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Calculation of the Number of Bp Units Inside the Virtual Sphere

In order to evaluate the space containing both the metal complex in the center and Bp units that can transfer excitation energy to the central metal complex, the spatial distribution of the Bp in **Bp–PMO** was formulated using an exact numerical model. According to the crystallographic and physical chemistry data of **Bp–PMO**,[S1] the Bp units should be placed in a double-layered hexagonal unit (xy-plane). The hexagonal units are accumulated along the column axis (z-axis) and construct a hexagonal column. Finally, the hexagonal columns are bundled together, as shown in Figure S1. The steric structures are characterized by the following parameters:

L: thickness of the hexagonal unit along the z-axis.
S: length of the side of the hexagonal unit.
ν_1, ν_2: the number of Bp units that are placed in the inner and outer layers of one side of the hexagonal unit.

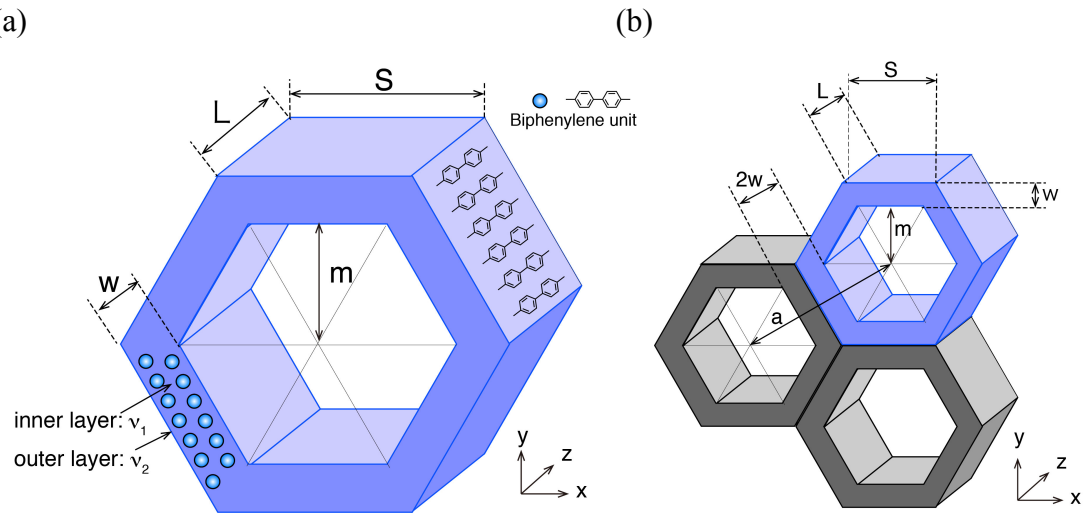

Figure S1. (a) Spatial distribution model of the Bp units in a unit cell (double layered hexagonal column structure) and (b) the hexagonal column bundle structure of **Bp–PMO**.

The numerical parameters were evaluated by using the crystallographic measurement results (a = 5.4 nm, L = 1.19 nm, and S = 3.13 nm). Using the BET pore size data (d_{BET} = 3.5 nm) obtained from measurement of the nitrogen adsorption, the thickness of the walls of the hexagonal units were estimated as w =1.08 nm.

In the hexagonal unit, the Bp units are located only in the cell wall region, and form a concentric double hexagon. Combining the density of **Bp–PMO** (d = 1.5 g cm^{-3}) and the formula weight of **Bp–PMO**: [$(O_{1.5}Si\text{-}C_{12}H_8\text{-}SiO_2H)_n$, 265.4 g mol^{-1}], the number of Bp units in one hexagonal unit was determined to be 66, and ν_1 and ν_2 were assumed to be 6 and 7, respectively.

For the calculation of the number of Bp units in a space, additional assumptions were employed as follows:

(i) The Bp units are evenly distributed in the walls of the hexagonal units (Fig. S1a).

(ii) The neighboring hexagonal units are bundled without any disorder. All Bp units are located on the common xy-plane among the bundled hexagonal units (Fig. 14).

(iii) The acceptor metal complex is located at the center of the hexagonal unit (g = 0.5).

Figure S2 shows the relationship between the number of Bp units in the virtual sphere (N_{calc}) and the radius of the sphere (R).

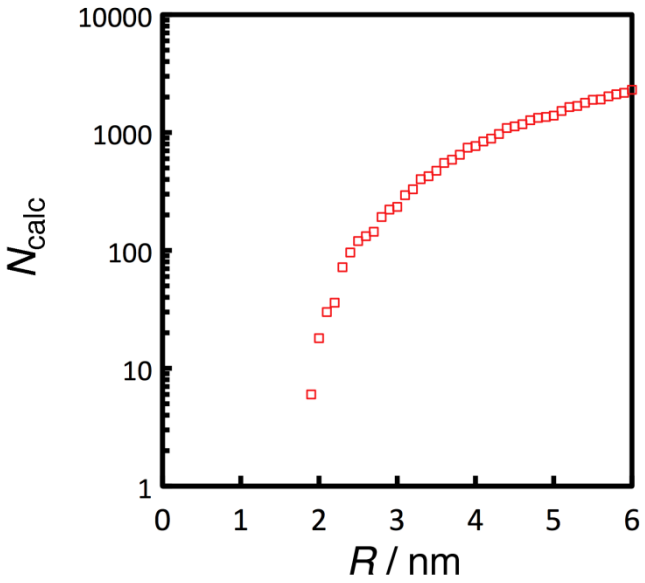

Figure S2. The number of Bp units (N_{calc}) inside of a virtual sphere with a radius R.

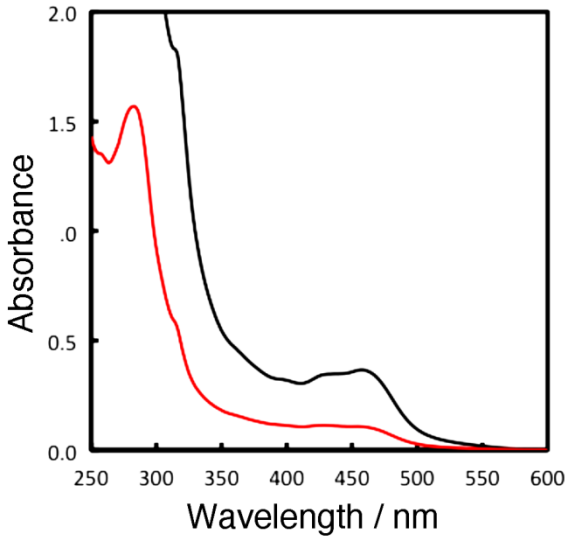

Figure S3. UV-vis absorption spectra of **Ru–Re$_5$** in an MeCN solution before the addition of **Bp–PMO** (black) and the filtrate after treatment with **Bp–PMO** (red).

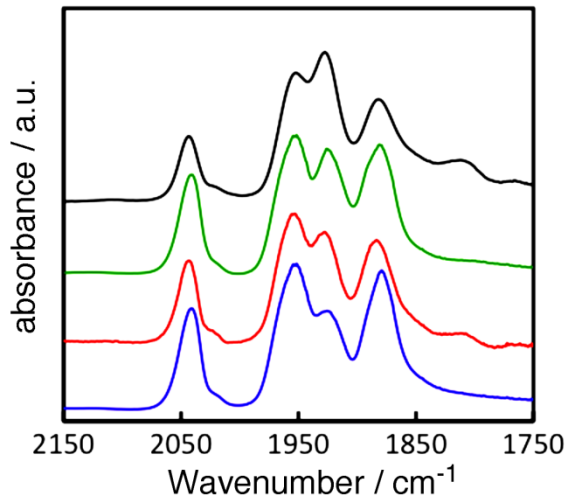

Figure S4. FT-IR spectra of **Re$_5$** (blue), **Re$_5$–Bp–PMO** (red), **Ru–Re$_5$** (green), and **Ru–Re$_5$–Bp–PMO** (black) measured in KBr disks. The peaks at 1956 and 1886 cm^{-1} are attributed to the ν_{CO} of the internal units, i.e., $[Re(dmb)(CO)_2(\text{-PP-})_2]^+$ and those at 2046, 1956, and 1930 cm^{-1} are the ν_{CO} of the edge units, i.e., $[Re(dmb)(CO)_3(\text{-PP-})]^+$.

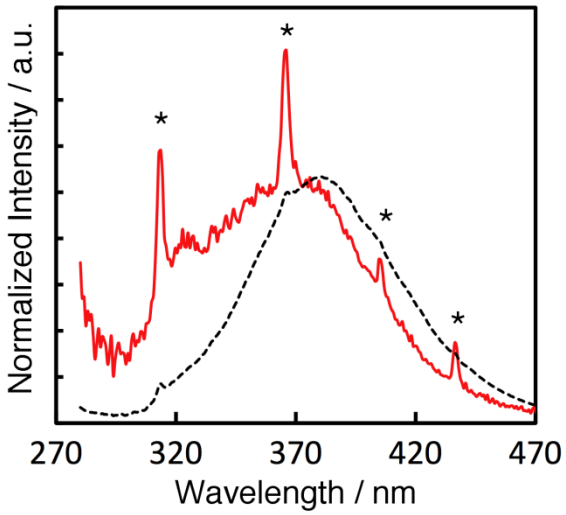

Figure S5. Normalized emission spectra of **Bp–PMO** (dashed) and **Ru–Bp–PMO** with 14.31×10^{-2} mmol g^{-1} of **Ru** (red). The asterisks indicate the emission lines from the light source.

Reference

S1. Kapoor, M. P.; Yang, Q.; Inagaki, S., "Self-Assembly of Biphenylene-Bridged Hybrid Mesoporous Solid with Molecular-Scale Periodicity in the Pore Walls" *J. Am. Chem. Soc.* **2002,** *124* (51), 15176-15177.