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Three-Component Cascade Energy Transfer with Use of Oligonaphthalene Skeletons

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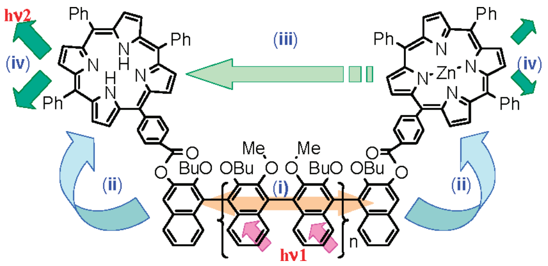
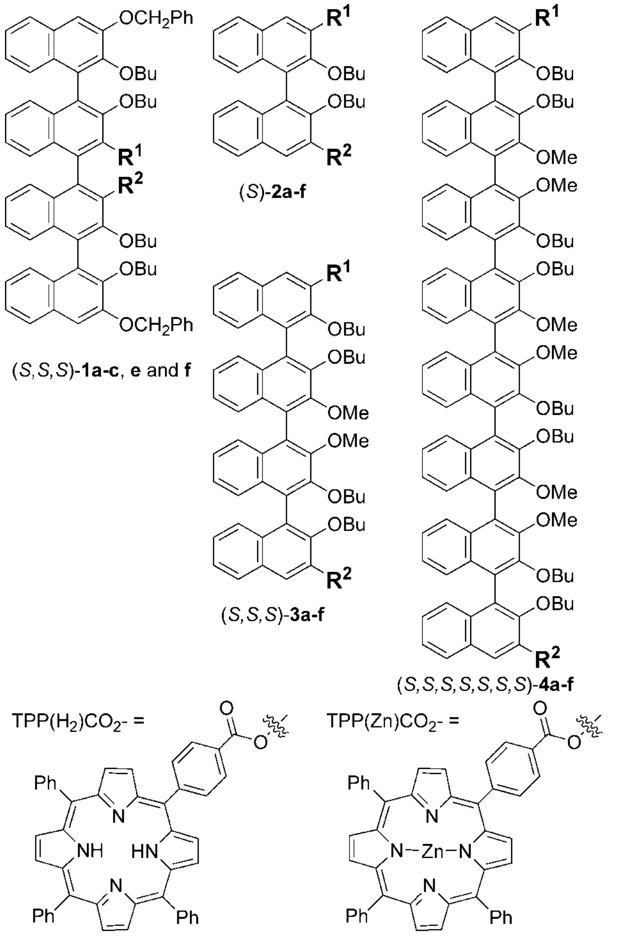


Three oligonaphthalenes with zinc porphyrin and free-base porphyrin moieties were synthesized, in which cascade energy transfer (from naphthalene to free-base porphyrin via zinc porphyrin) was observed when the zinc and free-base porphyrins were close to each other.

In the field of supramolecular chemistry, considerable research has focused on developing molecular devices and molecular machines such as molecular motors, ratchets, and logic gates.[1] At the same time, photosensitive functional molecules have been considered as input/output devices for information and as energy and/or electron transfer devices related to photosynthesis.[2] Several fully conjugated systems containing porphyrins have been applied and reported for the purpose.[3] On the other hand, we have focused our attention on the synthesis and function of oligonaphthalenes composed of a 2,3-dioxynaphthalene unit connected at the 1,4-position.[4] Herein, we report a three-component hierarchical energy transfer system[5] based on oligonaphthalenes with zinc porphyrins and/or free-base porphyrins **1a**−**c** ≈ **4a**−**c** (Figure 1).



For **5**,**6** and a-f,
5: TPP(H_2)CO_2H, **6**: TPP(Zn)CO_2H,
a: $R^1 = R^2$ = TPP(H_2)CO_2, **b**: R^1 = TPP(H_2)CO_2, R^2 = TPP(Zn)CO_2,
c: $R^1 = R^2$ = TPP(Zn)CO_2, **d**: $R^1 = R^2$ = OCH_2Ph
e: $R^1 = R^2$ = OH, **f**: R^1 = TPP(Zn)CO_2, R^2 = OH

FIGURE 1. Oligonaphthalenes **1a**−**4f** and porphyrins **5** and **6**.

Scheme 1 outlines the synthetic route of oligonaphthalenes.[6] Oligonaphthalenes with two hydroxy groups **1e**−**4e**[4c] were treated with 4-(10,15,20-triphenyl-21*H*,23*H*-porphin-5-yl)benzoic acid (TPP(H_2)CO_2H) (**5**) in the presence of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (WSC)·HCl and 4-dimeth-

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[6] Full experimental details: see the Supporting Information.

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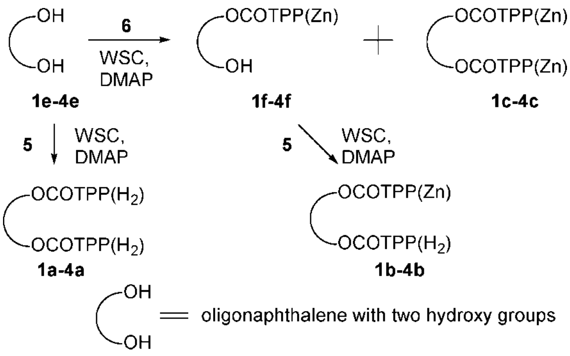
SCHEME 1. Synthetic Route of Oligonaphthalenes 1a−4f



ylaminopyridine (DMAP) to afford bis-TPP(H_2) **1a**−**4a** in 53−76% yields. On the other hand, diols **1e**−**4e** were treated with (TPP(Zn)CO_2H) (**6**) under the WSC/DMAP condition to give corresponding mono-TPP(Zn) **1f**−**4f** and bis-TPP(Zn) derivatives **1c**−**4c** in low to moderate yields, respectively. Oligonaphthalenes with both TPP(Zn) and TPP(H_2) **1b**−**4b** were prepared by the condensation of mono-TPP(Zn) **1f**−**4f** with the TPP(H_2)CO_2H (**5**) in 54−90% yields.

First, with **4b** as an example, the interaction among the oligonaphthalene skeleton, free-base porphyrin part, and zinc porphyrin part in the grand state was investigated. Figure 2 shows the UV−vis spectra of **4b** with all components, oligonaphthalene **4d**, free-base porphyrin **5**, and zinc porphyrin **6**, as well as their fluorescence spectra. Because the absorption spectrum of **4b** is the sum of the spectra of the constituent, **4d**, **5**, and **6**, each fragment in the grand state does not interact. A wide overlap with the emission of the donor naphthalene unit **4d** (around 380 nm) and absorption of the Soret band of acceptor porphyrin **5** and/or **6** (around 420 nm) was observed. Because porphyrins **5** and **6** have a negligible absorption near 320 nm, the naphthalene units can be excited with a high selectivity at this wavelength. Furthermore, because the fluorescence spectrum of zinc porphyrin **6** exhibits peaks at 596 and 647 nm and that of free-base porphyrin **5** displays a peak at 651 nm, the source of the fluorescence can be easily discriminated.

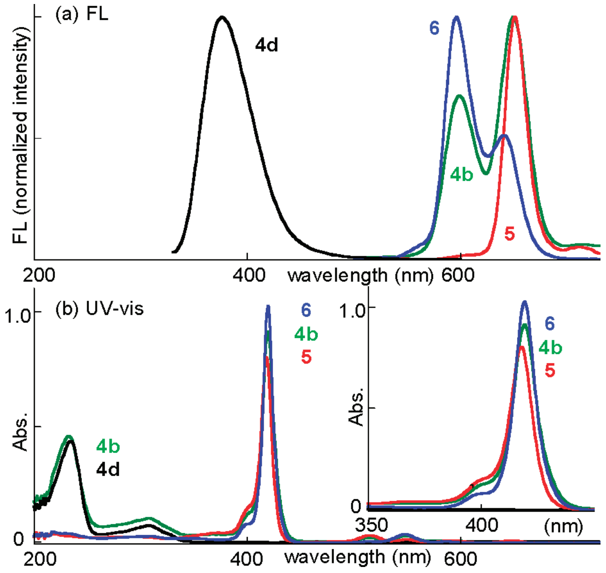


FIGURE 2. (a) Fluorescence spectra of **4b**, **4d**, **5**, and **6**. Conditions: CH_2Cl_2, 20 °C, $\lambda_{ext} = 320$ nm for **4d**, $\lambda_{ext} = 420$ nm for **4b**, **5**, and **6**. (b) UV−vis spectra of **4b**, **4d**, **5**. and **6**. Conditions: CH_2Cl_2 containing 1.0×10^{-8} M triethylamine to remove HCl. [**4b**] = [**4d**] = 1.0×10^{-5} M, [**5**] = [**6**] = 2.0×10^{-5} M, 20 °C, light path length = 1 mm. Inset: Expansion of the Soret absorption region.

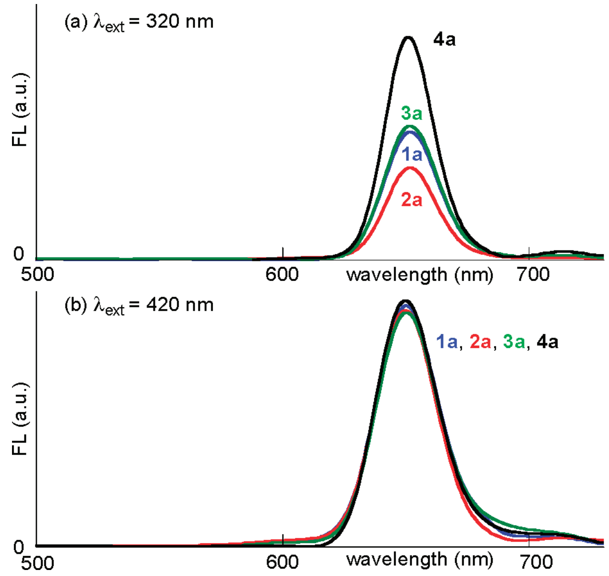


FIGURE 3. Fluorescence spectra of **1a**−**4a**. Conditions: CH_2Cl_2 containing 1.0×10^{-8} M triethylamine to remove HCl. [**1a**−**4a**] = 1.0 × 10^{-6} M, 20 °C, light path length = 10 mm. (a) $\lambda_{ext} = 320$ nm; (b) $\lambda_{ext} = 420$ nm.

When the naphthalene units of **1a**−**4a** were selectively irradiated at 320 nm, the fluorescence was not due to the naphthalene units, but rather the corresponding porphyrin units (Figure 3a). These results demonstrate that an effective intramolecular energy transfer occurs from the naphthalene units to the porphyrin units. Furthermore, the intensity of the fluorescence increased as the number of naphthalene rings increased. Because the fluorescent spectra of **1a** and **3a**, which were composed of four naphthalene units, excited at 320 nm are similar, it is concluded that the position of TPP on the oligonaphthalene skeleton is not related to the fluorescent intensity. It should be noted that the fluorescence spectra derived from the porphyrin units had nearly the same intensities and shapes when the porphyrin units of **1a**−**4a** were directly excited at 420 nm (Figure 3b).

It is also clarified that **1c**−**4c** with oligonaphthalene skeletons and two zinc porphyrins show similar behaviors against irradiation at 320 and 420 nm (Figure 4). These results indicate that (1) regardless of which naphthalene unit in the oligonaphthalene skeleton is excited, an effective and fast energy transfer should occur from the excited naphthalene unit to an adjacent naphthalene unit,[7] and (2) a through-space energy transfer, which determines the efficiency of the total energy transfer should occur from the naphthalene possessing TPP to the TPP unit.

Figure 5 shows the normalized fluorescence spectra of **1b**−**4b** with both free-base and zinc porphyrins as well as that of an equimolar mixture of **5** and **6**. The fluorescence spectrum of **4b**, in which the zinc porphyrin part and free-base porphyrin part are far from each other, overlapped with that of the equimolar mixture of **5** and **6**. As the two porphyrins became closer, the fluorescence derived from the zinc porphyrin clearly

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[7] For another interpretation of the energy transfer, the oligonaphthalene skeleton itself acts as a single chromophore. However, the AM1 calculation of the most stable conformation all-(*S*)-octamer, which was determined through CONFLEX-MM2 implemented in CAChe ver. 6.1.12 for Windows, indicates obitals from HOMO-5 to LUMO+5 are localized on only one or two naphthalene rings. Therefore, we adopted the interpretation in context.

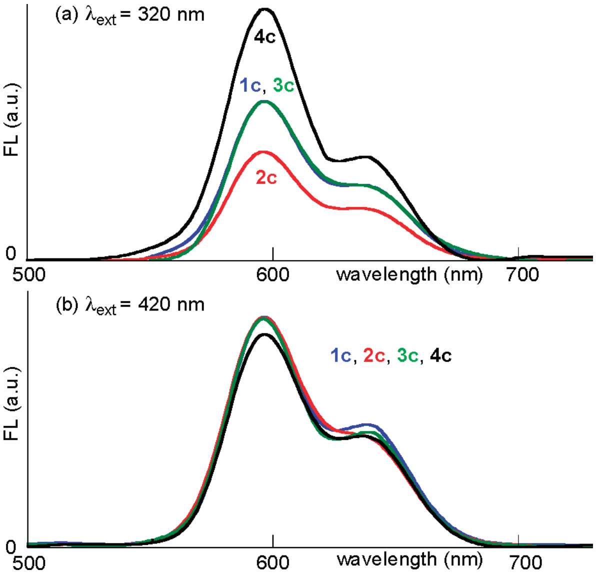

FIGURE 4. Fluorescence spectra of **1c**–**4c**. Conditions: CH_2Cl_2 containing 1.0×10^{-8} M triethylamine to remove HCl. [**1c**–**4c**] = 1.0×10^{-6} M, 20 °C, light path length = 10 mm. (a) λ_{ext} = 320 nm; (b) λ_{ext} = 420 nm.

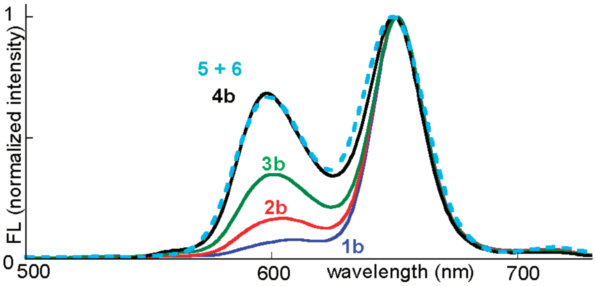

FIGURE 5. Normalized fluorescence spectra of **1b**–**4b** and a mixture of **5** and **6**. Conditions: CH_2Cl_2 containing 1.0×10^{-8} M triethylamine to remove HCl. [**1b**–**4b**] = 1.0×10^{-6} M (λ_{ext} = 320 nm), [**5**] = [**6**] = 1.0×10^{-6} M (λ_{ext} = 420 nm), 20 °C, light path length = 10 mm.

decreased. In particular, the fluorescence from the zinc porphyrin in **1b** was nearly quenched.[8]

Figure 6 shows the fluorescence spectrum of **3b**, in which partial quenching was observed, as well as those of **3a**, **3c**, and an equimolar mixture of **5** and **6**. Comparing **3b** to **5** + **6**, it is clear that the emission intensity from the zinc porphyrin part of **3b** near 600 nm is decreased, whereas that from the free-base porphyrin part near 650 nm is increased. The data indicate that the additional energy transfer from the zinc porphyrin part to the free-base porphyrin part[8] should occur after the energy transfer from the naphthalene rings to each porphyrin.

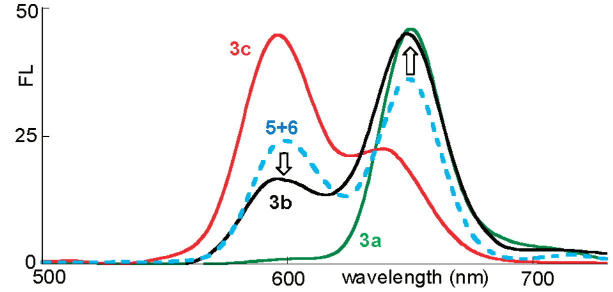

FIGURE 6. Fluorescence spectra of **3a**–**c** and a mixture of **5** and **6**. Conditions: CH_2Cl_2 containing 1.0×10^{-8} M triethylamine to remove HCl. [**3a**–**c**] = [**5**] = [**6**] = 1.0×10^{-6} M (λ_{ext} = 420 nm), 20 °C, light path length = 10 mm.

TABLE 1. Quantum Yields of Compounds 1a–4d

entry	compd	Φ_{320} (%)[a]	Φ_{420} (%)[b]	Φ_{320}/Φ_{420}
1	**5**		0.19	
2	**6**		0.36	
3	**1a**	0.11	0.19	0.58
4	**1b**	0.10	0.18	0.54
5	**1c**	0.17	0.33	0.53
6	**2a**	0.11	0.19	0.58
7	**2b**	0.11	0.21	0.55
8	**2c**	0.16	0.33	0.50
9	**2d**	19.0		
10	**3a**	0.12	0.20	0.59
11	**3b**	0.13	0.23	0.58
12	**3c**	0.17	0.32	0.53
13	**3d**	55.0		
14	**4a**	0.12	0.21	0.58
15	**4b**	0.14	0.28	0.50
16	**4c**	0.17	0.33	0.51
17	**4d**	60.8		

[a] λ_{ext} = 320 nm. [b] λ_{ext} = 420 nm. Conditions: CH_2Cl_2 containing 1.0×10^{-8} M triethylamine to remove HCl. The fluorescence quantum yields were determined by using a solution of quinine sulfate in 1 N H_2SO_4 as a reference standard (Φ = 0.546) for λ_{ext} = 320 nm and fluorescein in 0.1 N NaOH as a reference standard (Φ = 0.95) for λ_{ext} = 420 nm.

The quantum yields of the compounds are listed in Table 1. Compared to the quantum yields with irradiation at 320 nm (Φ_{320}), oligonaphthalenes with two free-base porphyrins **1a**–**4a** are about 0.11% (entries 3, 6, 10, and 14), and those with two zinc porphyrins **1c**–**4c** are 0.16% (entries 5, 8, 12, and 16). When porphyrins were directly excited at 420 nm (Φ_{420}), the corresponding quantum yields of **1a**–**4a** and **1c**–**4c** were 0.20% and 0.32%, respectively. As a result, the values of Φ_{320}/Φ_{420} were relatively constant at 0.57 for **1a**–**4a**, and at about 0.51 for **1c**–**4c**. The values of Φ_{320}/Φ_{420} were considered to reflect the efficiency of through-space energy transfer from the naphthalene possessing the porphyrin moiety to the porphyrin. Furthermore, for compounds **1b**–**4b** with zinc and free-base porphyrins, the quantum yields of **1b**–**4b** (Φ_{320} and Φ_{420}) gradually decrease as the distance between the zinc porphyrin and free-base porphyrin decreases, due to the additional energy transfer from the zinc porphyrin to the free-base porphyrin (entries 4, 7, 11, and 15).

The fluorescence lifetimes of some typical compounds were determined by time-resolved fluorometry (Table 2). The lifetime at 650 nm of the free-base porphyrin (**5**) irradiated at 420 nm was 8.8 ns, and the lifetimes at both 600 and 650 nm of zinc porphyrin (**6**) were ca. 1.9 ns. Oligonaphthalenes with either free-base or zinc porphyrin had lifetimes that reflected the corresponding fragmental porphyrins (entries 3, 5, 6, and 8). For **1b** and **4b** which have both porphyrins, **4b**, in which the two kinds of porphyrins are sufficiently separated from each other, indicated two lifetimes based on the zinc porphyrin (τ = 1.9 ns, λ_{em} = 600 nm) and free-base porphyrins (τ = 8.2 ns, λ_{em} = 650 nm) (entry 7). On the other hand, **1b**, in which the two porphyrins are near each other, showed one lifetime derived from the free-base porphyrin (τ = 8.2 ns, λ_{em} = 650 nm) and

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TABLE 2. Fluorescence Lifetimes of Some Typical Compounds[a]

entry	compd	τ (ns) (λ_{em} = 600 nm)[b]	τ (ns) (λ_{em} = 650 nm)[b]
1	**5**		8.8
2	**6**	1.9	2.0
3	**1a**		9.3
4	**1b**	nd[c]	8.2
5	**1c**	1.9	1.9
6	**4a**		8.9
7	**4b**	1.9	8.2
8	**4c**	1.7	1.7

[a] Conditions: CH_2Cl_2 containing 1.0 × 10^{-8} M triethylamine to remove HCl. [b] Lifetime was determined by curve-fitting of the decay profile assuming a single exponential function. [c] Lifetime could not be determined since it was shorter than the measurement limit (about 0.2 ns).

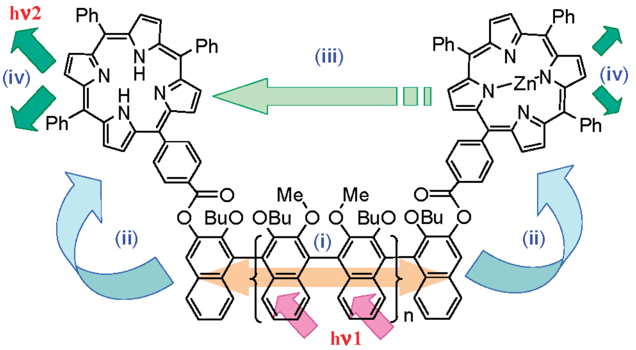

FIGURE 7. Energy transfer in oligonaphthalenes with zinc and free-base porphyrins.

no fluorescence from the zinc porphyrin (entry 4). These results indicate that rapid energy transfer (exceeding the detection limit <0.2 ns) occurs from zinc porphyrin to free-base porphyrin.

The energy transfer in oligonaphthalenes with zinc and free-base porphyrins is summarized in Figure 7. Thus, when a discrete naphthalene unit was selectively excited by irradiation at 320 nm, (i) an effective and fast energy transfer occurs from an excited naphthalene unit to an adjacent naphthalene unit. Next, (ii) a through-space energy transfer occurs from the naphthalene with a zinc and/or free-base porphyrin side chain to the porphyrin unit. (iii) If the zinc and free-base porphyrins are close to each other, additional energy transfer occurs from the zinc porphyrin unit to the free-base porphyrin unit. Finally, (iv) emission occurs from the corresponding porphyrin unit.

In the present study, we described the energy transfer from naphthalene rings to the porphyrin part using oligonaphthalene derivatives. In particular, in oligonaphthalenes **1b**−**3b** which have zinc porphyrin and free-base porphyrin moieties, cascade energy transfer (naphthalene → zinc porphyrin → free-base porphyrin) occurred. We are currently developing a more complicated energy transfer system as well as an electron transfer system using a combination of oligonaphthalene, porphyrin and fullerene C_{60}.

Experimental Section

General Procedure for the Synthesis of Compounds 1f−4f and 1c−4c. The preparation of **2f** and **2c** is typical. To a solution of (*S*)-**2e** (20 mg, 0.047 mmol) in CH_2Cl_2 (1.0 mL) were added TPP(Zn)CO_2H (**6**) (34 mg, 0.047 mmol), WSC·HCl (27 mg, 0.14 mmol), and DMAP (34 mg, 0.28 mmol) under argon atmosphere and the solution was stirred at room temperature for 24 h. The reaction mixture was quenched with water, extracted with $CHCl_3$, washed successively with water and brine, dried over Na_2SO_4, and evaporated to give a residue that was purified by recycling preparative HPLC (Japan Analytical Industry Co., Ltd. LC-908) with connected JAIGEL-1H (20 × 600 mm) and JAIGEL-2H (20 × 600 mm) under the conditions of 3.5 mL/min of flow rate with $CHCl_3$ detected by UV (254 nm) and RI (refractive index) to afford (*S*)-**2f** (24 mg, 0.021 mmol, 46%) and bis-adduct (*S*)-**2c** (17 mg, 0.0093 mmol, 20%).

(*S*)-**2f**: 46% yield; purple solid; mp 175 °C; $[\alpha]^{20}_D$ −3382 (*c* 0.054, $CHCl_3$); IR (KBr) 3503, 2955, 1739, 1598, 1339, 1243 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.51 (t, *J* = 7.3 Hz, 3H), 0.67 (t, *J* = 7.3 Hz, 3H), 0.8−1.5 (m, 8H), 3.5−3.7 (m, 3H), 3.89 (dt, *J* = 6.4 Hz, 9.2 Hz, 1H), 6.16 (s, 1H), 7.1−7.5 (m, 6H), 7.7−7.8 (m, 11H), 7.96 (d, *J* = 7.8 Hz, 1H), 8.01 (s, 1H), 8.1−8.3 (m, 6H), 8.39 (d, *J* = 7.8 Hz, 2H), 8.65 (d, *J* = 8.2 Hz, 2H), 8.91 (d, *J* = 4.6 Hz, 2H), 8.95−9.05 (m, 6H); HRMS (FAB^+) calcd for $C_{73}H_{56}N_4O_5Zn$ 1132.3542, found 1132.3524.

(*S*)-**2c**: 20% yield; purple solid; mp 281 °C; $[\alpha]^{20}_D$ −3990 (*c* 0.048, $CHCl_3$); IR (KBr) 2955, 1740, 1598, 1339, 1244 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.64 (t, *J* = 7.3 Hz, 6H), 0.8−1.5 (m, 8H), 3.7−3.9 (m, 2H), 3.9−4.1 (m, 2H), 7.3−7.5 (m, 6H), 7.6−7.8 (m, 18H), 7.98 (d, *J* = 8.1 Hz, 2H), 8.05 (s, 2H), 8.1−8.3 (m, 12H), 8.41 (d, *J* = 8.1 Hz, 4H), 8.69 (d, *J* = 7.8 Hz, 4H), 8.8−9.0 (m, 16H); MS (FAB^+) *m/z* 1835 $(M + H)^+$. Anal. Calcd for $C_{118}H_{82}N_8O_6Zn_2 \cdot 3CH_2Cl_2$: C, 69.42; H, 4.24; N, 5.35. Found: C, 69.72; H, 4.35; N, 5.24.

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Supporting Information Available: Full experimental details and characterization data of all new compounds, and fluorescence decay profiles of **1a**−**c** and **4a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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