens within oolitic succession (10)	Violet	3.0	5, 7, 8, 9	23.3	<0.1
Encrinida										
Chelocrinus schlotheimi	Stalk fragment	Middle Triassic, Upper Anisian, Trochitenkalk Formation, Gelbe Basisschichten	Willebadessen, North Rhine-Westphalia, Germany	SMNS 75557	Gray brown limestone	Violet	0.6	5, 8, 9, 10	3.7	0.4
Encrinus cf. *brahli*	Partial crown with proximal stalk	Middle Triassic, Lower Anisian, Jena Formation, Basiskonglomeratbänke	Weißenborn near Göttingen, Lower Saxony, Germany	SMNS 75556	Gray bioclastic, intraclast-bearing limestone (reworked hardground) (11)	Violet	0.1	5, 7	16.4	n.d.
Monobathrida										
Strimplecrinus inornatus	Crown fragment	Lower Carboniferous, Kinderhookian, Maynes Creek Formation	LeGrand, Iowa	FMNH PE 60748	Intraclastic crinoidal grainstone overlain by thin-bedded, dolomitic mudstone (12)	Gray–violet	2.6	n.d.	n.d.	n.d.
Order indet.										
Crinoidea	Stalk fragment	Silurian, Ludlovian	Burgen, Gotland, Sweden	SMNS, uncataloged specimen	Gray bioclastic limestone	Gray–violet	1.2	n.d.	n.d.	n.d.

n.d., not determined. Limits of detection (ESI-MS): fringelite F, 29 ppb; hypericin, 5 ppb.
*Molecular formulas of indicated compounds are listed in Table S3.

1. Wings O (2000) [A hardground as a new aspect in the interpretation of the Lower Tithonian Solnhofen Plattenkalk]. *Archaeopteryx* 18:75–92. German.
2. Bussert R, Heinrich W-D, Aberhan M (2009) The Tendaguru Formation (Late Jurassic to Early Cretaceous, southern Tanzania): Definition, palaeoenvironments, and sequence stratigraphy. *Fossil Record* 12(2):141–174.

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5. Loreau J-P, Tintant H (1968) [The limestone of Tonnerre and adjacent Upper Jurassic formations of Yonne: Stratigraphic and paleontologic observations]. *Bull Soc Géol Fr Sér 7* 10:341–357. French.
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7. Ausich WI, Wilson MA (2012) New Tethyan Apiocrinitidae (Crinoidea, Articulata) from the Jurassic of Israel. *J Paleontol* 86(6):1051–1055.
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10. Hess H (1999) Middle Jurassic of Northern Switzerland. *Fossil Crinoids*, eds Hess H, Ausich WI, Brett CE, Simms MJ (Cambridge Univ Press, Cambridge, UK), pp 203–215.
11. Bielert U, Bielert F (1995) [Encrinids from the Basiskonglomerat beds of the Lower Muschelkalk of Weißenborn (Lower Saxony)]. *Der Aufschluß* 46(1):23–31. German.
12. Gahn FJ, Baumiller TK (2004) A bootstrap analysis for comparative taphonomy applied to Early Mississippian (Kinderhookian) crinoids from the Wassonville Cycle of Iowa. *Palaios* 19(1):17–38.

Table S2. Hypericinoid pigment occurrence in colored extant crinoids

Species	Locality	Coordinates	Depth, m	Collection no.	Natural color of crinoid (ref.)	Hypericinoids*
Cyrtocrinida						
Cyathidium foresti	Southern Faial Channel, Azores	38°30′N, 28°40′W	500	MB.E 3333	Dark green (1)	8, 9, 12, 13, 15, 19
Hyocrinida						
Ptilocrinus amezianeae	Kerguelen Plateau	46°56.892′S, 70°25.422′E	544	MNHN-IE-2013-10376, MNHN-IE-2013-10377, MNHN-IE-2013-10378, MNHN-IE-2013-10379	Yellow-orange (2)	n.d.
Comatulida						
Porphyrocrinus cf. *verrucosus*	Osprey Reef, Australia	13°49.560′S, 46°32.520′E	498	LMU GW1168	Orange	n.d.
Isocrinida						
Proisocrinus ruberrimus	Aguni Knoll, central Okinawa Trough	27°00.71′N, 126°37.02′E	1,803–1,804	UMUT RE 29475	Red (3)	n.d.
Saracrinus nobilis	Western Pacific	31°24.33′N, 131°35.92′E to 31°24.18′N, 131°35.71′E	295–306	NUM-Az648a, NUM-Az648b, NUM-Az648c, NUM-Az648d	Dark green to almost black	2, 3, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 17, 19
Metacrinus levii	New Caledonia	22°45′S, 167°09′E	380–395	MNHN EcPs 74	Dark green	10, 13, 15
Metacrinus musorstomae	Bohol Sea, Philippines	9°39′N, 123°48′E	255–268	MNHN-IE-2007-5	Not documented	11, 13, 14, 15, 17, 19
Endoxocrinus (Diplocrinus) wyvillethomsoni	Bay of Biscay	48°41′N, 10°53′W	1,420–1,470	MNHN-IE-2012-836	Dark green	1, 2, 8, 9, 12, 15
Endoxocrinus (Diplocrinus) alternicirrus sibogae	New Caledonia	23°34′S, 169°36.8′E	700	MNHN EcPh 69	Not documented	n.d.
Hypalocrinus naresianus	Shima Spur, Kumano-nada Sea, Japan	33°59.6′N, 136°55.1′E to 33°58.9′N, 136°55.9′E	763–796	ZMB Ech 7415	Dark green	2, 3, 4, 5, 10, 11, 13, 14, 16, 17, 18, 19, 20

n.d., not determined.

*Molecular formulas of indicated compounds are listed in Table S4.

1. Wisshak M, Neumann C, Jakobsen J, Freiwald F (2009) The ‘living-fossil community’ of the cyrtocrinid *Cyathidium foresti* and the deep-sea oyster *Neopycnodonte zibrowii* (Azores Archipelago). *Palaeogeogr Palaeoclimatol Palaeoecol* 271(1–2):77–83.

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3. Oji T, Kitazawa K (2008) Discovery of two rare species of stalked crinoids from Okinawa Trough, southwestern Japan, and their systematic and biogeographic implications. *Zoolog Sci* 25(1):115–121.

Table S3. Accurate mass data of hypericinoid pigments from fossil crinoids (Fig. 2*A* and Table S1)

Peak (compound)	Molecular formula, [M–H]$^-$	*m/z* calculated	*m/z* observed
2	$C_{28}H_{11}O_6$	443.0561	443.0558
5 (fringelite F)	$C_{28}H_{11}O_8$	475.0459	475.0471
7, 9	$C_{29}H_{13}O_8$	489.0616	489.0619
1, 4	$C_{28}H_{11}O_9$	491.0409	491.0410
8 (hypericin)	$C_{30}H_{15}O_8$	503.0772	503.0772
10	$C_{31}H_{17}O_8$	517.0929	517.0929
3, 6	$C_{30}H_{15}O_9$	519.0722	519.0724

Mass data are from millericrinid, Upper Jurassic, Tanzania.

Table S4. Accurate mass data of hypericinoid pigments from extant crinoids (Fig. 2*B* and Table S2)

Peak (compound)	Molecular formula, $[M–H]^-$	*m/z* calculated, monoisotopic	*m/z* observed, monoisotopic
7	$C_{36}H_{25}Br_2O_{10}$	774.9820	774.9806 (S)
8	$C_{38}H_{29}Br_2O_{10}$	803.0133	803.0111 (S)
6	$C_{34}H_{20}Br_3O_{10}$	824.8612	824.8593 (S)
9, 11 (gymnochrome B)	$C_{36}H_{24}Br_3O_{10}$	852.8925	852.8912 (S)
12	$C_{38}H_{28}Br_3O_{10}$	880.9238	880.9241 (E)
10	$C_{34}H_{19}Br_4O_{10}$	902.7717	902.7696 (S)
13, 14 (gymnochrome A)	$C_{36}H_{23}Br_4O_{10}$	930.8030	930.8014 (H)
16	$C_{36}H_{21}Br_4O_{11}$	944.7823	944.7809 (H)
15, 17, 19	$C_{38}H_{27}Br_4O_{10}$	958.8343	958.8323 (S)
18	$C_{38}H_{25}Br_4O_{11}$	972.8136	972.8118 (H)
20	$C_{40}H_{29}Br_4O_{11}$	1000.8449	1000.8425 (H)
1	$C_{36}H_{23}Br_4O_{13}S$	1010.7598	1010.7608 (E)
2, 3	$C_{38}H_{27}Br_4O_{13}S$	1038.7911	1038.7899 (E)
4	$C_{38}H_{25}Br_4O_{14}S$	1052.7704	1052.7670 (H)
5	$C_{40}H_{29}Br_4O_{14}S$	1080.8017	1080.7946 (H)

Mass data are from the following: E, *Endoxocrinus*; H, *Hypalocrinus*; S, *Saracrinus*.