# Singlet energy transfer in bis(phenylethynyl)phenylene-bridged zinc–free base hybrid diporphyrins

**Shigeki Kawabata,*[,a] Iwao Yamazaki,[b] Yoshinobu Nishimura[b] and Atsuhiro Osuka*[,c]**

[a] *Department of Liberal Arts and Sciences, Faculty of Engineering,*
*Toyama Prefectural University, Kosugi, Toyama 939-03, Japan*
[b] *Department of Chemical Process Engineering, Faculty of Engineering, Hokkaido University,*
*Sapporo 060, Japan*
[c] *Division of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-01, Japan*

**A set of bis(phenylethynyl)phenylene-bridged diporphyrins 1–3 has been prepared by the acid-catalysed double condensation reaction of bis(4-formylphenylethynyl)benzene 8 and 9, and 3,5-di-*tert*-butylbenzaldehyde 11 with bis(3-hexyl-4-methylpyrrol-2-yl)methane 12 or the $Pd^0$-catalysed coupling reaction of acetylene-substituted porphyrin 14 with 1,4-diiodobenzene. Intramolecular singlet excitation energy transfer in Zn–free base hybrid diporphyrins 1–3(ZH) has been studied by picosecond time-resolved fluorescence spectroscopy. The determined $k_{EN}$ values are in the order of 1(ZH) > 2(ZH) ≈ 3(ZH). The energy transfer mechanism is discussed in terms of varying contribution of through-space and through-bond interactions.**

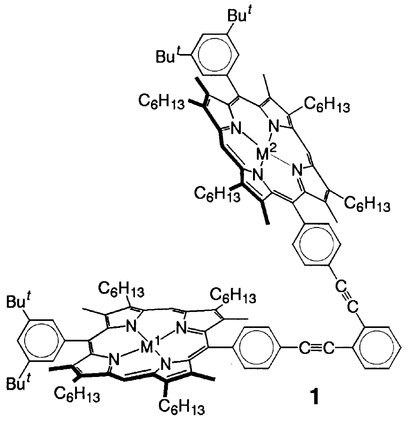
The absorption of solar energy by antenna pigments and the subsequent efficient transfer of excitation energy to photosynthetic reaction centres constitute key entries into the generation of energetic charge-separated products in photosynthesis.[1] For this purpose, photosynthetic organisms use light-harvesting complexes as an antenna that has an elegant alignment and fine-tuned photophysical and photochemical properties, suitable for achieving remarkably high quantum yield energy transfer over long distances through hundreds of photosynthetic pigments. It seems that control of the energy transfer may be achieved by holding each pigment in specific spatial arrangements.[2] This is also valid in artificial model systems where rates of intramolecular energy transfer have been shown to follow the trends predicted by Förster theory.[3]

On the other hand, recent reports have demonstrated that π-conjugated systems can significantly enhance through-bond electronic couplings between covalently linked energy donor and acceptor pairs. For example, π-conjugated bridges including ethyne,[4–9] diyne,[4,7–10] polyene[4,11] and oligothiophene linkages[11] have been demonstrated to mediate efficient electronic interactions between the donor and the acceptor, thereby enabling efficient energy transfer over long distances, over which the energy transfer is usually impossible without these π-conjugated bridges within the lifetime of the donor excited state. In these covalently linked π-conjugated systems, electronic coupling is not primarily determined by spatial arrangement but by through-bond electronic interactions. Therefore, it should be possible to construct a new energy-transfer network by combining both the spatial arrangements and the through-bond interactions of π-conjugated systems.

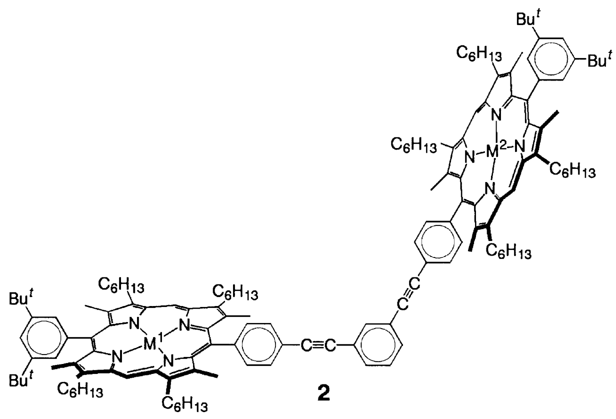
Recently, we prepared polyyne- and polyene-bridged diporphyrins and demonstrated that linear π-conjugated polyyne and polyene bridges can enhance through-bond electronic coupling between the donor and the acceptor, thus enabling efficient energy and electron transfer over long distances.[4] As part of our continuing programme of developing artificial photosynthetic systems, we have now prepared a set of bis(phenylethynyl)phenylene-bridged diporphyrins **1**–**3** and examined intramolecular singlet energy transfer from zinc–porphyrin donor to free-base porphyrin acceptor. It is expected that the through-space interactions would depend primarily on the distance, and thus decrease in the order **1** > **2** > **3**, while the through-bond interactions would be **1** ≈ **3** > **2**, since the two ethyne units are electronically conjugated in **1** and **3** but not conjugated in **2**. It is well-established that singlet–singlet energy transfer can occur by Förster and/or Dexter mechanisms. Discrimination of the two mechanisms may often be aided by examining the geometry dependence of the energy transfer. The Dexter mechanism may be predominant in the case of strong electron exchange interactions due to the close contact of the donor and the acceptor or the presence of π-conjugated bridge between the donor and the acceptor, while the Förster mechanism may be predominant in the case of large spectral overlap of the emission of the donor and the absorption of the acceptor. In this paper, we report the synthesis and singlet energy transfer of bis(phenylethynyl)phenylene-bridged diporphyrins.

## Results and discussion

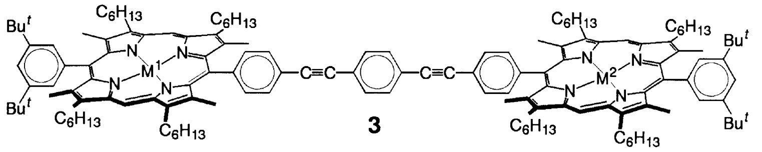
Synthetic schemes to bis(phenylethynyl)phenylene linkers and diporphyrins are shown in Schemes 1–3. Palladium(0) mediated coupling reactions between 4-(4,4-dimethyl-2,6-dioxan-1-yl)-phenylacetylene (**4**) and 1,2-, 1,3- and 1,4-diiodobenzenes in triethylamine[12] gave protected bridges **5**–**7**, which were hydrolysed under acidic conditions to give dialdehydes **8**–**10**, respectively (Scheme 1). 1,2- and 1,3-Bis(phenylethynyl)phenylene-bridged diporphyrins **1**(**HH**) and **2**(**HH**) were prepared in moderate yields by the trichloroacetic acid catalysed double condensation[4,13] of dialdehydes **8** and **9** with 3,5-di-*tert*-butylbenzaldehyde (**11**) and bis(3-hexyl-4-methylpyrrol-2-yl)-methane (**12**) in acetonitrile–dichloromethane followed by *p*-chloranil oxidation, respectively (Scheme 2). However, the very poor solubility of **10** hampered the application of this double condensation method. We therefore sought an alternative route based on the palladium catalysed coupling reaction (Scheme 3).[6,9] The acid catalysed condensation of 4-ethynylbenzaldehyde (**13**) and **11** with **12** in a mixture of acetonitrile–dichloromethane followed by oxidation with a *p*-chloranil afforded ethynylporphyrin **14** in 20% yield. In these mild reaction conditions, a terminal ethyne does not need to be protected. In the presence of $PdCl_2$ and triphenylphosphine in triethylamine, the



**1**

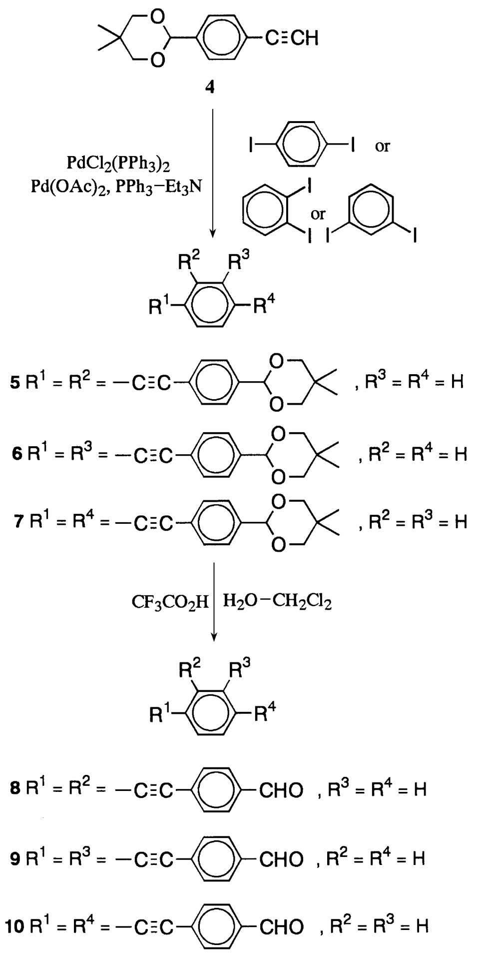


**2**



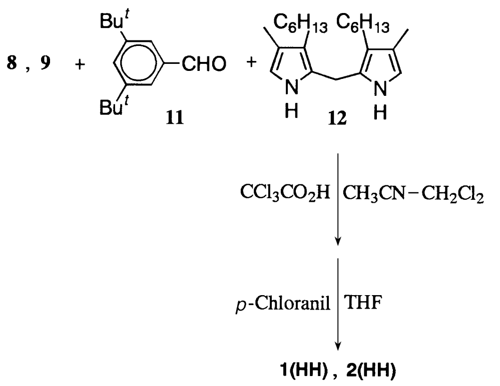
**3**

$M^1 = H_2, M^2 = Zn$

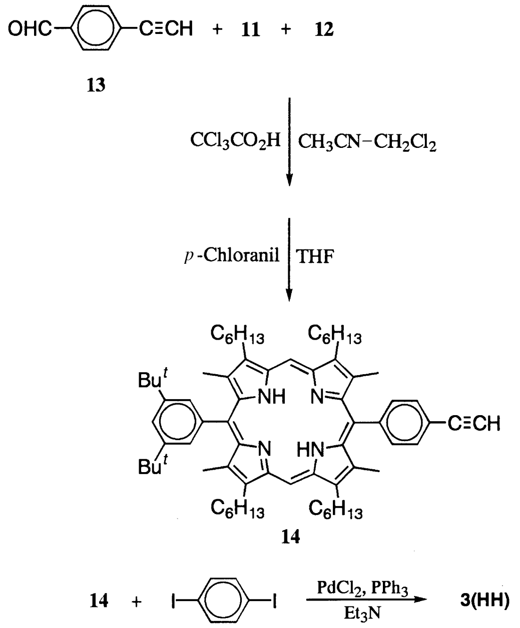


**Scheme 1** Synthetic procedure of bis(phenylethynyl)phenylene linker

coupling reaction of **14** with 1,4-diiodobenzene proceeded smoothly to provide 1,4-bridged diporphyrin **3(HH)** in 35% yield.[9] Partial zinc metallation was carried out by treatment of **1–3(HH)** with a small amount of $Zn(OAc)_2$–MeOH while the extent of the metallation was monitored by TLC. After a suitable time, the metallation was stopped by addition of water and the products were separated by silica gel column chromatography, giving singly zinc-metallated diporphyrins **1–3(ZH)**.



**Scheme 2** Synthetic procedure of bis(phenylethynyl)phenylene diporphyrins **1** and **2**



**Scheme 3** Synthetic procedure of bis(phenylethynyl)phenylene diporphyrin **3**

The absorption spectra of dialdehydes **8–10** in tetrahydrofuran (THF) are shown in Fig. 1. The absorption maximum of **10** is observed at a longer wavelength than those of **8** and **9**,

**Table 1** Data for **1**–**3**

| Compound | $k_{EN}$/s$^{-1}$ [a] | $\tau$/ps [b] | $\tau$/ps [c] | $k_{EN}$/s$^{-1}$ [d] | $r$/$10^{-10}$ m | $J$/cm$^6$ mmol$^{-1}$ | $\kappa^2$ | $k_{EN}$/s$^{-1}$ [e] |
|---|---|---|---|---|---|---|---|---|
| **1**(**ZH**) | $4.8 \times 10^9$ | 195 | 217 | $4.4 \times 10^9$ | 13.1 | $4.7 \times 10^{-14}$ | 0.69 | $3.7 \times 10^{10}$ |
| **2**(**ZH**) | $9.4 \times 10^8$ | 793 | 692 | $5.7 \times 10^8$ | 22.7 | $3.7 \times 10^{-14}$ | 0.97 | $1.5 \times 10^9$ |
| **3**(**ZH**) | $9.3 \times 10^8$ | 796 | 723 | $5.7 \times 10^8$ | 26.2 | $3.5 \times 10^{-14}$ | 1.1 | $7.1 \times 10^8$ |

[a] Rates of singlet energy transfer calculated on the basis of the steady-state fluorescence intensity at 585 nm according to the eqn. (1). [b] The decay lifetime of the fluorescence of zinc porphyrin at 585 nm. [c] The increase time of the fluorescence of free base porphyrin at 700 nm. [d] Rates of singlet energy transfer calculated on the basis of the fluorescence lifetime according to eqn. (2). [e] Predicted Förster energy transfer rate constant.

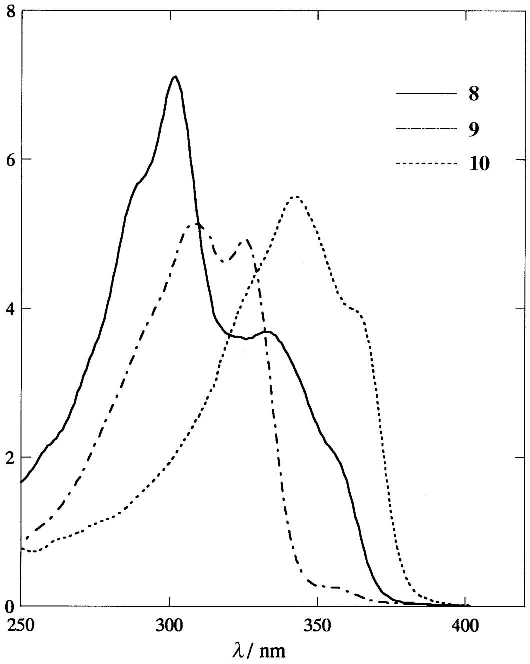


**Fig. 1** UV–VIS absorption spectra of **8**–**10** in THF

suggesting larger electronic interactions in a 1,4-substituted bridge than those in 1,2- and 1,3-substituted ones.

The absorption spectra of diporphyrins **1**–**3**(**HH**) and **1**–**3**(**ZH**) in THF, however, do not display significant difference between the isomers (Fig. 2). The absorption bands due to the bridge moieties are slightly broadened and hidden by the strong absorption of porphyrin. The absorption spectra of **1**–**3**(**ZH**) are essentially a superposition of those of free base and zinc porphyrin components. The Soret absorption peak in **3**(**HH**) and **3**(**ZH**) are somewhat red-shifted relative to those in other diporphyrins **1**(**HH**) and **1**(**ZH**), and **2**(**HH**) and **2**(**ZH**), but the difference is not so large. Therefore we conclude that the electronic interaction between the porphyrins is not strong in the ground state in this series.

The fluorescence spectra of **1**–**3**(**ZH**) are different from the superposition of those of the individual chromophores (Fig. 3). The fluorescence intensity of the zinc porphyrin is reduced ($\lambda_{em}$/nm = 585 and 643) whereas that of the free base porphyrin is enhanced ($\lambda_{em}$/nm = 632 and 695). This observation shows the efficient singlet excitation energy transfer from the zinc porphyrin to the free base porphyrin. Under our dilute conditions (*ca.* $10^{-7}$ M), intermolecular singlet energy transfer reactions from zinc porphyrin to free base porphyrin can be excluded. Rate constants ($k_{EN}$) of the intramolecular energy transfer have been calculated using eqn. (1), where $\tau_0$ is the fluorescence lifetime of

$$k_{EN} = (1/\tau_0)(I_0 - I)/I \qquad (1)$$

the reference zinc porphyrin (1.46 ns), $I$ is the fluorescence intensity of **1**–**3**(**ZH**) at 585 nm, and $I_0$ is the fluorescence intensity of 1:1 mixture of corresponding **1**–**3**(**ZZ**) and **1**–**3**(**HH**) at 585 nm, respectively (Table 1).

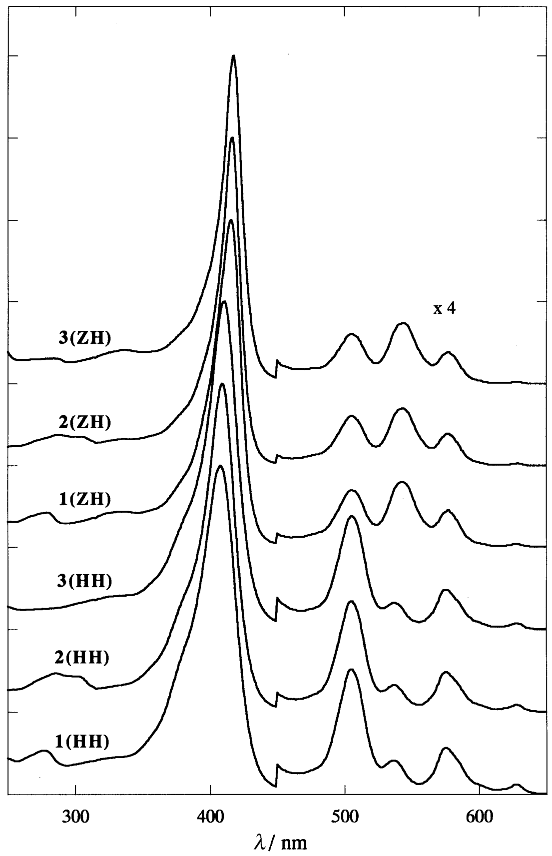


**Fig. 2** UV–VIS absorption spectra of **1**–**3**(**HH**) and **1**–**3**(**ZH**) in THF. Each spectrum is normalized to the Soret absorption.

The energy transfer reaction in these compounds has also been investigated by picosecond time-resolved fluorescence spectroscopy.[3] Time-resolved fluorescence spectra of **1**(**ZH**) taken by excitation at 532 nm in THF are shown in Fig. 4. The fluorescence spectrum at 36 ps was assigned as primarily due to the emission from the zinc porphyrin. Decay of the zinc porphyrin fluorescence was followed by an increase in the free base porphyrin fluorescence. Essentially the same time-resolved fluorescence spectra were observed for **2**(**ZH**) and **3**(**ZH**). The fluorescence decay times of the zinc porphyrin were roughly the same as the fluorescence increase times of the free base porphyrins (Table 1). Since the fluorescence decay times are more reliable than the fluorescence increase times, we used the former values in calculating the rate of the energy transfer ($k_{EN}$) according to eqn. (2).

$$k_{EN} = 1/\tau - 1/\tau_0 \qquad (2)$$

The two calculated $k_{EN}$ values based either on eqn. (1) or on eqn. (2) display a similar trend; **1**(**ZH**) > **2**(**ZH**) ≈ **3**(**ZH**). The calculated $k_{EN}$ values based on eqn. (2) should be more reliable

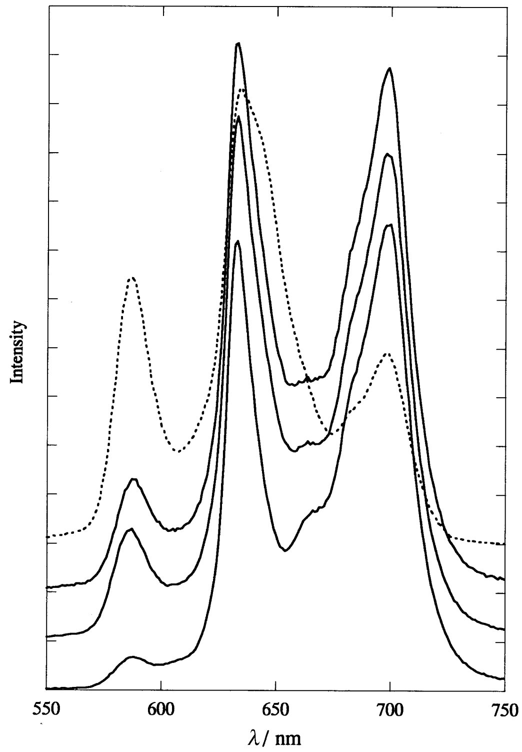


**Fig. 3** Fluorescence spectra of **1**(**ZH**) (lower solid line), **2**(**ZH**) (centre solid line), **3**(**ZH**) (upper solid line) and 1:1 mixture of **1**(**ZZ**) and **1**(**HH**) (dotted line) in THF

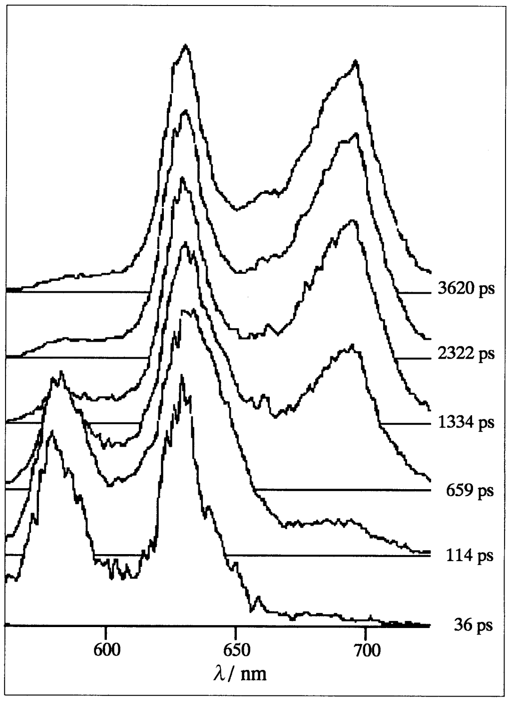


**Fig. 4** Time-resolved fluorescence spectra of **1**(**ZH**) in THF. The excitation wavelength is 532 nm. Each spectrum is normalized to the maximum intensity.

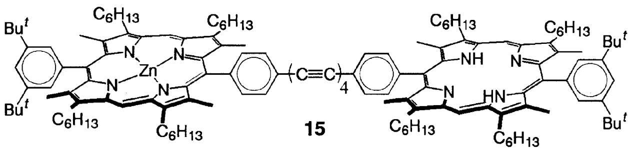
than those based on eqn. (1), since the comparison of the steady-state fluorescence intensity suffers from errors derived from the presence of fluorescent impurities.

If the energy transfer occurs only by a simple Coulombic interaction, the energy transfer rate constant can be predicted by Förster theory.[14] In this theory the rates of singlet energy transfer are expressed in terms of the orientation factor ($\kappa$), the centre-to-centre distance ($r$) between the transition dipole moment and the spectral overlap integral ($J$) [eqn. (3)].

$$k_{EN} = 8.37 \times 10^{-27} \kappa^2 r^{-6} J \tau_0^{-1} \text{ (solvent: THF, } \varphi_{ZnP} = 0.037) \quad (3)$$

The calculated values of $r$, $J$, $\kappa^2$ and energy transfer rate constant $k_{EN}$ are summarized in Table 1. The centre-to-centre distances ($r$) between the zinc porphyrin and the free base porphyrin are estimated by CPK model, assuming neither fluctuation nor bend. Orientation factors are calculated by assuming free rotation about the ethyne unit and by dynamic averaging in the case that one porphyrin is fixed at 0°, 90°, 180° and 270° about the ethyne unit and the other porphyrin rotates freely.

Comparison of the rates of the energy transfer in **1**–**3**(**ZH**) gave some insight into the mechanism of the energy transfer. First, the fact that **2**(**ZH**) and **3**(**ZH**) display almost the same $k_{EN}$ values is clear evidence for the through-bond electronic interaction in **3**(**ZH**), since the centre-to-centre distance is shorter in **2**(**ZH**) and thus a larger $k_{EN}$ value is expected through dipole–dipole interaction (Förster mechanism). Second, the through-bond electronic interaction is inferred to be weaker than the direct dipole–dipole interaction in **1**(**ZH**) since the $k_{EN}$ value observed is *ca.* one order of magnitude larger than that in **3**(**ZH**). The dipole–dipole interaction can operate even at a long distance and becomes 'steeply' important at a shorter distance between the donor and the acceptor. Thus, such through-space interaction is predominant over the through-bond interaction in **1**(**ZH**). The calculated $k_{EN}$ value for **1**(**ZH**) is one order of magnitude larger than the observed value. This may show the limitation of the theory based on the point-dipole approximation at a small distance as reported previously.[3] Comparison of the rate of the energy transfer of the linear dimer **3**(**ZH**) ($k_{EN} = 5.7 \times 10^8$ s$^{-1}$; $r = 26.2 \times 10^{-10}$ m) with that of the diphenylpolyyne-bridged hybrid dimer **15** ($k_{EN} = 1.9 \times 10^9$ s$^{-1}$; $r = 27.0 \times 10^{-10}$ m)[4] indicates lower ability of a 1,4-bis(phenylethynyl)phenylene bridge in mediating the through-bond electronic interactions than that of diphenylpolyyne bridges of analogous length.[15]



**15**

As an extension of this model study, the synthesis of the related hybrid diporphyrins for study of intramolecular electron transfer is now in progress, since the electron exchange interaction is more important in electron transfer reactions. Bis(phenylethynyl)phenylene bridges are useful in keeping donors and acceptors at well-defined geometry, and are capable of mediating the through-bond electronic interactions.

## Experimental

UV–VIS spectra were recorded on a Hitachi 150-20 spectrometer and steady-state fluorescence spectra were taken on a Shimadzu RF-5300PC spectrofluorometer. $^1$H NMR spectra were recorded on a JEOL JNM EX-400 spectrometer, and coupling constants ($J$) are given in Hz. Mass spectra were recorded on JEOL HX-100 and AX-500 spectrometers. For porphyrin compounds, the positive-FAB ionization method was used, accelerating voltage 10 kV, Xe atom as the primary ion source, and a mixture of 3-nitrobenzyl alcohol–$CHCl_3$ as the FAB matrix. IR spectra were recorded on a Shimadzu FTIR-8100 spectrometer. Fluorescence lifetimes were measured on $10^{-7}$ M air-saturated solutions with a picosecond timecorrelated single photon counting system.[16] Solvents and reagents were purified by standard methods before use.

**1,2-Bis[4-(4,4-dimethyl-2,6-dioxan-1-yl)phenylethynyl]benzene 5**
4-(4,4-Dimethyl-2,6-dioxan-1-yl)phenylacetylene **4** (1.30 g, 6 mmol) and 1,2-diiodobenzene (0.99 g, 3 mmol) were dissolved in dry triethylamine.[12] Pd(OAc)$_2$ (28 mg), triphenylphosphine (66 mg), and a small amount of PdCl$_2$(PPh$_3$)$_2$ were added, and the mixture was refluxed under Ar for 2 h, then stirred overnight at room temp. The mixture was poured into 2 M HCl and extracted with benzene, washed with aqueous NaHCO$_3$, and dried over anhydrous Na$_2$SO$_4$. The product was purified by silica gel column chromatography with benzene, recrystallized from THF–hexane. Yield 340 mg, 22%; white powder, mp 194 °C (Found: C, 80.41; H, 6.71. $C_{34}H_{34}O_4$ requires C, 80.60; H, 6.76%); $\nu_{max}$/cm$^{-1}$ 2951m, 2857m, 1385m, 1096s, 1018m and 831m; $\delta_H$(CDCl$_3$) 7.57 (4 H, d, *J* 8.3, ArH), 7.56 (2 H, dd, *J* 5.4 and 3.9, centre-ArH), 7.49 (4 H, d, *J* 8.3, ArH), 7.30 (2 H, dd, *J* 5.6 and 3.2, centre-ArH), 5.40 (2 H, s, acetal), 3.78 (4 H, d, *J* 11.2, CH$_2$), 3.66 (4 H, *J* 10.3, d, CH$_2$), 1.30 (6 H, s, Me) and 0.80 (6 H, s, Me); *m*/*z* 506.2445 (Calc. 506.2457 for $C_{34}H_{34}O_4$).

**1,3-Bis[4-(4,4-dimethyl-2,6-dioxan-1-yl)phenylethynyl]benzene 6**
The synthetic procedure was the same as for **5** except for using 1,3-diiodobenzene instead of 1,2-diiodobenzene. Yield 395 mg, 26%; pale-yellow powder; mp 231 °C (Found: C, 80.26; H, 6.81. $C_{34}H_{34}O_4$ requires C, 80.60; H, 6.76%); $\nu_{max}$/cm$^{-1}$ 2953m, 2853m, 1385m, 1100s, 1021m and 831m; $\delta_H$(CDCl$_3$) 7.72 (1 H, s, centre-ArH), 7.54 (4 H, d, *J* 8.3, ArH), 7.50 (4 H, d, *J* 8.3, ArH), 7.48 (2 H, d, *J* 6.4, centre-ArH), 7.33 (1 H, t, *J* 7.6, centre-ArH), 5.40 (2 H, s, acetal), 3.78 (4 H, d, *J* 11.2, CH$_2$), 3.66 (4 H, d, *J* 10.74, CH$_2$), 1.30 (6 H, s, Me) and 0.81 (6 H, s, Me); *m*/*z* 506.2446 (Calc. 506.2457 for $C_{34}H_{34}O_4$).

**1,4-Bis[4-(4,4-dimethyl-2,6-dioxan-1-yl)phenylethynyl]benzene 7**
The synthetic procedure was the same as for **5** except for using 1,4-diiodobenzene instead of 1,2-diiodobenzene. Yield 477 mg, 31%; white powder; mp 305 °C (Found: C, 80.46; H, 6.82. $C_{34}H_{34}O_4$ requires C, 80.60; H, 6.76%); $\nu_{max}$/cm$^{-1}$ 2955m, 2853m, 1383m, 1102s, 1019m, 837m and 814m; $\delta_H$(CDCl$_3$) 7.54 (4 H, d, *J* 8.3, ArH), 7.50 (4 H, d, *J* 8.3, ArH), 7.50 (4 H, s, centre-ArH), 5.40 (2 H, s, acetal), 3.78 (4 H, d, *J* 11.2, CH$_2$), 3.66 (4 H, d, *J* 11.2, CH$_2$), 1.30 (6 H, s, Me) and 0.81 (0.81, s, Me); *m*/*z* 506.2501 (Calc. 506.2457 for $C_{34}H_{34}O_4$).

**1,2-Bis(4-formylphenylethynyl)benzene 8**
A solution of **5** (203 mg, 0.4 mmol) in CH$_2$Cl$_2$ (20 ml) was stirred overnight with 50% trifluoroacetic acid (20 ml) at 0 °C. The solution was washed with saturated NaHCO$_3$ solution and dried over Na$_2$SO$_4$. Product was recrystallized from THF–hexane. Yield 103 mg, 77%; pale-yellow powder; mp 154 °C (Found: C, 85.95; H, 4.18. $C_{24}H_{14}O_2$ requires C, 86.21; H, 4.22%); $\lambda_{max}$(THF)/nm 302 ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 71 000) and 333 (37 000); $\nu_{max}$/cm$^{-1}$ 2361m, 1698s, 1603m, 1210m and 828m; $\delta_H$(CDCl$_3$) 10.04 (2 H, s, CHO), 7.88 (4 H, d, *J* 7.8, ArH), 7.71 (4 H, d, *J* 8.3, ArH), 7.62 (2 H, dd, *J* 5.6 and 3.2, centre-ArH) and 7.40 (2 H, dd, *J* 5.9 and 3.4 centre-ArH); *m*/*z* 334.0996 (Calc. 334.0994 for $C_{24}H_{14}O_2$).

**1,3-Bis(4-formylphenylethynyl)benzene 9**
The synthetic procedure was the same as for **8**. Yield 113 mg, 85%; pale-yellow powder; mp 183 °C (Found: C, 85.98; H, 4.27. $C_{24}H_{14}O_2$ requires C, 86.21; H, 4.22%); $\lambda_{max}$(THF)/nm 308 ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 52 000) and 325 (49 000); $\nu_{max}$/cm$^{-1}$ 2361m, 1688s, 1603m, 1210m and 824m; $\delta_H$(CDCl$_3$) 10.04 (2 H, s, CHO), 7.89 (4 H, d, *J* 8.3, ArH), 7.77 (1 H, s, centre-ArH), 7.69 (4 H, d, *J* 8.3, ArH), 7.56 (2 H, d, *J* 7.6, centre-ArH) and 7.40 (1 H, t, *J* 7.6, centre-ArH); *m*/*z* 334.0990 (Calc. 334.0994 for $C_{24}H_{14}O_2$).

**1,4-Bis(4-formylphenylethynyl)benzene 10**
The synthetic procedure was the same as for **8**. This compound was hardly soluble in common organic solvents. Yield 133 mg, quant.; milky white powder; mp 270 °C (decomp.) (Found: C, 82.00; H, 4.22. $C_{24}H_{14}O_2$ requires C, 86.21; H, 4.22%); $\lambda_{max}$(THF)/nm 342 ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 55 000); $\nu_{max}$/cm$^{-1}$ 1703s, 1601m, 1206m and 828m; $\delta_H$(CDCl$_3$) 10.04 (2 H, s, CHO), 7.89 (4 H, d, *J* 7.8, ArH), 7.69 (4 H, d, *J* 8.3, ArH) and 7.57 (4 H, s, centre-ArH); *m*/*z* 334.0995 (Calc. 334.0994 for $C_{24}H_{14}O_2$).

**1,2-Bis{4-[5-(3,5-di-*tert*-butylphenyl)-2,8,12,18-tetrahexyl-3,7,13,17-tetramethyl-15-porphyrinyl]phenylethynyl}benzene 1(HH)**
Dialdehyde **8** (50 mg, 0.15 mmol), **11** (263 mg, 1.2 mmol) and **12** (513 mg, 1.5 mmol) were dissolved in dry CH$_3$CN (8 ml) and dry CH$_2$Cl$_2$ (5 ml).[4,13] Trichloroacetic acid (74 mg, 0.45 mmol) in dry CH$_3$CN (3 ml) was added and stirred at room temperature overnight under Ar in the dark. A solution of *p*-chloranil (588 mg, 2.4 mmol) in dry THF (30 ml) was added, and the mixture was stirred further for 1 d. After evaporation of the solvent, the residue was dissolved in a small amount of CHCl$_3$ and the solution was passed through a short activated alumina column. The products were separated by silica gel column chromatography with CH$_2$Cl$_2$, and recrystallized from CH$_2$Cl$_2$–MeOH. Yield 36 mg, 12% based on the amount of **8** used; violet crystals; $\lambda_{max}$(THF)/nm 408 (relative absorption intensity 1000), 506 (95), 537 (25), 576 (35) and 628 (7); $\delta_H$(CDCl$_3$) 10.13 (4 H, s, *meso*-H), 8.16 (4 H, d, *J* 8.3, ArH), 8.12 (4 H, d, *J* 8.3, ArH), 7.86 (4 H, s, ArH), 7.84–7.86 (2 H, dd, *J* 5.9 and 3.4, centre-ArH), 7.77 (2 H, s, ArH), 7.50–7.52 (2 H, dd, *J* 5.9 and 3.4, centre-ArH), 3.90 (8 H, t, *J* 7.8, Hex-1), 3.85 (8 H, t, *J* 7.8, Hex-1), 2.58 (12 H, s, Me), 2.40 (12 H, s, Me), 2.11 (8 H, p, *J* 7.6, Hex-2), 2.01 (8 H, p, *J* 7.1, Hex-2), 1.65 (8 H, m, Hex-3), 1.47 (44 H, s + m, Bu$^t$ + Hex-3), 1.40 (8 H, m, Hex-4), 1.30 (8 H, m, Hex-5), 1.15–1.20 (8 H, m, Hex-4), 1.08–1.15 (8 H, m, Hex-5), 0.82 (12 H, t, *J* 7.3, Hex-6), 0.69 (12 H, t, *J* 7.3, Hex-6) and −2.45 (4 H, br, NH); *m*/*z* 2058 (Calc. 2056 for $C_{146}H_{190}N_8$).

**Monozinc complex 1(ZH)**
To a solution of **1**(**HH**) (20 mg) in CH$_2$Cl$_2$ (20 ml) were added a few drops of a saturated MeOH solution of Zn(OAc)$_2$. After a while, the solution was washed with water, dried with anhydrous Na$_2$SO$_4$, and concentrated *in vacuo*. The products were separated by silica gel column chromatography with CH$_2$Cl$_2$, recrystallized from CH$_2$Cl$_2$–MeOH. Yield 5 mg, 25%; violet crystals; $\lambda_{max}$(THF)/nm 416 (relative absorption intensity 1000), 506 (44), 543 (50), 577 (28) and 628 (2); *m*/*z* 2120 (Calc. 2117 for $C_{146}H_{188}N_8{}^{64}Zn$).

**Bis(phenylethynyl)-1,3-phenylene-bridged dimer 2(HH)**
The synthetic procedure was the same as for **1**(**HH**). Yield 34 mg, 11% based on the amount of **9** used; violet crystals; $\lambda_{max}$(THF)/nm 409 (relative absorption intensity 1000), 506 (84), 537 (20), 576 (30) and 628 (6); $\delta_H$(CDCl$_3$) 10.25 (4 H, s, *meso*-H), 8.14 (4 H, d, *J* 7.8, ArH), 8.07 (1 H, s, centre-ArH), 7.99 (4 H, d, *J* 7.8, ArH), 7.92 (4 H, s, ArH), 7.80 (2 H, s, ArH), 7.76 (2 H, d, *J* 7.3, centre-ArH), 7.55 (1 H, t, *J* 7.6, centre-ArH), 4.00 (16 H, t + t, Hex-1), 2.58 (12 H, s, Me), 2.46 (12 H, s, Me), 2.20 (16 H, m, Hex-2), 1.74 (16 H, m, Hex-3), 1.51 (36 H, s, Bu$^t$), 1.49 (16 H, m, Hex-4), 1.38 (16 H, m, Hex-5), 0.91 (24 H, t, *J* 7.1, Hex-6) and −2.39 (4 H, br, NH); *m*/*z* 2058 (Calc. 2056 for $C_{146}H_{190}N_8$).

**Monozinc complex 2(ZH)**
The synthetic procedure was the same as for **1**(**ZH**). Yield 8 mg, 40%; violet crystals; $\lambda_{max}$(THF)/nm 417 (relative absorption intensity 1000), 506 (38), 543 (44), 577 (24) and 628 (2); *m*/*z* 2121 (Calc. 2117 for $C_{146}H_{188}N_8{}^{64}Zn$).

### 5-(3,5-Di-*tert*-butylphenyl)-15-(4-ethynylphenyl)-2,8,12,18-tetrahexyl-3,7,13,17-tetramethylporphyrin 14

3,5-Di-*tert*-butylbenzaldehyde **11** (656 mg, 3 mmol), bis(3-hexyl-4-methylpyrrol-2-yl)methane **12** (2.06 g, 6 mmol) and 4-ethynylbenzaldehyde **13** (390 mg, 3 mmol) were dissolved in dry $CH_3CN$ (32 ml) and dry $CH_2Cl_2$ (10 ml).[13] Trichloroacetic acid (74 mg, 0.45 mmol) in dry $CH_3CN$ (3 ml) was added and stirred at room temp. overnight under Ar in the dark. A solution of *p*-chloranil (2.94 g, 12 mmol) in dry THF (100 ml) was added, and the mixture was stirred further for 1 d. After evaporation of the solvent, the residue was dissolved in a small amount of $CHCl_3$ and the solution was passed through a short activated alumina column. The products were separated by silica gel column chromatography with $CH_2Cl_2$ (second fraction), recrystallized from $CH_2Cl_2$–MeOH. Yield 605 mg, 20%; violet crystals; $\delta_H$($CDCl_3$) 10.23 (2 H, s, *meso*-H), 8.07 (2 H, d, *J* 8.3, ArH), 7.91 (2 H, s, ArH), 7.89 (2 H, d, *J* 8.3, ArH), 7.80 (1 H, s, ArH), 3.98 [8 H, m(t + t), Hex-1], 3.34 (1 H, s, CCH), 2.50 (6 H, s, Me), 2.45 (6 H, s, Me), 2.17 (8 H, m, Hex-2), 1.72 (8 H, m, Hex-3), 1.50 (26 H, s + m, $Bu^t$ + Hex-4), 1.36 (8 H, m, Hex-5), 0.90 (12 H, t, *J* 7.3, Hex-6) and −2.42 (2 H, br, NH); *m*/*z* 991 (Calc. 991 for $C_{70}H_{94}N_4$).

### Bis(phenylethynyl)-1,4-phenylene-bridged dimer 3(HH)

Ethynylporphyrin **14** (100 mg, 0.1 mmol) and 1,4-diiodobenzene (10.9 mg, 0.033 mmol) were dissolved in triethylamine (7 ml).[9] $PdCl_2$ (10 mg) and $PPh_3$ (20 mg) were added, and the mixture was refluxed under Ar for 4 h, then stirred overnight at room temp. The solvent was removed *in vacuo*, the residue was dissolved in $CH_2Cl_2$ and washed with 1 M HCl, then water, dried over $Na_2SO_4$. The products were purified by silica gel column chromatography (Wakogel C-200 + Merck Kieselgel 7736, vol. 2 : 1) with $CHCl_3$ containing stabilizer (EtOH 0.4–0.9%) (second fraction), and recrystallized from $CH_2Cl_2$–MeOH. Yield 23.4 mg, 35%; violet crystals; $\lambda_{max}$(THF)/nm 411 (relative absorption intensity 1000), 506 (86), 537 (20), 576 (30) and 628 (5); $\delta_H$($CDCl_3$) 10.26 (4 H, s, *meso*-H), 8.14 (4 H, d, *J* 7.6, ArH), 7.99 (4 H, d, *J* 7.8, ArH), 7.92 (4 H, s, ArH), 7.81 (2 H, s, ArH), 7.80 (4 H, s, centre-ArH), 4.0 (16 H, m, Hex-1), 2.58 (12 H, s, Me), 2.47 (12 H, s, Me), 2.21 (16 H, m, Hex-2), 1.75 (16 H, m, Hex-3), 1.51 (36 H, s, $Bu^t$), 1.50 (16 H, m, Hex-4), 1.38 (16 H, m, Hex-5), 0.91 (24 H, t, *J* 7.3, Hex-6) and −2.40 (4 H, br, NH); *m*/*z* 2058 (Calc. 2056 for $C_{146}H_{190}N_8$).

### Monozinc complex 3(ZH)

The synthetic procedure was the same as for **1**(**ZH**). Yield 3 mg, 15%; violet crystals; $\lambda_{max}$(THF)/nm 418 (relative absorption intensity 1000), 506 (38), 544 (46), 578 (24) and 628 (2); *m*/*z* 2120 (Calc. 2117 for $C_{146}H_{188}N_8{}^{64}Zn$).

## Acknowledgements

Work at Kyoto was partly supported by Grants-in-Aid for Scientific Research (No. 07228232 and 07454249) from the Ministry of Education, Science, Sports and Culture of Japan and by Iwatani Naoji Foundation.

## References

1 R. Van Grondelle, J. P. Dekker, T. Gillbro and V. Sundstrom, *Biochim. Biophys. Acta*, 1994, **1187**, 1.

2 G. Mcdermott, S. M. Prince, A. A. Freer, A. M. Hawthornthwaite-Lawless, M. Z. Papiz, R. J. Cogdell and N. W. Isaacs, *Nature*, 1995, **374**, 517; T. Pullerits and V. Sundström, *Acc. Chem. Res.*, 1996, **29**, 381.

3 A. Osuka, K. Maruyama, I. Yamazaki and N. Tamai, *Chem. Phys. Lett.*, 1990, **165**, 392.

4 S. Kawabata, N. Tanabe and A. Osuka, *Chem. Lett.*, 1994, 1797; A. Osuka, N. Tanabe, S. Kawabata, I. Yamazaki and Y. Nishimura, *J. Org. Chem.*, 1995, **60**, 7177.

5 S. Prathapan, T. E. Johnson and J. S. Lindsey, *J. Am. Chem. Soc.*, 1993, **115**, 7519; R. W. Wagner and J. S. Lindsey, *J. Am. Chem. Soc.*, 1994, **116**, 9759; J. Seth, V. Palaniappan, T. E. Johnson, S. Prathapan, J. S. Lindsey and D. F. Bocian, *J. Am. Chem. Soc.*, 1994, **116**, 10 578; R. W. Wagner, J. S. Lindsey, J. Seth, V. Palaniappan and D. F. Bocian, *J. Am. Chem. Soc.*, 1996, **118**, 3996.

6 J. S. Lindsey, S. Prathapan, T. E. Johnson and R. W. Wagner, *Tetrahedron*, 1994, **50**, 8941; R. W. Wagner, T. E. Johnson, F. Li and J. S. Lindsey, *J. Org. Chem.*, 1995, **60**, 5266.

7 V. S.-Y. Lin, S. G. DiMagno and M. J. Therien, *Science*, 1994, **264**, 1105; P. J. Angiolillo, V. S.-Y. Lin, J. M. Vanderkooi and M. J. Therien, *J. Am. Chem. Soc.*, 1995, **117**, 12 514.

8 D. P. Arnold and L. J. Nitschinsk, *Tetrahedron*, 1992, **48**, 8781; D. P. Arnold and G. A. Heath, *J. Am. Chem. Soc.*, 1993, **115**, 12 197; J. J. Gosper and M. Ali, *J. Chem. Soc., Chem. Commun.*, 1994, 1707.

9 Pd-catalysed coupling reaction of *meso*-(ethynyl)NiOEP with 1,4-diiodobenzene was reported to give a 1,4-bis(ethynyl)phenylene bridged dimer in 60% yield, but the similar reaction with 1,2-diiodobenzene gave the corresponding 1,2-bis(ethynyl)phenylene bridged dimer in some amount which was not isolated due to thermal unstability. D. P. Arnold and L. J. Nitschinsk, *Tetrahedron Lett.*, 1993, **34**, 693; D. P. Arnold, D. A. James, C. H. L. Kennard and G. Smith, *J. Chem. Soc., Chem. Commun.*, 1994, 2131.

10 H. L. Anderson, S. J. Martin and D. D. C. Bradley, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 655; H. L. Anderson, *Inorg. Chem.*, 1994, **33**, 972.

11 F. Effenberger, H. Schlosser, P. Bauerle, S. Maier, H. Port and H. C. Wolf, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 281; N. Holl, H. Port, H. C. Wolf, H. Stobel and F. Effenberger, *Chem. Phys.*, 1993, **176**, 215; F. Wurthner, M. S. Vollmer, F. Effenberger, P. Emele, D. U. Meyer, H. Port and H. C. Wolf, *J. Am. Chem. Soc.*, 1995, **117**, 8090.

12 J. R. Weir, B. A. Patel and R. F. Heck, *J. Org. Chem.*, 1980, **45**, 4926.

13 A. Osuka, B.-L. Liu and K. Maruyama, *J. Org. Chem.*, 1993, **58**, 3582; A. Osuka, B.-L. Liu and K. Maruyama, *Chem. Lett.*, 1993, 949; A. Osuka, N. Tanabe, S. Nakajima and K. Maruyama, *J. Chem. Soc., Perkin Trans. 2*, 1996, 199.

14 T. Förster, *Discuss. Faraday Soc.*, 1959, **27**, 7.

15 Albinsson *et al.* have studied similar energy transfer reaction in diporphyrins close related to **3**(**ZH**). They found the rate of energy transfer in **3**(**ZH**) is *ca.* one-third of that in a model where the central 1,4-phenylene unit was replaced by a 9,10-anthracenyl unit. K. K. Jensen and B. Albinsson, XVI IUPAC Symposium on Photochemistry at Helsinki, 1996, abstr. p. 313.

16 I. Yamazaki, N. Tamai, H. Kume, H. Tuchiya and K. Oba, *Rev. Sci. Instrum.*, 1985, **56**, 1187.

*Paper* 6/06700J
*Received* 30*th September* 1996
*Accepted* 29*th October* 1996