Stacked nanocarbon photosensitizer for efficient blue light excited Eu(III) emission

Yuichi Kitagawa*1,3, Fumiya Suzue1, Takayuki Nakanishi2, Koji Fushimi1, Tomohiro Seki1, Hajime Ito1,3 & Yasuchika Hasegawa*1,3

1Faculty of Engineering, Hokkaido University, Kita-13, Nishi-8, Sapporo, Hokkaido, 060-8628, Japan.
2Faculty of Industrial Science and Technology, Tokyo University of Science, 6-3-1, Niijuku, Katsushika-ku, Tokyo 125-8585, Japan.
3Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, Sapporo, Hokkaido 001-0021, Japan.

Correspondence and requests for materials should be addressed to Y.K. (email: y-kitagawa@eng.hokudai.ac.jp) or Y.H. (email: hasegaway@eng.hokudai.ac.jp)
Supplementary Methods

Materials

Magnesium sulfate, anhydrous (> 98.0% (titration)), n-butyllithium in hexane (for organic synthesis), and chloroform-d1 (99.8%) were purchased from Kanto Chemical Co., Inc. Tetrahydrofuran (THF), super dehydrated, with a stabilizer (for organic synthesis), hydrogen peroxide (30%), bromine (Guaranteed Reagent), and dichloromethane (spectroscopic grade) were purchased from Wako Pure Chemical Industries, Ltd. Coronene (> 83.0%), chlorobenzene (> 98.0%), and chlorodiphenylphosphine (> 97.0%) were purchased from Tokyo Chemical Industry Co., Ltd.

Preparation of 1,6-dibromo-coronene

Chlorobenzene (20 ml) containing Br₂ (5.0 g, 31.3 mmol) was added dropwise to a solution of coronene (5.3 g, 17.7 mmol) in chlorobenzene (650 ml) under Ar. After stirring for 12 h at 110 °C, the solution was stirred for 3 h at RT. After decantation, the solution was filtered and washed with hot toluene and water, yielding a yellow powder.

EI-MS: m/z calcd for C$_{24}$H$_{10}$Br$_2$ [M]$^+$ = 457.91; found: 457.87.
Preparation of Gd(III) complex (Fig. 7, 5)

Dichloromethane (30 mL) containing Gd(hfa)$_3$(H$_2$O)$_2$ (100 mg, 0.12 mmol) and ligand I (40 mg, 0.057 mmol) was refluxed under stirring for 2 h at 40 °C. The reaction mixture was filtrated, and the filtrate was concentrated using a rotary evaporator. Recrystallization from CH$_2$Cl$_2$/hexane solution gave yellow crystals (Yield: 3 %, 5.0 mg).

ESI-MS: m/z calcd for C$_{121}$H$_{65}$Gd$_2$F$_{30}$O$_{14}$P$_4$ [M-hfa]$^+$ = 2751.13; found: 2751.11.

Elemental analysis (%): calcd for C$_{126}$H$_{66}$Gd$_2$F$_{36}$O$_{16}$P$_4$+CH$_2$Cl$_2$: C 50.13, H 2.25. found: C 49.72, H 2.01.
**Supplementary Table 1.** Crystal data of Eu(III) complex (2)

|                      | Eu(III) complex (2) |
|----------------------|---------------------|
| chemical formula     | C₁₂₆H₆₆Eu₂F₃₆O₁₆P₄ |
| formula weight       | 2947.61             |
| crystal color, habit | yellow, needle      |
| crystal system       | monoclinic          |
| space group          | P2₁/n               |
| a / Å                | 13.5541(6)          |
| b / Å                | 25.6188(10)         |
| c / Å                | 18.0509(8)          |
| α / deg              | 90                  |
| β / deg              | 95.759(7)           |
| γ / deg              | 90                  |
| volume / Å           | 6236.3(5)           |
| Z                    | 2                   |
| density / g cm⁻³     | 1.570               |
| Temperature / °C     | −150                |
| μ (Mo Kα) / cm⁻¹     | 12.22               |
| max 2θ / deg         | 54.972              |
| Reflections          | 14305               |
| R₁                   | 0.0698              |
| wR₂                  | 0.2023              |
Supplementary Note 1 (Structural analysis)

The continuous shape measure factor $S$ was calculated to estimate distortion degree of the coordination structure in the first coordination sphere based on the crystal structure data. The $S$ value is given by following Supplementary Equation 1.\textsuperscript{1}

$$S = \min \frac{\sum_{k}^{N} |Q_k - P_k|^2}{\sum_{k}^{N} |Q_k - Q_0|^2} \times 100 \quad (1),$$

where $Q_k$ is the vertices of an actual structure, $Q_0$ is the center of mass of an actual structure, $N$ is the number of vertices and $P_k$ is the vertices of an ideal structure. The 8-coordinated lanthanide complexes exhibit square antiprism (SAP, point group: $D_{4d}$), trigonal dodecahedron (TDH, point group: $D_{2d}$), and biaugmented trigonal prism (BTP, point group: $C_{2v}$) structures, according to evaluation of the $S$ values. From the calculation, complex 2 is categorized to be asymmetric coordination geometry of TDH ($D_{2d}$) structure ($S$(SAP) = 1.37, $S$(TDH) = 0.56, $S$(BTP) = 1.54).
The exciton coupling strength between two molecules is expressed as Supplementary Equation 2:

\[ V = \frac{|M|^2}{|r|^3} (\cos \alpha - 3 \cos \theta_1 \cdot \cos \theta_2) \]  

(2),

where \( M \) is the transition dipole moment of the monomer. The other parameters are expressed in Supplementary Figure 1. We calculated the exciton coupling strength between two ligands (1) using the orientation parameter based on the X-ray crystal structure (Fig. 3b). The calculated exciton coupling strength is positive (0.87\(|M|^2/|r|^3 > 0\)), indicating the formation of an H-type orientation.

**Supplementary Figure 1.** Oblique arrangement of two transition dipole moments.
Supplementary Note 2 (DFT calculation of ligand 1)

To clarify the electronic properties of ligand 1, its electronic absorption spectrum was calculated using the time-dependent density functional theory method with the B3LYP/6-31G(d, p) basis set using the structure of the ligand moiety identified in the single-crystal X-ray data. The characteristic weak absorption bands at longer wavelength and strong absorption bands at shorter wavelength (Supplementary Figure 3, black line) were reproduced in the calculated spectrum (Supplementary Table 2). The origins of these bands can be qualitatively explained by configuration interactions involving four $\pi$ molecular orbitals (HOMO−1, HOMO, LUMO, and LUMO+1, Supplementary Figure 2; HOMO is highest occupied molecular orbital and LUMO is lowest unoccupied molecular orbital) and four electronic configurations ((HOMO−1 $\rightarrow$ LUMO), (HOMO−1 $\rightarrow$ LUMO+1), (HOMO $\rightarrow$LUMO), and (HOMO $\rightarrow$LUMO+1)). Because of the small energy difference between HOMO and HOMO−1, a heavy admixture forms between the electronic configurations composed of these orbitals, resulting in both the intense high-energy bands and weak low-energy bands.
**Supplementary Figure 2.** Molecular orbitals of ligand 1.

**Supplementary Table 2.** Information about the main electronic configurations in the absorption bands.

|   | $\lambda_{\text{abs}}$/nm | f   | main contribution                                                                 |
|---|---------------------------|-----|-----------------------------------------------------------------------------------|
| $S_1$ | 391                      | 0.0096 | 19%($\text{HOMO-1} \rightarrow \text{LUMO}$), 23%($\text{HOMO-1} \rightarrow \text{LUMO+1}$), 44%($\text{HOMO} \rightarrow \text{LUMO}$), 14%($\text{HOMO} \rightarrow \text{LUMO+1}$) |
| $S_2$ | 370                      | 0.0580 | 47%($\text{HOMO-1} \rightarrow \text{LUMO}$), 8%($\text{HOMO-1} \rightarrow \text{LUMO+1}$), 24%($\text{HOMO} \rightarrow \text{LUMO}$), 20%($\text{HOMO} \rightarrow \text{LUMO+1}$) |
| $S_3$ | 316                      | 0.7632 | 26%($\text{HOMO-1} \rightarrow \text{LUMO}$), 56%($\text{HOMO} \rightarrow \text{LUMO+1}$) |
| $S_4$ | 310                      | 0.4108 | 54%($\text{HOMO-1} \rightarrow \text{LUMO+1}$), 26%($\text{HOMO} \rightarrow \text{LUMO}$) |
Supplementary Note 3 (Experimental data of ligand 1)

Electronic absorption and phosphorescence spectra of the ligand 1 are shown in Supplementary Figure 3. The $T_1$ level of Eu(III) complex 2 (Fig. 8, 18,900 cm$^{-1}$) was red-shifted from that of the free nanocarbon ligand 1 (Supplementary Figure 3, 19,100 cm$^{-1}$), thus delocalizing $T_1$ of the integrated photosensitized antenna through charge-resonance interactions.

Supplementary Figure 3. Electronic absorption (black line, $1.4 \times 10^{-5}$ M, CH$_2$Cl$_2$) and phosphorescence (red line, $2.0 \times 10^{-5}$ M, 2Me-THF, 90 K, delay: 50 ms, $\lambda_{ex} = 430$ nm) spectra of the ligand 1.
Supplementary Figure 4. Emission (black solid line, $\lambda_{ex} = 450$ nm) and excitation (black broken line, $\lambda_{em} = 613$ nm) spectra of Eu(III) complex (2) in CH$_2$Cl$_2$ (3.0 × 10$^{-5}$ M).
Supplementary Note 4 (Excited state dynamics)

Energy transfer from the triplet state of an organic ligand to a lanthanide ion becomes reversible when the triplet state can be thermally repopulated from the lanthanide-centered excited state, resulting in an excited state equilibrium. The lifetime measurement dependence on the oxygen concentration for the lanthanide complex is a useful method for confirming the existence of the excited state equilibrium between the T₁ state and lanthanide-centered excited state.³-⁴ This can be attributed to the existence of the T₁ and 4f-4f excited states that are sensitive and insensitive toward O₂, respectively. The existence of the excited state equilibrium manifests the dependence of the lanthanide emission lifetime (time-dependent concentration of excited ⁵D₀) on the oxygen concentration, which involves a deactivation process from the T₁ state upon reaction with oxygen molecules (Supplementary Figure 5).
**Supplementary Figure 5.** Schematic energy levels for the equilibrium processes in an Eu(III) complex and the effect of dissolved oxygen. \( k_{12} \): Forward energy transfer rate constant, \( k_{21} \): back energy transfer rate constant, \( k_{21} = k_{12} \exp(-\Delta E/RT) \).^3

The emission decay curves of Eu(III) complex (2) and (3) in non-degassed CH\(_2\)Cl\(_2\) and degassed CH\(_2\)Cl\(_2\) are shown in Supplementary Figure 6. The emission lifetime of Eu(III) complex (2) in degassed CH\(_2\)Cl\(_2\) (0.7 ms) is longer than that in non-degassed CH\(_2\)Cl\(_2\) (0.5 ms), which is caused by T\(_1\) quenching by oxygen. The results reveal the existence of equilibrium between the excited state (T\(_1\)) and the emitting level (\( ^5D_0 \)) of Eu(III) ion. The emission lifetime of Eu(III) complex 3 (Supplementary Figure 7) in degassed CH\(_2\)Cl\(_2\) (0.82 ms) is almost the same as that in non-degassed CH\(_2\)Cl\(_2\) (0.81 ms), which reveals the nonexistence of equilibration between the excited state (T\(_1\)) and the emitting level (\( ^5D_0 \)) of the Eu(III) ion. The non-emissive phosphorescence of the ligand moiety of the Eu(III) complex (2) during equilibration might be due to a very slow radiative rate constant (<
0.2 s\(^{-1}\) from the T\(_1\) state of stacked nanocarbon.

**Supplementary Figure 6.** Emission decay curves of Eu(III) complex 2 in the degassed (black line) and the non-degassed CH\(_2\)Cl\(_2\) solution (blue line) (3.0 \(\times\) 10\(^{-5}\) M, \(\lambda_{ex} = 356\) nm, \(\lambda_{em} = 613\) nm).

**Supplementary Figure 7.** Emission decay curves of Eu(III) complex 3 in the degassed (black line) and the non-degassed CH\(_2\)Cl\(_2\) solution (blue line) (1.0 \(\times\) 10\(^{-3}\) M, \(\lambda_{ex} = 356\) nm, \(\lambda_{em} = 613\) nm).
**Supplementary Note 5 (Excitation spectrum of Eu(III) complex (2))**

Excitation spectrum of Eu(III) complex (2) is shown in Supplementary Figure 8. The spectrum is similar to the absorption spectrum, and shows the characteristic strong band at around 310 nm and weak bands at 420 nm and 440 nm. The absorption peak intensity ratio ($\text{Abs}_{310\text{nm}}/\text{Abs}_{420\text{nm}} = 89$) is comparable with the excitation peak intensity ratio ($\text{Ex}_{310\text{nm}}/\text{Ex}_{420\text{nm}} = 96$), which indicates that the excitation wavelength-dependent emission quantum yields are small.

**Supplementary Figure 8.** Excitation spectrum of Eu(III) complex (2) in dilute solution ($\text{CH}_2\text{Cl}_2$, $1.0 \times 10^{-6} \text{ M}$, $\lambda_{em} = 613$ nm).
Supplementary Note 6 (Eu(III) emission excited by a blue light)

The development of red phosphors excited by a blue LED is required to fabricate high-efficiency white LEDs. Recently, the efficient red luminescence of a brick-type Eu(III) complex excited by a blue LED was achieved for the first time.\(^5\) \(I_{450}\) of Eu(III) complex 2 \((5.5 \times 10^2 \text{ M}^{-1}\text{cm}^{-1})\) is much larger than that of the previous brick-type Eu(III) complex \((0.9 \times 10^2 \text{ M}^{-1} \text{cm}^{-1})\). Although several blue-light excitable Eu(III) complexes in solid state (high concentration states to compensate a very weak absorption coefficient at 450 nm) have been reported\(^6\), the reports on blue-light excitable Eu(III) complexes in dilute solutions are very few.\(^7\) To the best of our knowledge, only two Eu(III) complexes (2 and 4) showing effective Eu(III) emission and long absorption peak wavelengths (> 440 nm) are reported till date.
Supplementary Figure 9. Fluorescence spectrum of Gd(III) complex (5) in 2Me-THF (8.0 × 10^{-6} M, \lambda_{ex} = 350 nm).
Supplementary Note 7 (Energy transfer analysis using LUMPAC)

To obtain a deeper understanding of excited state dynamics for complexes 3 and 2, we calculated the energy transfer rates between ligands and Eu(III) ions using LUMPAC software.\textsuperscript{8} The ground-state coordination geometries of the Eu(III) complexes 2 and 3 as isolated molecules (vacuum condition) were calculated using the Sparkle/RM1 model. We used the optimized structure of complex 2 and 3 to estimate the singlet and triplet excited states with the configuration interaction singles (CIS) method based on the intermediate neglect of differential overlap/spectroscopic (INDO/S) technique, as proposed in previous reports.\textsuperscript{8-13} The calculations were performed using ORCA software (v.4.2.0).\textsuperscript{14} We used a point charge (+3) to represent the trivalent europium ion. The $S_1$ energies of 3 and 2 were estimated to be 31,500 and 25,700 cm$^{-1}$, respectively. The $T_1$ energies of complexes 3 and 2 were estimated to be 20,100 and 18,900 cm$^{-1}$, respectively. Although the calculated $T_1$ energies of 3 were underestimated, they were similar to the experimental values (3: 21,700 cm$^{-1}$, 2: 18,900 cm$^{-1}$). Using the electronic structures, we calculated the total emission quantum yields and rate constants using LUMPAC. For complex 3, the calculated emission quantum yield (68%) closely resembles the experimental value (59%), which indicates the validity of the calculation. The calculated Judd-Ofelt parameters ($\Omega_2$: $28.07 \times 10^{-20}$ cm$^4$, $\Omega_4$: $6.49 \times 10^{-20}$ cm$^4$) were also similar
with the experimental results ($\Omega_2$: 29.81 $\times 10^{-20}$ cm$^{-1}$, $\Omega_4$: 7.23 $\times 10^{-20}$ cm$^{-1}$). The rate constants for the excited states of 3 are shown in Supplementary Figure 10. The energy transfer rates from $S_1$ to $^5D_4$ and $^5D_4$ to $S_1$ are $2.4 \times 10^3$ and $3.0 \times 10^{15}$ s$^{-1}$, respectively.

We also calculated the energy transfer rates from singlet states using the singlet energy calculated by DFT calculation at the B3LYP level (6-31G(d, p)).$^{15-16}$ The $S_1$ energy is estimated to be 29500 cm$^{-1}$, and the calculated energy transfer rates from singlet state to $^5D_4$ and $^5D_4$ to singlet state are $2.8 \times 10^4$ and $7.8 \times 10^9$ s$^{-1}$, respectively. The results indicate that energy transfers from $S_1$ state are ineffective. On the other hand, the energy transfer rates from $T_1$ to $^5D_1$, $T_1$ to $^5D_0$, $^5D_1$ to $T_1$, and $^5D_0$ to $T_1$ are $3.1 \times 10^6$, $3.9 \times 10^6$ s$^{-1}$, $2.1 \times 10^4$, and $6.0$ s$^{-1}$, respectively. The results indicate that energy transfers from $T_1$ state are effective. These calculations also indicate that the back energy transfer from the Eu(III) ion to ligands is suppressed by the high $T_1$ energy level (Fig. 1a). On the other hand, the calculated emission quantum yield of 2 is very low (under 0.01%), which is in contradiction with the experimentally obtained value of 36%. The calculated Judd-Ofelt parameters ($\Omega_2$: $30.27 \times 10^{-20}$ cm$^{-1}$, $\Omega_4$: $7.98 \times 10^{-20}$ cm$^{-1}$) is similar with the experimental results ($\Omega_2$: $30.41 \times 10^{-20}$ cm$^{-1}$, $\Omega_4$: $7.55 \times 10^{-20}$ cm$^{-1}$). The disparity in emission quantum yields likely results from the very slow energy transfer rates calculated for this complex ($T_1 \rightarrow ^5D_1$: $2.4 \times 10^4$ s$^{-1}$, and $T_1 \rightarrow ^5D_0$: $3.9 \times 10^1$ s$^{-1}$). The inaccuracy of this result may be
due to difficulties in precisely calculating the characteristic electronic structure of the phosphine oxide ligand containing the coronene framework as an energy donor. The electronic interactions between the coronene framework and the phosphine oxide moiety (P=O) are complex. In addition, the ligands containing coronene show a relatively high HOMO energy level (DFT calculation: -5.59 eV; Supplementary Figure 2), which induces the formation of an LMCT band with a relatively low energy level. The formation of an LMCT band with low energy (ca. 25,000 cm⁻¹) has been shown to affect the electronic character of 4f-4f excited states. We propose that the LMCT perturbation might account for some of the inaccuracy in the calculations.
Supplementary Figure 10. Energy level diagram for complex 3 showing the energy transfer processes (\(W_{ET1}: S_1 \rightarrow 5^D_4\), \(W_{ET2}: T_1 \rightarrow 5^D_1\), \(W_{ET3}: T_1 \rightarrow 5^D_0\), \(W_{BET1}: S_1 \leftarrow 5^D_4\), \(W_{BET2}: T_1 \leftarrow 5^D_1\), \(W_{BET3}: T_1 \leftarrow 5^D_0\)).
Supplementary Note 8 (Temperature dependent emission lifetime of 5)

Temperature-dependent emission lifetimes were measured for Gd(III) complex (5) in 2-Me-THF. We used Arrhenius plots of these measurements to estimate the $T_1$ lifetime of 5 at 300 K (Supplementary Figure 11, 145 K-163 K) as reported.$^{18}$ We have assumed that the decay rate does not change below 100 K ($\tau = 6.2$ s), as a similar decay rate is observed at 100 K and 110 K. The estimated $T_1$ lifetime at 300 K is 40 ms, which is approximately 50 times longer than the Eu(III) emission lifetime.

Supplementary Figure 11. Arrhenius plots of Gd(III) complex (5).
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