Structures were determined by direct methods and refined on $F^2$. Crystal data for **4**: $C_{11}H_{10}Mn_{1.5}O_6S$, $fw = 352.66$, monoclinic, space group $P2_1/c$, $a = 8.3033(5)$, $b = 12.4987(8)$, $c = 12.9551(8)$ Å, $\beta = 90.228(1)^\circ$, $V = 1344.48(14)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.742\ g\,cm^{-3}$, $\mu = 1.604\ mm^{-1}$, $F(000) = 710$, $\theta$ range 2.26–26.39°, 180 variables refined with 2757 independent reflections to final $R$ indices $[I > 2\sigma(I)]$ of $R_1 = 0.0512$ and $wR_2 = 0.1330$, and $GOF = 1.137$. Crystal data for **5**: $C_{11}H_{10}MnCd_{0.5}O_6S$, $fw = 381.39$, monoclinic, space group $P2_1/c$, $a = 8.4067(9)$, $b = 12.4128(13)$, $c = 12.9325(14)$ Å, $\beta = 90.089(2)^\circ$, $V = 1349.5(2)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.877\ g\,cm^{-3}$, $\mu = 1.918\ mm^{-1}$, $F(000) = 756$, $\theta$ range 2.27–25.09°, 219 variables refined with 2383 independent reflections to final $R$ indices $[I > 2\sigma(I)]$ of $R_1 = 0.0685$ and $wR_2 = 0.1559$, and $GOF = 1.149$. Crystal data for **6**: $C_{36}H_{16}Mn_4Zn_2O_{20}$, $fw = 1118.99$, tetragonal, space group $P4_3$, $a = 15.4449(13)$, $c = 15.664(2)$ Å, $V = 3736.4(7)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.989\ g\,cm^{-3}$, $\mu = 2.663\ mm^{-1}$, $F(000) = 2208$, $\theta$ range 1.85–26.42°, 559 variables refined with 7684 independent reflections to final $R$ indices $[I > 2\sigma(I)]$ of $R_1 = 0.0680$ and $wR_2 = 0.1560$, and $GOF = 1.154$. Crystal data for **7**: $C_{16}H_{14}Mn_{1.5}NO_6S$, $fw = 430.75$, monoclinic, space group $P2_1/c$, $a = 11.7056(10)$, $b = 12.3216(10)$, $c = 12.7812(10)$ Å, $\beta = 98.154(2)^\circ$, $V = 1824.8(3)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.568\ g\,cm^{-3}$, $\mu = 1.199\ mm^{-1}$, $F(000) = 874$, $\theta$ range 1.76–26.47°, 253 variables refined with 3757 independent reflections to final $R$ indices $[I > 2\sigma(I)]$ of $R_1 = 0.0567$ and $wR_2 = 0.1161$, and $GOF = 1.304$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-161517 (**4**), CCDC-161518 (**5**), CCDC-161519 (**6**), and CCDC-161520 (**7**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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# A Large Dendritic Multiporphyrin Array as a Mimic of the Bacterial Light-Harvesting Antenna Complex: Molecular Design of an Efficient Energy Funnel for Visible Photons**

Myung-Seok Choi, Takuzo Aida,* Tomoko Yamazaki, and Iwao Yamazaki

Photosynthesis is triggered by the absorption of a photon by the light-harvesting antenna system, which has a large absorption cross-section. This process is followed by a rapid and efficient transfer of the excitation energy to the reaction center, where conversion of solar energy into chemical potentials in the form of a charge-separated state takes place.[1, 2] To mimic the natural photosynthetic systems, artificial light-harvesting antennae consisting of many porphyrin units linked through covalent[3] and noncovalent[4] bonds have been synthesized which can provide a large absorption cross-section to capture dilute photons. However, utilization of the light energy requires further molecular design to realize a long-range vectorial transfer of the excitation energy to a designated point. An efficient cooperation of chromophore units is essential if this is to be achieved. Such a molecular design could be inspired by the successful crystal-structure analysis of the light-harvesting antenna complex (LH2) from purple photosynthetic bacterium *Rhodopseudomonas acidophila* strain 10050, where highly efficient light-driven energy migration and transfer are realized by the wheel-like arrays of a large number of bacteriochlorophyll *a* (Bchl *a*) units.[5]

Recently, dendritic architectures have attracted attention as potential scaffolds for the incorporation of many light-absorbing units to enable the efficient capturing of photons.[6] Herein we report on a designed large multiporphyrin array $(7P_{Zn})_4P_{FB}$[7] consisting of four dendritic wedges of a zinc porphyrin heptamer ($7P_{Zn}$) as the energy-donating units which are anchored by a focal free-base porphyrin unit ($P_{FB}$) which functions as the energy acceptor. This star-shaped dendritic macromolecule is intended to mimic the unique morphology of the wheel-like chromophore array in LH2, and is expected to operate as an efficient energy funnel for visible

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[+] Time-resolved spectroscopy

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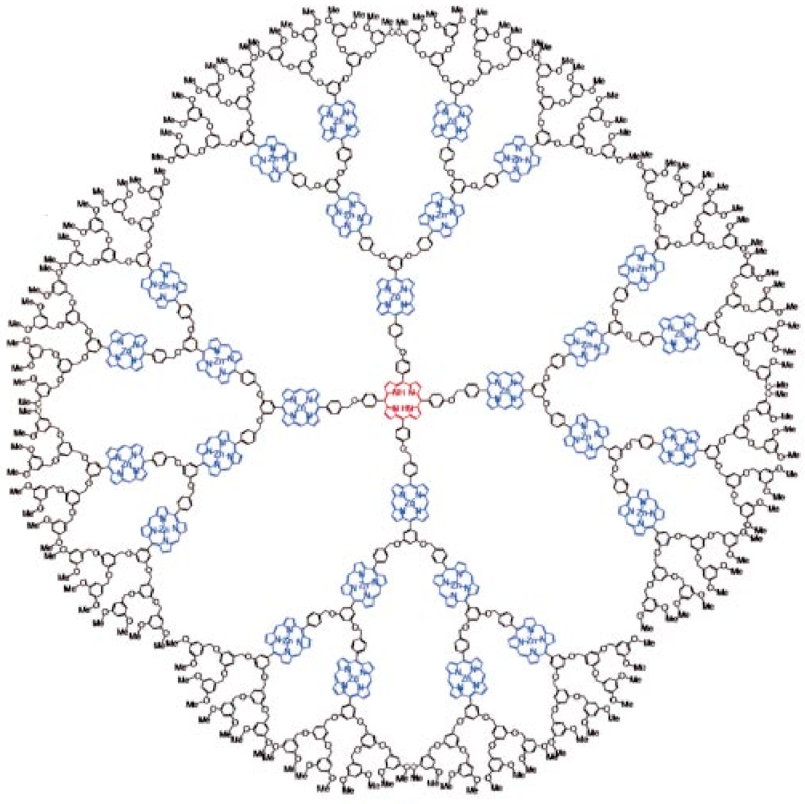
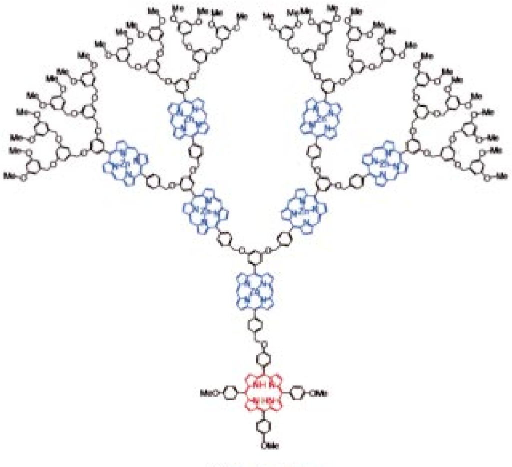


$(7P_{Zn})_4P_{FB}$



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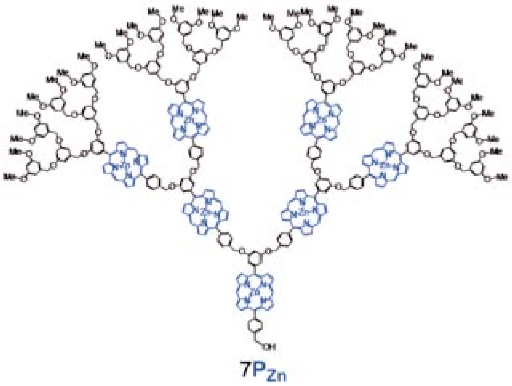
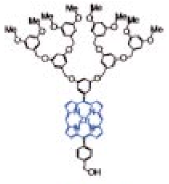
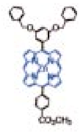


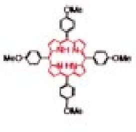
$7P_{Zn}$



$P_{Zn}^{EXT}$



$P_{Zn}^{INT}$



$P_{FB}^{CORE}$

**Monomeric References**

photons in an analogous fashion to the natural antennae. Although the importance of π-electronic conjugation between chromophore units for facilitating energy transfer has been suggested,[8] our light-harvesting molecule $(7P_{Zn})_4P_{FB}$, in contrast, is devoid of any π-electronic bridges, while the chromophore units are simply suspended by the dendritic scaffold through flexible ether linkers. A point to be highlighted here is how the cooperativeness of the chromophore units in energy migration and transfer is affected by the morphology of the multiporphyrin array.[9] Thus, conically shaped $(7P_{Zn})_1P_{FB}$ with only a single dendritic wedge of the zinc porphyrin heptamer ($7P_{Zn}$) was synthesized as a morphological reference for star-shaped $(7P_{Zn})_4P_{FB}$.[7] The presence of poly(benzyl ether) dendritic wedges[10] at the periphery makes both of these multiporphyrin arrays highly soluble in common organic solvents such as $CH_2Cl_2$, $CHCl_3$, and THF.

A solution of $(7P_{Zn})_4P_{FB}$ in THF at 25 °C showed an intense Soret absorption band at 415.8 nm ($\varepsilon = 5\,130\,000\ \mathrm{L\,cm^{-1}\,mol^{-1}}$).[7] This band was red-shifted by 1.3 nm with a slight broadening (FWHM = 19200 $\mathrm{cm^{-1}}$) relative to a noncovalent reference prepared by simply mixing three monomeric porphyrins $P_{Zn}^{EXT}$, $P_{Zn}^{INT}$, and $P_{FB}^{CORE}$ at a molar ratio of 16:12:1 ($\lambda_{Soret} =$ 414.5 nm, FWHM = 12600 $\mathrm{cm^{-1}}$). The Q-bands, however, showed neither substantial shift nor broadening, which indicates there is a weak ground-state interaction between the $P_{zn}$ units in the dendritic array.[11]

When a solution of the noncovalent reference mixture $P_{Zn}^{EXT}$, $P_{Zn}^{INT}$, and $P_{FB}^{CORE}$ (16:12:1) in THF was excited at 544 nm, only a fluorescence from the $P_{Zn}$ units ($Q(0,0) = 589$, $Q(0,1) = 637$ nm) was detected (Figure 1 A, broken line). In contrast, excitation of star-shaped $(7P_{Zn})_4P_{FB}$ under identical conditions to the above resulted in the detection of an emission predominantly from the focal $P_{FB}$ unit ($Q_X(0,0) = 658$, $Q_X(0,1) = 723$ nm), with only a weak emission from the $P_{Zn}$ units (Figure 1 A, solid line). This result suggests there is an efficient transfer of energy from the excited singlet states of the dendritic $P_{Zn}$ units to the focal $P_{FB}$ unit. Accordingly, the excitation spectrum of $(7P_{Zn})_4P_{FB}$ monitored at 725 nm (fluorescence from $P_{FB}$) displayed substantial absorption characteristics of the 28 $P_{Zn}$ units.

Although the absorption spectrum of conically shaped $(7P_{Zn})_1P_{FB}$ in THF at 25 °C was quite similar to that of star-shaped $(7P_{Zn})_4P_{FB}$ ($\lambda_{Soret} =$ 416.6 nm, $\varepsilon = 2\,290\,000\ \mathrm{L\,cm^{-1}\,mol^{-1}}$),[7] the luminescence profile was much different: Excitation of $(7P_{Zn})_1P_{FB}$ at 544 nm resulted in an emission spectrum (Figure 1 B, solid line) in which the fluorescence intensity from the focal $P_{FB}$ unit,

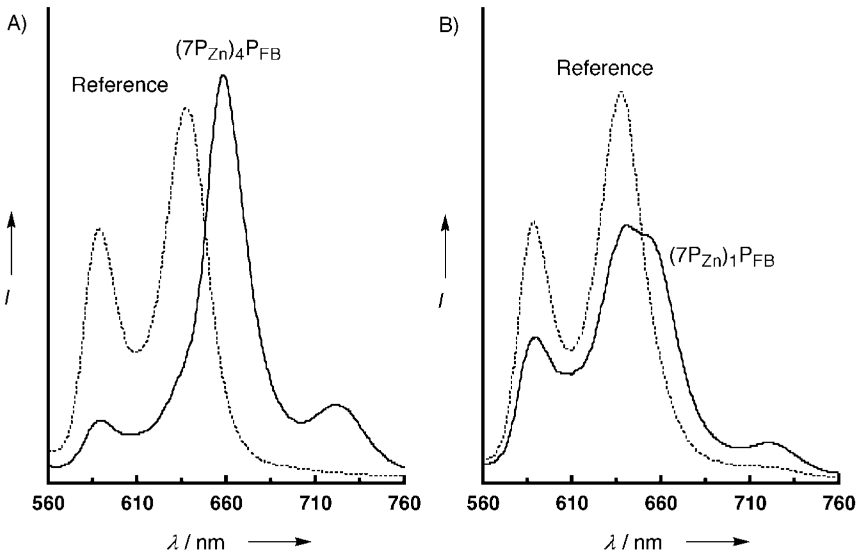


Figure 1. Steady-state fluorescence spectra upon excitation of a solution of star-shaped $(7P_{Zn})_4P_{FB}$ (A; solid line) and conically shaped $(7P_{Zn})_1P_{FB}$ (B; solid line) in THF (25 °C) at 544 nm together with those of their noncovalent references (broken lines) consisting of $P_{Zn}^{EXT}$, $P_{Zn}^{INT}$, and $P_{FB}$ at molar ratios of 16:12:1 and 4:3:1, respectively. All the spectra were normalized to a constant absorbance ($A = 0.03$) at the excitation wavelength.

relative to that from the dendritic $P_{Zn}$ units, was much less pronounced than in the case of $(7P_{Zn})_4P_{FB}$. On the other hand, a noncovalent reference of $P_{Zn}^{EXT}$:$P_{Zn}^{INT}$:$P_{FB}^{CORE}$ (4:3:1) again showed, under identical conditions to the above, a fluorescence predominantly from the zinc porphyrin components, with only a little contribution from the free-base porphyrin (Figure 1 B, broken line). These observations suggest a much less efficient $P_{Zn} \rightarrow P_{FB}$ energy transfer in conically shaped $(7P_{Zn})_1P_{FB}$ than in star-shaped $(7P_{Zn})_4P_{FB}$.

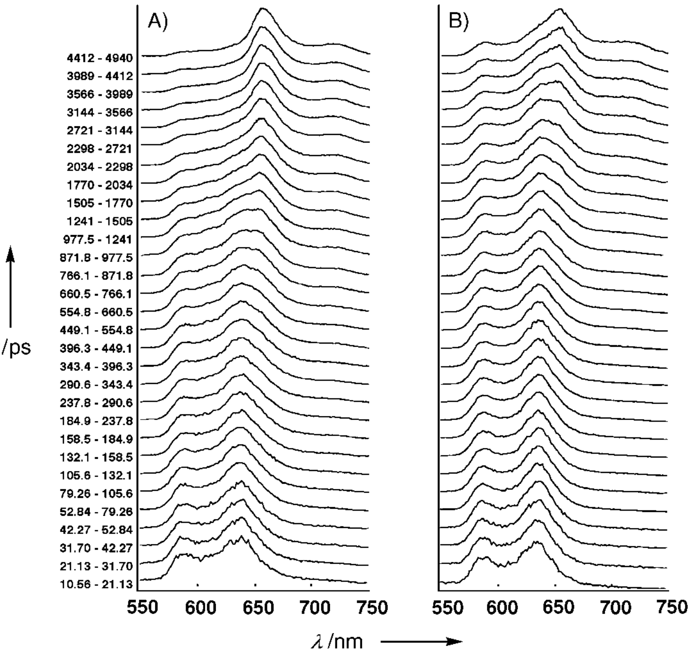


Figure 2. Time-resolved fluorescence spectra upon excitation at 415 nm of star-shaped $(7P_{Zn})_4P_{FB}$ (A) and conically shaped $(7P_{Zn})_1P_{FB}$ (B) in THF at 25 °C.

Picosecond time-resolved fluorescence spectroscopy of $(7P_{Zn})_4P_{FB}$ and $(7P_{Zn})_1P_{FB}$ was conducted to evaluate the intramolecular energy transfer events in a more quantitative manner. When star-shaped $(7P_{Zn})_4P_{FB}$ was excited at 415 nm, the time-resolved fluorescence spectrum (Figure 2 A) initially showed a rise in the fluorescence from the $P_{Zn}$ units (589, 637 nm) which then decayed progressively to allow a rise in a new fluorescence from the $P_{FB}$ core. Although a similar time-resolved spectral change was observed for conically shaped $(7P_{Zn})_1P_{FB}$ (Figure 2 B), the rise in the fluorescence from the $P_{FB}$ units (658, 723 nm) was much slower than in the case of star-shaped $(7P_{Zn})_4P_{FB}$. For comparison, a dendritic zinc porphyrin heptamer $7P_{Zn}$[7] without the energy-accepting free-base porphyrin ($P_{FB}$) core showed, upon excitation at 415 nm, a fluorescence decay profile at 585 nm (Figure 3 C), which could be fitted with a single exponential decay for a lifetime ($\tau_D$) of 2309 ps ($\chi^2 = 1.13$). Since this decay profile was quite similar to that of a monomeric zinc porphyrin such as $P_{Zn}^{EXT}$ ($\tau_D = 2305$ ps, $\chi^2 = 1.28$), self-quenching of the photoexcited $P_{Zn}$ units in the dendritic $7P_{Zn}$ wedges is unlikely to occur. In contrast, $(7P_{Zn})_4P_{FB}$ showed a remarkable quenching signature in the fluorescence decay profile (Figure 3 A), which was analyzed as the sum of three exponential components ($\chi^2 = 0.99$) with $\tau_{DA}$ values of 70 (21 %), 500 (56 %), and 1674 (23 %) ps. The conically shaped $(7P_{Zn})_1P_{FB}$, however, displayed only a little quenching in the fluorescence decay curve (Figure 3 B), which gave three exponential components ($\chi^2 = 1.03$) with $\tau_{DA}$ values of 79 (3 %), 640 (25 %), and 2367

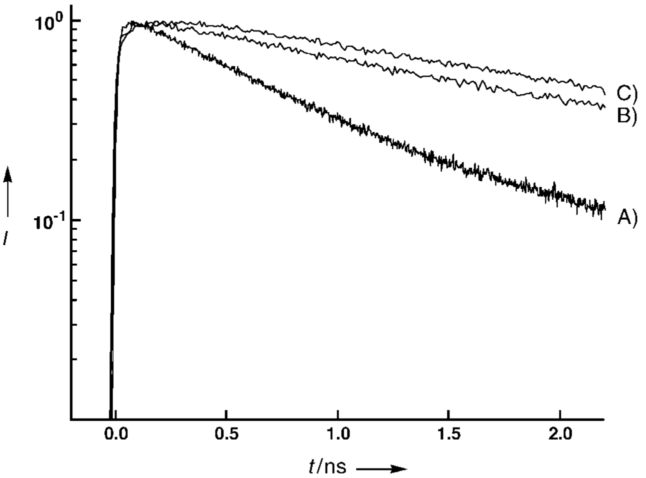


Figure 3. Fluorescence decay profiles upon excitation at 415 nm of star-shaped $(7P_{Zn})_4P_{FB}$ (A), conically shaped $(7P_{Zn})_1P_{FB}$ (B), and reference $7P_{Zn}$ (C) in THF ($A_{ext} < 0.1$) at 25 °C, monitored at 585 nm.

(72 %) ps. Since these values are roughly consistent with the fluorescence rise-times of the $P_{FB}$ units in $(7P_{Zn})_4P_{FB}$ and $(7P_{Zn})_1P_{FB}$,[12] the decay profiles in Figure 3 can be utilized for the kinetic analysis of the transfer of excitation energy in the dendritic multiporphyrin arrays. Thus, the energy-transfer rate constant $k_{ENT}$ for star-shaped $(7P_{Zn})_4P_{FB}$ could be evaluated from the average $\tau_{DA}$ value ($\tau_{DA}^{av}$) to be $1.04 \times 10^9\ s^{-1}$, which is one order of magnitude larger than that for conically shaped $(7P_{Zn})_1P_{FB}$ ($0.10 \times 10^9\ s^{-1}$). The energy-transfer efficiencies $\Phi_{ENT}$, calculated from these $k_{ENT}$ values, were 71 and 19 % for $(7P_{Zn})_4P_{FB}$ and $(7P_{Zn})_1P_{FB}$, respectively.[13] Such large differences in the $k_{ENT}$ and $\Phi_{ENT}$ values for $(7P_{Zn})_4P_{FB}$ and $(7P_{Zn})_1P_{FB}$ clearly demonstrate a significant role of the morphology of the chromophore array in energy transfer.

In the photochemical events in bacterial light-harvesting antenna complex LH2, the excitation energy is considered to be maintained in the wheel-like chromophore array without radiative decay as a result of a superb cooperativity among the chromophore units for energy migration. In order to evaluate the energy migration characteristics in morphologically different $(7P_{Zn})_4P_{FB}$ and $(7P_{Zn})_1P_{FB}$, a steady-state fluorescence depolarization was investigated in a viscous medium of polyethylene glycol (MW = 200) at 25 °C, where molecular motions that lead to fluorescence depolarization should be suppressed. In such a case, fluorescence depolarization should occur mostly by energy migration between randomly oriented chromophore units in the dendritic array. Excitation of $(7P_{Zn})_4P_{FB}$ at 544 nm ($A = 0.03$) with polarized light resulted in a highly depolarized fluorescence from the $P_{Zn}$ units, where the fluorescence anisotropy ($P$) was evaluated to be only 0.03. This value is considerably smaller than that of monomeric $P_{Zn}^{EXT}$ ($P = 0.19$), used as an isolated chromophore reference. This observation indicates the occurrence of an efficient migration of excitation energy over the dendritic zinc porphyrin array in star-shaped $(7P_{Zn})_4P_{FB}$ before transfer to the focal free-base porphyrin unit.[9] Conically shaped $(7P_{Zn})_1P_{FB}$ bearing only a single dendritic zinc porphyrin wedge, however, showed a larger $P$ value (0.10) than $(7P_{Zn})_4P_{FB}$. These contrasting trends indicate a possible cooperation of the four dendritic zinc porphyrin wedges in large $(7P_{Zn})_4P_{FB}$ for facilitating the energy migration among the $P_{Zn}$ units.[14] Such a long-range energy migration in $(7P_{Zn})_4P_{FB}$ is quite interesting when the absence of any π-electronic conjugations among the $P_{zn}$ units is considered.

In conclusion, by mimicking the natural light-harvesting antenna complex LH2, we designed a novel large multiporphyrin array $(7P_{Zn})_4P_{FB}$ by incorporating 28 light-absorbing zinc porphyrin units into a dendritic scaffold having a focal free-base porphyrin unit as the energy acceptor. The large number of chromophore units in $(7P_{Zn})_4P_{FB}$ allows an efficient capture of visible photons. More importantly, the zinc porphyrin units in star-shaped $(7P_{Zn})_4P_{FB}$ cooperate with one another, to facilitate long-range energy migration and transfer without any assistance of π-electronic conjugation. Thus, the bio-inspired approach reported herein provides a new paradigm for the rational molecular design of highly efficient light-harvesting antennae.

## *Experimental Section*

$(7P_{Zn})_4P_{FB}$, $(7P_{Zn})_1P_{FB}$, and reference $7P_{Zn}$ were synthesized by the convergent approach using a 5,15-diarylporphyrin as the fundamental building block.[7] Time-resolved fluorescence spectra and decay curves were measured with a picosecond pulse laser and a single-photon timing apparatus. The laser system was a mode-locked titanium-sapphire laser (Coherent, Mira 900) and pumped by an Ar ion laser (Coherent, Innova 300) combined with a pulse picker (Coherent, Model 9200). The decay curve was obtained with an excitation wavelength of 415 nm by using a microchannel-plate photomultiplier (Hamamatsu R2809U-01). The pulse width of the instrumental response function was 30 ps (full width of half maximum height, FWHM). The energy-transfer rate constant ($k_{ENT}$) was calculated according to: $k_{ENT} = 1/\tau_{DA}^{av} - 1/\tau_D$, where $\tau_{DA}^{av}$ represents the average fluorescence lifetime of $P_{Zn}$ units in a dendritic multiporphyrin array, while $\tau_D$ denotes the fluorescence lifetime of the $P_{Zn}$ units in $7P_{Zn}$. The energy-transfer efficiency ($\Phi_{ENT}$) was calculated according to: $\Phi_{ENT} = k_{ENT}\tau_{DA}^{av} = 1 - \tau_{DA}^{av}/\tau_D$. The fluorescence anisotropy ($P$) was evaluated according to: $P = (I_{\parallel} - GI_{\perp})/(I_{\parallel} + GI_{\perp})$, where $I_{\parallel}$ and $I_{\perp}$ are fluorescence intensities observed through polarizers oriented parallel and perpendicular, respectively, to a vertically polarized excitation light, $G$ is an instrumental correction factor for depolarization effects arising from the instrument and is given by: $i_{\parallel}/i_{\perp}$, where $i_{\parallel}$ and $i_{\perp}$ denote the fluorescence intensities observed through the polarizers.

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[12] The rise-times of the $P_{FB}$ emissions were evaluated from Figure 2 to be 88 and 345 ps for $(7P_{Zn})_4P_{FB}$, and 80 and 652 ps for $(7P_{Zn})_1P_{FB}$ as negative amplitudes.

[13] Apparent energy-transfer efficiencies ($\Phi_{EXT}$), as estimated from the steady-state fluorescence profiles (Figure 1), were 75 and 44% for $(7P_{Zn})_4P_{FB}$ and $(7P_{Zn})_1P_{FB}$, respectively (R. L. Brookfield, M. Ellul, A. Harriman, G. Porter, *J. Chem. Soc. Faraday Trans. 2* **1986**, *82*, 219).

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# Color Indicators of Molecular Chirality Based on Doped Liquid Crystals

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With the rapidly increasing role of combinatorial methods in chemistry and (bio)catalysis there is an ever-growing need for fast screening processes for activity and selectivity.[1] This is particularly evident in the search for high enantioselectivity in asymmetric catalysis, which is often a time-consuming process. Recently reported methods for enantiomeric excess (*ee*) determination employ,[2] in an elegant way, UV/Vis spectroscopy,[3] fluorescence,[4] mass spectrometry,[5] and IR thermography.[6] One ingenious assay involves the different fluorescence emission of enantiomers and using a method based on four synthetic steps including a kinetic resolution.[7] Traditional techniques for chiral chromatographic analysis are currently being miniaturized to allow rapid screening and, although enantiomer separation is still necessary, new methods such as parallel chiral capillary electrophoresis offer promising alternatives.[8] Direct visualization of molecular chirality is a fundamental challenge which ultimately could have considerable practical importance for the rapid screening of libraries of nonracemic compounds. Here we report a simple color test for enantiomeric excess (*ee*) based on the chirality-dependent color generation in doped films of liquid crystals. Our design for a color test of chirality is based on the consideration that a change from a nematic to a cholesteric phase in liquid crystalline (LC) materials can be induced upon doping with suitable chiral guest compounds.[9] For example, we have shown by using chiral molecular switches as dopants that LC materials can function as amplifiers of chirality.[10, 11]

The chirality of a cholesteric LC material is indicated by the sign and magnitude of the cholesteric pitch. The pitch is dependent on: 1) the concentration ($c$ in wt%) of the dopant; 2) the helical twisting power ($\beta$) of the dopant, and 3) the enantiomeric excess (*ee*) of the dopant [Eq. (1)].

$$\text{pitch}\ (p) = (c\beta ee)^{-1} \qquad (1)$$

The helical twisting power is an intrinsic property of any chiral dopant which indicates how efficient this molecule is in inducing a chiral orientation in the LC material.

The pitch, for a given chiral substrate doped in an LC matrix at a fixed concentration, is dependent only on the *ee* value of the dopant. This property, therefore, might be used as a measure for the enantiopurity of any chiral compound that can induce a cholesteric phase.

The pitch is generally determined by the Grandjean–Cano technique,[12] a method which requires an aligned LC sample to be placed between a plane-convex lens and a flat surface. The pitch can then be obtained from the distances between distinct lines seen through a polarizing microscope. It is evident that for screening purposes this technique for the determination of *ee* values can hardly compete with other techniques because of laborious sample preparation. Cholesteric materials, however, show interesting optical properties when the pitch of the liquid crystal lies in the region of the wavelength of visible light. Liquid crystalline samples which are oriented by a linearly rubbed polyimide-covered glass plate show reflection at a specific wavelength ($\lambda$) that is dependent on the angle of the incident light ($\alpha$) relative to the normal of the surface and on the average refractive index of the material ($n$) [Eq. (2)].[13]

$$\lambda(\alpha) = np\cos[\sin^{-1}(\sin\alpha/n)] = n(c\beta ee)^{-1}\cos[\sin^{-1}(\sin\alpha/n)] \qquad (2)$$

The color, and hence the chiral nature, of such a phase, which is readily prepared, can be instantly assessed by eye. Doped, colored LC materials are therefore promising candidates for color indicators of *ee* values, with potential use in the combinatorial screening of enantioselective catalysts.

The major problem to overcome in the development of such a screening technique is that the helical twisting powers of common products of enantioselective catalysis are negligible (and therefore no cholesteric phase can be induced) or they are very small (only pitches in the range of micrometers can be obtained). Color induction is normally only achieved with specially designed dopants.[9] We reasoned that compounds that structurally resemble the LC material can be expected to

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