Electronic supplementary information

S1. Instrumental techniques

UV-vis absorption spectra were measured using a JASCO V-570 spectrometer. CD measurements were performed using a JASCO J-725 spectrodichrometer or a JASCO E-250 magnetooptical meter. MCD measurements were performed using the JASCO E-250 magnetooptical meter equipped with a JASCO electromagnet (+1.35 to –1.35 T). For the MChD measurements, monochromatic light emitted from a Xe lamp (JASCO PS-X150B) equipped with a monochromator (JASCO CT-25E) and a mechanical chopper was detected using a photomultiplier (Hamamatsu Photonics R928) as it travelled through a sample in the JASCO electromagnet (+1.35 or –1.35 T). The photomultiplier signals obtained through a lock-in amplifier (Stanford Research SR830) were recorded point-by-point at 1 nm in the J-band regions (700–760 nm). To evaluate only the effects of reversing the externally applied magnetic field (**H**), we measured the absorbance in directions parallel to **H**, followed by the absorbance in directions antiparallel to **H**. We then measured the antiparallel absorbance, followed by the parallel absorbance. Repeating this procedure 20 times, data was accumulated, and thus, the averaged MChD spectrum was evaluated from the difference between the parallel and antiparallel absorption spectra.

S2. Analytical data

Zinc 3-devinyl-3-methoxymethylpyropheophorbide-*a* tetraethylene glycol monoester (ZnChl)

ZnChl was prepared with reference to the reported procedure.[14] UV-vis, ^{1}H-NMR, HRMS (FAB) and elemental analysis were satisfactory. UV-vis (CH_2Cl_2) λ_{max} = 651 (0.70), 606 (0.18), 516 (0.13), 425 (1.00), 307 (0.37). ^{1}H-NMR ($CDCl_3$) δ = 9.52, 9.23, 8.34 (each 1H, s, 5-, 10-, 20-H), 5.61 (2H, s, 3-CH_2), 5.21, 5.08 (each 1H, d, *J*=20 Hz, 13^2-H_2), 4.45 (1H, dq, *J*=2, 7 Hz, 18-H), 4.27 (1H, dt, *J*=8, 2 Hz, 17-H), 4.10 (2H, m, $COOCH_2$), 3.90 (2H, q, *J*=7 Hz, 8-CH_2), 3.70, 3.69, 3.33, 3.26 (each 3H, s, 3^1-OCH_3, 2-, 7-, 12-CH_3), 3.17-3.45 (12H, m, $COOCH_2C\underline{H}_2O(C\underline{H}_2C\underline{H}_2O)_2C\underline{H}_2CH_2OH$), 2.40-2.61, 2.20-2.45 (each 2H, m, 17-CH_2CH_2), 1.80 (3H, d, *J*=8 Hz, 18-CH_3), 1.71 (3H, t, *J*=7 Hz, 8^1-CH_3). HRMS (FAB) m/z (M^+) calcd for $C_{41}H_{50}N_4O_8Zn$: 790.2920; found: 790.2974. Elemental analysis calcd. for $C_{41}H_{50}N_4O_8Zn\cdot H_2O$: C, 60.77; H, 6.47; N, 6.91; found: C, 61.07; H, 6.29; N, 6.67.

S3. Preparation of the ZnChl monomer and the chiral J-aggregates of ZnChls

The aqueous solutions of ZnChl were prepared by diluting the methanol solution of ZnChl (2000 μM) with a 99-fold volume of water. The form (monomer or J-aggregates) was controlled by changing the concentration of Triton X-100 (1500 μM and 180 μM for the monomer and J-aggregates, respectively). The obtained J-aggregates of ZnChls mimicked a supramolecular LH system in a chlorosome from the viewpoints of both the sharp J-band indicating the formation of highly ordered J-aggregates and the intense, inverse-S shaped CD signal (Figure 2A, C).[14]

S4. UV-vis, MCD, and CD spectra of the ZnChl monomer and the chiral J-aggregates of ZnChls in the B and Q band regions

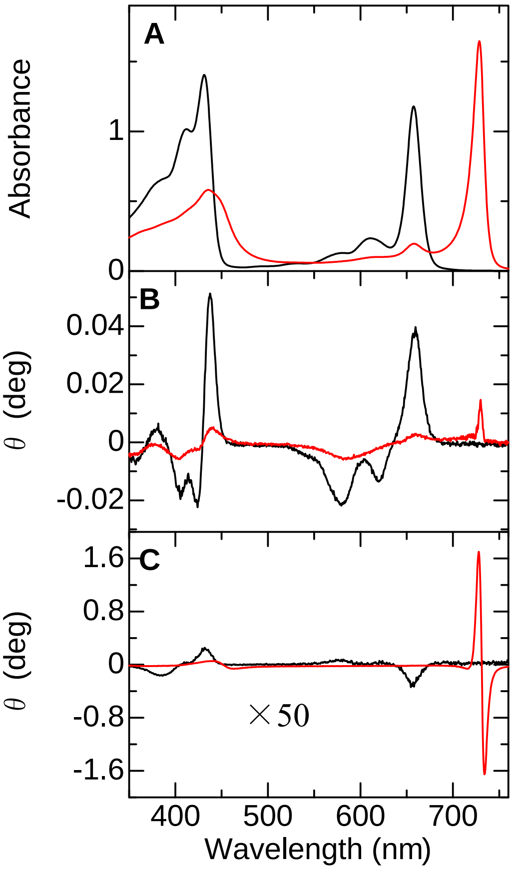

Figure S1. UV-vis (A), MCD (B), and CD (C) spectra of the chiral J-aggregates of ZnChls (red line) and the ZnChl monomer (black line).

S5. Electronic properties of the ZnChl monomer

First, the optimum structure of the ZnChl monomer was calculated by the DFT method (B3LYP/6-31G* Gaussian 03). Herein, we employed the structure of a ZnChl derivative having an ethyl group at position 17. The optimum structure of the ZnChl monomer shows the planar structure (Figure S2). Molecular orbitals (MOs) and an MO energy diagram are shown in Figure S3. An electronic absorption spectrum was calculated for the optimum structure of the ZnChl derivative using the TD-DFT (B3LYP/6-31G* Gaussian 03) method. The spectral characteristics, such as intense B and Q_y bands and a weak Q_x band (Figure S4A), were well-reproduced by these calculations (Figure S4B), whereas the excitation energies were overestimated. These spectroscopic properties of the B and Q absorption bands are reasonably explained by the Gouterman's four orbital model.[17] In this model, HOMO-1, HOMO, LUMO, and LUMO+1 are considered, which are called b_1, b_2, c_2, and c_1, respectively, according to the Gouterman's notation. Thus, four configurations, ((b_1c_2), (b_2c_2), (b_1c_1), and (b_2c_1)) are considered. Since the energy difference between the (b_2c_2) and (b_1c_1) configurations is relatively large, the Q_y and B_y transitions mainly originate from the (b_2c_2) and (b_1c_1) configurations, respectively. On the other hand, because of the small energy difference between the (b_1c_2) and (b_2c_1) configurations, the (b_1c_2) configuration is heavily admixed with the (b_2c_1) configuration, which results in both the intense B_x band and weak Q_x band (Table S1).

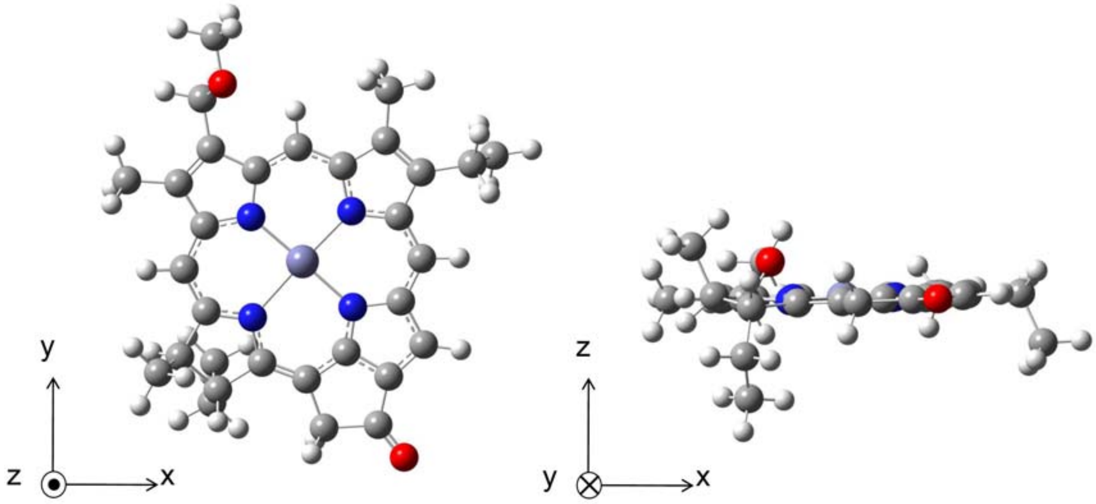

Figure S2. Optimum structures of the ZnChl monomer. In the coordinate system, the point and the cross denote the tip of an arrow and the tail of an arrow, respectively.

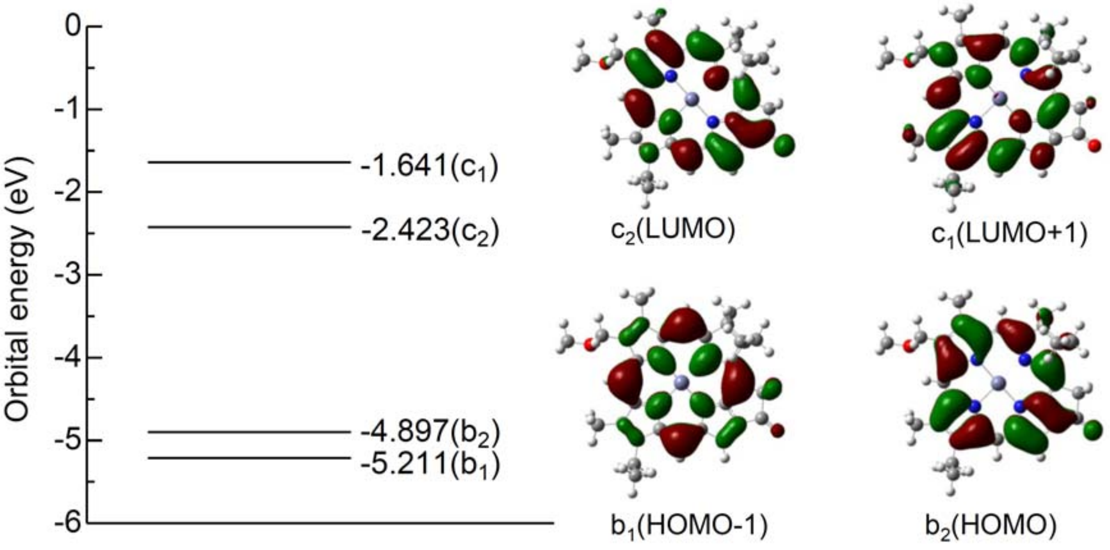

Figure S3. MOs and an MO energy diagram for the ZnChl monomer.

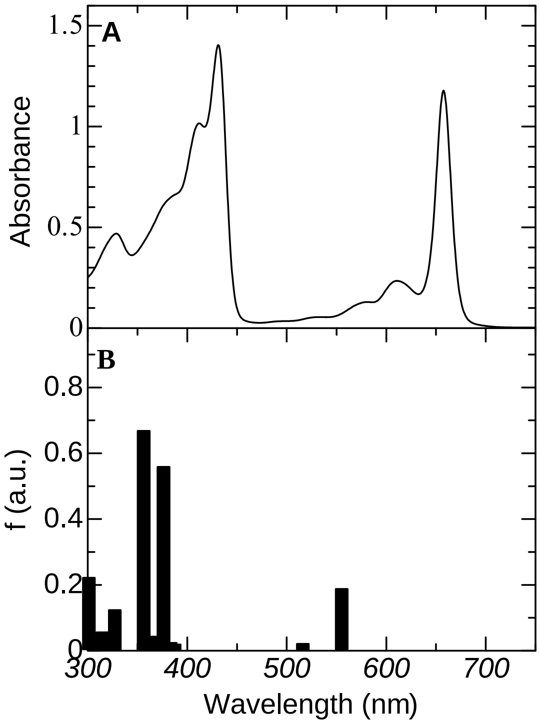

Figure S4. UV-vis (A) and calculated (B) spectra of the ZnChl monomer.

Table S1. Information about the main electronic configurations in the Q_y, Q_x, B_y, and B_x bands.

	λ/nm	f	main contribution
Q_y	556	0.188	70%(b_2c_2), 20%(b_1c_1)
Q_x	517	0.021	64%(b_1c_2), 33%(b_2c_1)
B_x	377	0.559	13%(b_1c_2), 43%(b_2c_1)
B_y	357	0.668	5%(b_2c_2), 51%(b_1c_1)

S6. Relative configuration between ZnChl constituents in the J-aggregates

In order to obtain information about the configurations between the ZnChl constituents, DFT (B3LYP/6-31G* Gaussian 03) calculations were carried out for the ZnChl dimer. In the optimum structure (Figure S5), the 3^1-methoxy group of one ZnChl coordinates to the Zn ion of another ZnChl. In addition, the transition dipole moments of the Q_y band are almost parallel to the long axis of the dimer, which is consistent with the observed J-band.

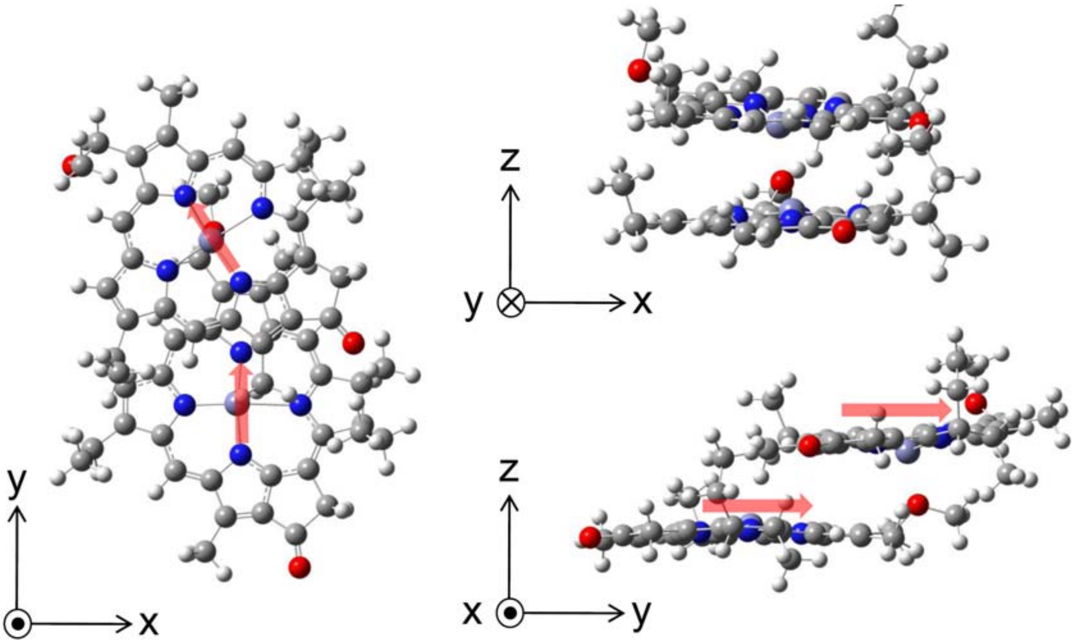

Figure S5. Optimum structures of the ZnChl dimer. The red arrows indicate the transition dipole moments of the ZnChl constituents at the Q_y band. In the coordinate system, the point and the cross denote the tip of an arrow and the tail of an arrow, respectively.