# Intramolecular Singlet Excited Energy Transfer in a Zinc Porphyrin–Free-base Porphyrin Dyad Linked with an Si–Si $\sigma$ Bond

Yuki Shibano,[1] Mikio Sasaki,[2] Yutaka Kawanishi,[1] Yasuyuki Araki,[2] Hayato Tsuji,*[1,†]
Osamu Ito,*[2,††] and Kohei Tamao*[1,3]
[1]*International Research Center for Elements Science (IRCELS), Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011*
[2]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira, Aoba-ku, Sendai 980-8577*
[3]*RIKEN Frontier Research System, Wako 351-0198*

(Received May 16, 2007; CL-070534; E-mail: tsuji@chem.s.u-tokyo.ac.jp)

We have synthesized the diphenyldisilane-linked zinc porphyrin–free-base porphyrin dyad **ZnP–[Si$_2$]–H$_2$P** and measured its photophysical properties. These measurements indicate that energy transfer from the ZnP to the H$_2$P moiety occurs at the rate constant of $9.5 \times 10^9$ s$^{-1}$. The silicon–silicon bond is found to effectively mediate the singlet excited energy transfer.

Energy and electron transfer play important roles in multicomponent architectures, such as molecular logic gates, photovoltaic systems, and bioimagings. To achieve effective transfer systems, much effort has been devoted to developing organic molecular[1] and supramolecular[2] systems consisting of $\pi$-conjugated donor, acceptor, and linker, because of their synthetic accessibility and their tailorable photophysical and electronic properties. Besides the carbon $\pi$-conjugated systems, polysilane $\sigma$-conjugated systems[3,4] have drawn attention as another class of functional materials, and they have been used as donors in electron-transfer systems[5,6] as well as linkers for superexchange electron-transfer systems[7] and through-space energy-transfer systems.[8] We now report the synthesis of a zinc porphyrin–disilane–free-base porphyrin hybrid molecule (**ZnP–[Si$_2$]–H$_2$P**, Chart 1) and intramolecular singlet energy transfer (EnT) between the porphyrin moieties.

Syntheses of **ZnP–[Si$_2$]–H$_2$P** and the reference compounds shown in Chart 1 are based on Suzuki–Miyaura cross-coupling reactions between the porphyrins and the disilane moieties.[7b,7c] Details are described in Supporting Information.[9]

Figure 1a shows the steady-state UV-to-NIR absorption spectra of the dyad **ZnP–[Si$_2$]–H$_2$P** and the reference compounds **ZnP–[Si$_2$]** and **[Si$_2$]–H$_2$P** in toluene. The spectrum of the dyad is almost reproduced by the summed spectrum of those

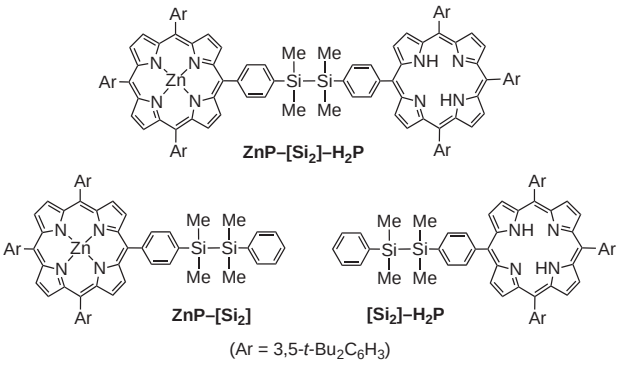


**Chart 1.**

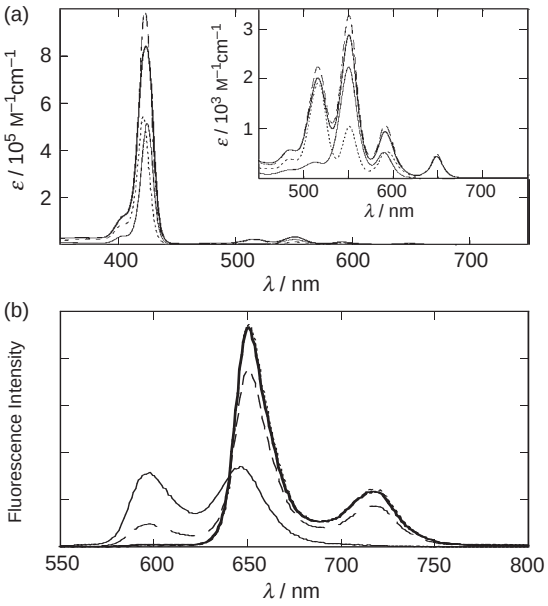


**Figure 1.** Steady-state spectra of the dyad **ZnP–[Si$_2$]–H$_2$P** (—) and the reference compounds **ZnP–[Si$_2$]** (—) and **[Si$_2$]–H$_2$P** (·····) in toluene at room temperature, together with the summed spectrum (**ZnP–[Si$_2$]** + **[Si$_2$]–H$_2$P**; – –): (a) absorption (inset; expanded spectra at the Q-band region) and (b) fluorescence spectra. The summed fluorescence spectrum is synthesized with considering the excitation ratio of the ZnP and H$_2$P moiety (3:7) at 400 nm.

of the reference compounds, suggesting that the ZnP and H$_2$P moieties of the dyad have little or no significant interaction in the ground state.

Figure 1b shows the steady-state fluorescence spectra in toluene observed with excitation at 400 nm, where the concentrations of all solutions were adjusted to give the same absorbance, and the ZnP and H$_2$P moieties of the dyad are excited in the ratio of 3:7. In the spectrum of the dyad, the emission band characteristic of the ZnP moiety at 600 nm almost disappears relative to the summed fluorescence spectrum, and the spectral shape closely resembles that of **[Si$_2$]–H$_2$P**. The relative fluorescence quantum yield of the ZnP moiety of the dyad to **ZnP–[Si$_2$]** (rel$\Phi_F$) evaluated from the fluorescence intensity ratio was 0.093. The excitation spectrum of the H$_2$P fluorescence of the dyad (Supporting Information)[9] shows good agreement with the absorption spectrum. These results imply that efficient EnT from the ZnP to the H$_2$P moieties occurs.[10] It should be also mentioned that the

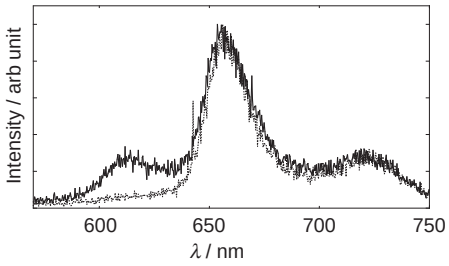


**Figure 2.** Normalized time-resolved fluorescence spectra of **ZnP–[Si$_2$]–H$_2$P** at 658 nm; 0–50 ps (solid curve) and 890–940 ps (dotted curve) with excitation at 400 nm.

spectrum of the dyad does not include any other fluorescence bands than those of **ZnP–[Si$_2$]** and **[Si$_2$]–H$_2$P**, which rules out any formation of emissive exciplexes in the excited state.

For a detailed study of the EnT, time-resolved fluorescence measurements of the dyad **ZnP–[Si$_2$]–H$_2$P** were performed. The time-resolved fluorescence spectra are shown in Figure 2, and the time profiles of the emission bands are shown in Supporting Information.[9] The time profile at 600 nm corresponding to the ZnP moiety is composed of fast [$100 \pm 2$ ps (fraction = 90%)] and slow [$5.84 \pm 0.57$ ns (fraction = 10%)] decay components, and that at 720 nm, corresponding to the H$_2$P moiety, has a rise ($91 \pm 10$ ps) and a decay ($9.35 \pm 0.32$ ns). The fast decay rate of the ZnP moiety matches the rise rate of the H$_2$P moiety, supporting the occurrence of a single-step EnT. The minor slow decay component is attributable to the tail of the H$_2$P fluorescence, considering that the fluorescence lifetimes of **ZnP–[Si$_2$]** and **[Si$_2$]–H$_2$P** are $1.99 \pm 0.02$ and $8.00 \pm 0.50$ ns, respectively. The relative fluorescence quantum yield of the ZnP moiety of the dyad to **ZnP–[Si$_2$]** based on the fluorescence lifetime (rel$\tau_F$) was 0.11. This value is almost the same as rel$\Phi_F$, supporting the view that the quenching of the ZnP moiety of the steady-state fluorescence spectrum of the dyad can be attributed exclusively to EnT to the H$_2$P moiety without any other quenching processes, such as non-emissive exciplex formation. Thus, the rate and quantum yield of EnT are estimated to be $k_{EnT} = 9.5 \times 10^9\ s^{-1}$ and about 0.90, respectively.

The optimized geometry of the dyad was obtained by PM3MM calculations as shown in Figure 3. The center-to-center distance between the two porphyrin moieties ($R_{cc}$) was estimated to be 20.0 Å. Based on this geometry and the steady-state spectrum overlap,[11] the Förster EnT rate constant was estimated to be $k_{EnT}^{Förster} = 2.4 \times 10^9\ s^{-1}$. The estimated Förster EnT rate constant is smaller than the observed EnT rate constant ($k_{EnT}$), suggesting either the presence of a closer conformer or the coexistence of through-bond (Dexter) EnT. Because the closer

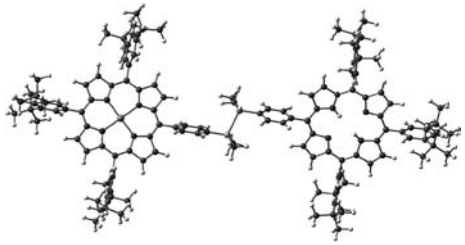

**Figure 3.** Optimized geometry of the dyad **ZnP–[Si$_2$]–H$_2$P** using PM3MM parameters.

conformer is rejected as a result of its higher energy,[12] Dexter EnT is the most plausible. Thus, the rate constant of the Dexter EnT ($k_{EnT}^{Dexter}$) is calculated to be $7.1 \times 10^9\ s^{-1}$. This is somewhat slower than that for meso-linked *meso*-tetraaryl-substituted porphyrin dyads,[8a,13,14] because of the higher LUMO energy level of the disilane linkage compared with the $\pi$-conjugated linkage found in diphenylacetylene and *N*-phenylbenzamide.[7c]

The unique point of the present dyad **ZnP–[Si$_2$]–H$_2$P** that distinguishes it from other silicon-linked donor–acceptor systems is that the EnT from one pigment to the other was definitely observed, whereas in preceding systems the charge-transfer (CT) band between two pigments and/or that between a pigment and a silicon moiety was mainly detected.[13] This is because the ZnP and H$_2$P moieties are spatially separated from each other by the diphenyldisilane linker in the present dyad, as supported by the absorption spectra and the PM3MM calculations. Thus, we have achieved effective EnT through the Si–Si $\sigma$ bond via both Förster and Dexter mechanisms for the first time.

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**References and Notes**

† Present address: Department of Chemistry, School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033.
†† Present address: RIKEN, Wako 351-0198.
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