# **Supplementary Information**

## Sandwich Rare Earth Complexes Simultaneously Involving Aromatic

Phthalocyanine and Antiaromatic Hemiporphyrazine Ligands Showing

### **Predominant Aromatic Nature**

Wenbo Liu, Houhe Pan, Ziqian Wang, Kang Wang\*, Dongdong Qi\*, and

Jianzhuang Jiang\*

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**Table S5**. Light induced electron transferring direction (LIETD) and light harvesting efficiency (LHE) for Lu[H(Pc)(Hp)].

#### **Experimental Section**

**General Remarks:** *n*-Pentanol was distilled from sodium. Anhydrous 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), phthalonitrile, and 2,6-diaminopyridine were purchased from Aldrich. The compounds  $Eu(acac)_3 nH_2O$ ,<sup>S1</sup> Lu(Pc)(acac),<sup>S2</sup> and  $H_2Hp^{S3,S4}$  were prepared according to the literature methods. All other reagents and solvents were of reagent grade and used as received.

<sup>1</sup>H NMR spectra were recorded on a Bruker DPX 400 spectrometer in [D<sub>8</sub>]THF or [D<sub>6</sub>]DMSO. Spectra were referenced internally using the residual solvent resonance ( $\delta$  = 3.58 or 2.50 for <sup>1</sup>H NMR) relative to SiMe<sub>4</sub>. The electronic absorption spectra were obtained on Hitachi U-4100 spectrophotometer. MALDI-TOF mass spectra were taken on a Bruker BIFLEX III ultra-high-resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with 1,8,9-trihydroxyanthracene as the matrix. IR spectra were recorded as KBr pellets using a Bruker Tensor 37 spectrometer with 2 cm<sup>-1</sup> resolution. Elemental analyses were performed on an ElementarVavio El III. Crystal data for **1** were determined by X-ray diffraction analysis at 150 K, using Oxford Diffraction Gemini E system with Cu K $\alpha$  radiation  $\lambda$  = 1.5418 Å, and details of the structure refinement are given in Table S2. CCDC-1480590 and 1532414 containing the supplementary crystallographic data for this paper can be obtained free of charge from the Cambridge Crystallographic Data Centre *via*www.ccdc.cam.ac.uk/data request/cif.

Synthesis of Eu[H(Pc)(Hp)] (1): A mixture of hemiporphyrazine (44.0 mg, 0.10 mmol), Eu(Pc)(acac) nH<sub>2</sub>O (76.5 mg, 0.10 mmol), and DBU (0.1 ml) in *n*-pentanol (1 ml) was refluxed under N<sub>2</sub> atmosphere for 4 h. The reaction mixture was then cooled to room

temperature. The volatiles were removed under reduced pressure and the residue was purified by chromatography on a silica-gel column with CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (20:1 v/v) as eluent. The blue fraction containing compound **1** was collected and evaporated. Repeated chromatography followed by recrystallization from  $CH_2Cl_2$  and  $CH_3OH$  provided 1 as a blue powder in the yield of 33.5%. <sup>1</sup>H NMR (400 MHz,  $[D_8]$ THF, 298 K),  $\delta = 15.84$  (s, 1H, acidic proton), 11.99 (br, 1H, pyridine), 11.41 (br, 1H, pyridine), 11.18 (br, 1H, pyridine), 10.85 (br, 1H, pyridine), 10.77 (br, 1H, pyridine), 9.83 (br, 1H, pyridine), 8.79 (br, 8H, Pc-H), 7.99 (br, 2H, benzene H), 7.38 (br, 1H, benzene H), 7.22 (br, 1H, benzene H), 6.26 (br, 2H, benzene H), 5.94 (br, 1H, benzene H), 5.66 (br, 1H, benzene H); UV-Vis (DMSO), λmax (lgε): 330 (4.85), 350 (4.83), 562 (3.87), 630 (4.25), 688 nm (4.74); MS (MALDI-TOF): Calcd. for  $C_{58}H_{32}N_{16}Eu [M+H]^+$  1104.9; found m/z 1105.4; Elemental analysis calcd. (%) for C<sub>58</sub>H<sub>30</sub>N<sub>16</sub>Eu CH<sub>2</sub>Cl<sub>2</sub> 2CH<sub>3</sub>OH: C 58.52, H 3.22, N 17.90; found: C 58.72, H 3.06, N 18.19.

Synthesis of Lu[H(Pc)(Hp)] (2): By employing the above-mentioned synthesis procedure of compound 1 with Lu(Pc)(acac) nH<sub>2</sub>O instead of Eu(Pc)(acac) nH<sub>2</sub>O as starting material, compound 2 was isolated in the yield of 26.7%. <sup>1</sup>H NMR (400 MHz, <sup>1</sup>H NMR (400 MHz, [D<sub>8</sub>]THF, 298 K),  $\delta = 10.84$  (s, 1H, acidic proton) 9.23 (d, 2H, Pc- $\alpha$ -H), 9.18 (t, 2H, Pc- $\beta$ -H), 8.83 (m, 3H, Pc-H), 8.73 (d, 1H, Pc- $\alpha$ -H), 8.05 (m, 8H, Pc-H), 7.73 (t, 1H, benzene  $\beta$ -H), 7.66 (t, 1H, benzene  $\beta$ -H), 7.45 (m, 3H, benzene H), 7.40 (m, 2H, pyridine) ,7.24 (d, 1H, benzene  $\alpha$ -H), 7.09 (d, 1H, benzene  $\alpha$ -H), 7.05 (d, 1H, benzene  $\alpha$ -H), 6.21 (d, 2H, pyridine), 6.17 (d, 1H, pyridine), 6.01 (d, 1H, pyridine); UV-Vis (DMSO),  $\lambda_{max}$  (lg $\varepsilon$ ): 326 (4.85), 352 (4.86), 426 (4.43), 566 (4.06), 680 (4.51), 704 nm (4.55); MS (MALDI-TOF): Calcd. for C<sub>58</sub>H<sub>32</sub>N<sub>16</sub>Lu [M+H]<sup>+</sup> 1127.9; found m/z 1127.5; Elemental analysis calcd. (%) for  $C_{58}H_{30}N_{16}Lu CH_2Cl_2 CH_3OH$ : C 57.98, H 2.92, N 18.03; found: C 58.37, H 3.15, N 18.06.

Synthesis of Eu[H(Hp)<sub>2</sub>] (3): A mixture of hemiporphyrazine (88.0 mg, 0.20 mmol), Eu(acac)<sub>3</sub> nH<sub>2</sub>O (45.2 mg, 0.10 mmol), and DBU (0.1 ml) in *n*-pentanol (1 ml) was refluxed under N<sub>2</sub> atmosphere for 4 h. The reaction mixture was cooled to room temperature. The volatiles were removed under reduced pressure and the residue was purified by chromatography on a silica-gel column with CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (20:1 v/v) as eluent. The brown fraction containing compound **3** was collected and evaporated. Repeated chromatography followed by recrystallization from CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>OH provided **3** as a brown powder in the yield of 53.5%.<sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO-TBAOH, 333 K),  $\delta = 10.98$  (t, 4H, pyridine), 9.76 (b, 8H, pyridine), 6.80 (b, 8H, benzene), 6.52 (b, 8H, benzene); UV-Vis (DMSO),  $\lambda_{max}$  (lg $\varepsilon$ ): 362 (4.88), 398 nm (4.74); MS (MALDI-TOF): Calcd. for C<sub>52</sub>H<sub>30</sub>N<sub>16</sub>Eu [M+H]<sup>+</sup> 1030.9; found m/z 1031.5; Elemental analysis calcd. (%) for C<sub>52</sub>H<sub>28</sub>N<sub>16</sub>Eu 0.5CH<sub>2</sub>Cl<sub>2</sub> 2CH<sub>3</sub>OH: C 57.65, H 3.28, N 19.74; found: C 57.29, H 3.11, N 20.06.

Synthesis of Lu[H(Hp)<sub>2</sub>] (4): By employing the above-mentioned synthesis procedure of compound **3** with Lu(acac)<sub>3</sub> nH<sub>2</sub>O instead of Eu(acac)<sub>3</sub> nH<sub>2</sub>O as starting material, compound **4**was isolated in the yield of 18.0%. <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO-TBAOH, 333 K),  $\delta = 7.34$  (b, 8H, benzene), 7.30 (b, 8H, benzene), 7.20 (t, 4H, pyridine), 6.16 (b, 8H, pyridine); UV-Vis (DMSO),  $\lambda_{max}$  (lg $\varepsilon$ ): 362 (4.86), 398 nm (4.74); MS (MALDI-TOF): Calcd. for C<sub>52</sub>H<sub>30</sub>N<sub>16</sub>Lu [M+H]<sup>+</sup> 1053.9; found m/z 1053.5; Elemental analysis calcd. (%) for C<sub>52</sub>H<sub>28</sub>N<sub>16</sub>Lu 0.5CH<sub>2</sub>Cl<sub>2</sub> 2CH<sub>3</sub>OH: C 56.51, H 3.22, N 19.35; found: C 56.45, H 3.21, N 19.27.

<sup>1</sup>**H** NMR spectra of **1** and **2**. Satisfactory <sup>1</sup>H NMR spectra were obtained for **1** and **2** in  $[D_8]$ THF, Figs. S2 and S3. With the help of two-dimensional and variable temperature NMR spectroscopy, Figs. S4-S6, all the signals could be assigned to respective proton species in an unambiguous manner, Table S1. In the <sup>1</sup>H NMR spectrum of **2**, Fig. S3, the three doublets at  $\delta = 9.23$ , 8.85, and 8.73 ppm are assigned to the four Pc  $\alpha$  protons, two triplets at  $\delta = 9.18$  and 8.81 ppm to the four Pc  $\beta$  protons, and one multiplet at  $\delta = 7.73$  and 7.66, one multiplet at  $\delta = 7.45$ , and three doublets at  $\delta = 7.24$ , 7.09, and 7.05 ppm are assigned to the aromatic benzene protons of the Hp moiety. The pyridine ring protons of the Hp moiety exhibit a multiplet at  $\delta = ca$ . 7.40 and three doublets at  $\delta = 6.21$ , 6.17, and 6.01 ppm. In particular, a singlet at  $\delta = 10.84$  ppm (the integral of which to those of the Pc moiety protons is 1 : 16) is assigned to the acidic proton, revealing the protonated nature of double-decker **2** and suggesting the location of this acid proton on the Hp rather than Pc ligand.

Fig. S2 shows the <sup>1</sup>H NMR spectrum of **1** in [D<sub>8</sub>]THF at room temperature. As can be seen, **1** shows a singlet at  $\delta = 15.84$  ppm assigned to the acidic proton, six broad signals at  $\delta = 11.99$ , 11.41, 11.18, 10.85, 10.77 and 9.83 ppm due to the protons on the pyridine rings of the Hp moiety, six broad signals at  $\delta = 7.99$ , 7.38, 7.22, 6.26, 5.94 and 5.66 ppm due to the protons on the aromatic benzene ring of the Hp moiety. Owing to the rotation of two macrocyclic ligands, eight protons of the Pc moiety exhibit a broad signal at  $\delta = 8.79$  ppm, while the signals for eight protons of the Pc moiety are too broad to be observed. At lower temperatures, the ring rotation process is retarded, resulting in these broad signals were resolved into fourteen broad signals, Fig. S6.

**IR** spectra of 1-4 as well as  $H_2Hp$ . The IR spectra of 1-4 as well as  $H_2Hp$  are shown in Fig. S19. In addition to the bands associated with the Pc and Hp moieties such as the C-H wagging and torsion vibrations, the isoindole ring and the C=N aza group stretching vibrations,<sup>S5</sup> the bands at 1633-1638, 1572-1590, 1423-1430, and 1236-1242 cm<sup>-1</sup> are assigned to the stretching vibrations of the pyridine rings of the Hp moieties.<sup>S6</sup> In particular, observation of a very weak absorption at *ca*.3300 cm<sup>-1</sup> due to the asymmetrical N-H stretching vibration in the IR spectra of 1-4 not only indicates the protonated nature of these four double-decker complexes but also confirms the location of the acid proton at the Hp rather than Pc side.<sup>S7</sup>

**Location of Acid Proton.** Quantum chemistry investigations were carried out to gain insight into the special conformation of the protonated Lu[H(Pc)(Hp)]. at the level of M06-D3/6-311++G(2df,2pd)/SDD.<sup>S8</sup> Calculating results suggest that the proton locates at the pyridine N atom of Hp macrocycle due to the lowest molecular energy, Fig. S20.

Why one pyridine moiety is significantly tilted away from the metal in Eu[H(Pc)(Hp)]? Fig. 2 shows the molecular structure of Eu[H(Pc)(Hp)] (1) in two different perspective views. As can be seen, the two isoindole moieties and one pyridine moiety are almost coplanar with the corresponding N<sub>4</sub> mean plane of Hp ligand, while the other pyridine moiety is significantly tilted away from the metal with the dihedral angle

of the NC<sub>5</sub> mean plane of the pyridine moiety with respect to the corresponding  $N_4$  mean plane of Hp ligand. The reason is just the chain deformation induced by the introduction of the acid proton, Fig. S21. First, the hydrogen ion is introduced to the N1 atom of one pyridine moiety, leading to the formation of N1-H bond and the reduction of N1-M bond. Second, due to the reduction of N1-M bond, part of the electron density in the N1-M bond is transferred to the N2-M bond, leading to the enhanced and shorted N2-M bond. And at last, the shorted N2-M bond causes the rotation of pyridine ring.

**Electron Transition Manners.** To enhance our understanding of the optical properties of these novel sandwich double-decker systems, time-dependent density functional theory (TD-DFT) method<sup>S9a-g</sup> of hybrid B3LYP functional<sup>S9h</sup> was used to calculate the electronic absorption spectra of M<sup>III</sup>[H(Pc)(Hp)] and M<sup>III</sup>[H(Hp)<sub>2</sub>] using Gaussian 09 D.01 program<sup>S10a</sup> and TD-Analy 1.13.<sup>S10b</sup> A mixed basis set, which is a combination of the 6-311+G(d) basis set for C/H/N and the SDD effective core basis set for Lu, was chosen.<sup>S11</sup>

Fig. S22 shows the frontier orbital coupling of the two Hp rings in  $Lu[H(Hp)_2]$ . According to the calculation results, both the HOMO and HOMO-1 for  $Lu[H(Hp)_2]$  originate from the orbital coupling of the two HOMOs of Hp. In the case of the mixed ring double-decker Lu[H(Pc)(Hp)], the delocalized HOMO originates from the orbital coupling of the HOMO of Pc ligand with the primary contribution of 78% and the HOMO of Hp ligand with the contribution of 22%, Fig. S23.

According to previous investigation result,<sup>S12</sup> the HOMO( ${}^{1}e_{g}$ ) $\rightarrow$ LUMO( ${}^{1}e_{g}$ ) transition in the monomeric Hp macrocycle is completely forbidden due to the same

symmetry of these two frontier orbitals originating from its anti-aromatic electronic structure. After being fabricated into Lu[H(Hp)<sub>2</sub>], the double-decker molecule seems to inherit the forbidden nature for related transitions. As shown in Fig. S24 and Table S4, the very slight transition coupling between ground state  $({}^{1}A_{g})$  and exited state  $({}^{1}B_{1})$  and between ground state  $({}^{1}A_{g})$  and exited state  $({}^{1}B_{1})$  and between ground state  $({}^{1}A_{g})$  and exited state  $({}^{1}B_{2})$  leads to quite weak transition dipole moment. This in turn results in the very weak absorption bands of Lu[H(Hp)<sub>2</sub>] in the region of 550-700 nm with the light harvestingefficiency (LHE) as low as 5%, due to the transitions of HOMO-1(b\_2) $\rightarrow$ LUMO(b\_3) and HOMO(b\_3) $\rightarrow$ LUMO+1(b\_2), and in the region of 470-550 nm with the LHE of 2%, due to the transitions of HOMO-1(b\_2) $\rightarrow$ LUMO+3(a) and HOMO(b\_3) $\rightarrow$ LUMO+2(b\_2). As a total result, Lu[H(Hp)<sub>2</sub>] shows nearly a vanished absorption band beyond 470 nm. This is in full agreement with the experimental findings, Fig. S25.

In good contrast, in Lu[H(Pc)(Hp)] significantly enhanced transition coupling between ground states and exited states due to the electronic symmetry breaking induces enhanced transition dipole moment, which in turn leads to intense absorptions for this compound in comparison with those for Lu[H(Hp)<sub>2</sub>] as disclosed by experimental findings. As shown in Fig. S26 and Table S5, the broad Q band of Lu[H(Pc)(Hp)] in the region of 500-800 nm is actually contributed by the transitions from HOMO to LUMO/LUMO+1/LUMO+2/LUMO+3. Nevertheless, the nature of the light induced electron density movements between Pc and Hp macrocycles for all these transitions, including the Pc $\rightarrow$ Hp electron density moving for Region I (800-600 nm), Region III (500-400 nm), and Region IV (400-300 nm) together with the Hp $\rightarrow$ Pc moving for Region II (600-500 nm), Fig. S25, reveals the intense electronic communication between Hp and Pc macrocycles in Lu[H(Pc)(Hp)]. This endows Lu[H(Pc)(Hp)] the predominant aromatic electronic structure.

**AICD calculating results.** The the anisotropy of the induced current density (AICD) calculation at the level of M06/6-311++G(2df,2pd)/SDD<sup>S8</sup> was also carried out for the analysis of Lu[H(Pc)(Hp)]. As can be found in Fig. S27, the current ring direction of Lu[H(Pc)(Hp)] is in good agreement with the 3D-NICS results.

**The reason for the Hp change anti-aromatic nature to a weak aromatic one in 1 and 2.** As shown in previous investigations,<sup>S13</sup> the average chemical shift of hydrogens locating at the periphery of the aromatic phthalocyanine, the non-aromatic benziporphyrin, and the anti-aromatic hemiporphyrazine is 8.03, 7.65, and 7.57 ppm, respectively. As can be found, the peripheral hydrogen chemical shift in the aromatic phthalocyanine moves to the lower-field as intensely as 0.38 ppm in comparison with the benchmark of benziporphyrin, while in the anti-aromatic hemiporphyrazine only moves to the higher-field as slightly as 0.08 ppm, indicating the much more intense ring current density in phthalocyanine macrocycle than in the hemiporphyrazine one.

In compounds 1 and 2, the Pc/Hp rings can be viewed as a co-axial di-coil system. Because of the very short distance between Pc ring and Hp ring, an intense mutual inductance is induced in these two coils. In the present case of Pc-M-Hp molecule, the original clockwise ring current in Coil Pc attempts to drive an induced clockwise ring current in Coil Hp. In contrast, the original anti-clockwise ring current in Coil Hp ring attempts to drive an induced anti-clockwise ring current in Coil Pc. Because of the stronger ring current density of Coil Pc in comparison with that of Coil Hp, the Coil Hp is forced to change its moderate-strong anti-aromatic nature to a weak aromatic one.

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Scheme S1. Synthesis of  $M^{III}[H(Pc)(Hp)]$  and  $M^{III}[H(Hp)_2]$  (M=Eu, Lu).



Fig. S1. (a) Experimental and (b) simulated isotopic pattern for the molecular ion of 1. (c) Experimental and (d) simulated isotopic pattern for the molecular ion of 3. (e) Experimental and (f) simulated isotopic pattern for the molecular ion of 2. (g) Experimental and (h) simulated isotopic pattern for the molecular ion of 4 shown in the MALDI–TOF mass spectra.



Fig. S2. <sup>1</sup>H NMR spectrum of 1 recorded in  $[D_8]$ THF at 25 °C. \*denotes the solvent impurity.



Fig. S3. <sup>1</sup>H NMR spectrum of 2 recorded in  $[D_8]$ THF at 25 °C. \*denotes the solvent impurity



**Fig. S4.**  ${}^{1}H^{-1}H$  COSY spectrum of **1** recorded in [D<sub>8</sub>]THF at 25 °C. \*denotes the solvent impurity.



**Fig. S5.**  ${}^{1}H-{}^{1}H$  COSY spectrum of **2** recorded in [D<sub>8</sub>]THF at 25 °C. \*denotes the solvent impurity.



Fig. S6. Variable-temperature <sup>1</sup>H NMR spectra of 1 in  $[D_8]$ THF. \*denotes the solvent impurity.



**Fig. S7.** <sup>1</sup>H NMR spectrum of **1** recorded in  $[D_8]$ THF with adding 1.0 equiv tetrabutylammonium hydroxide at 25 °C. \*denotes the solvent impurity.



**Fig. S8.**  ${}^{1}H-{}^{1}H$  NOSY spectrum of **2** recorded in [D<sub>8</sub>]THF at 25 °C. \*denotes the solvent impurity.



**Fig. S9.**  ${}^{1}H^{-1}H$  NOSY spectrum of **1** recorded in [D<sub>8</sub>]THF at 25 °C. \*denotes the solvent impurity.



**Fig. S10.** <sup>1</sup>H NMR spectrum of **3** recorded in  $[D_6]DMSO$  with adding 1.0 equiv tetrabutylammonium hydroxide at 60 °C. \*denotes the solvent impurity.



**Fig. S11.** <sup>1</sup>H NMR spectrum of **4** recorded in  $[D_6]DMSO$  with adding 1.0 equiv tetrabutylammonium hydroxide at 60 °C. \*denotes the solvent impurity.



**Fig. S12.**  ${}^{1}\text{H}-{}^{1}\text{H}$  COSY spectrum of **3** recorded in [D<sub>6</sub>]DMSO with adding 1.0 equiv tetrabutylammonium hydroxide at 60 °C. \*denotes the solvent impurity.



**Fig. S13.**  $H^{-1}H$  COSY spectrum of **4** recorded in [D<sub>6</sub>]DMSO with adding 1.0 equiv tetrabutylammonium hydroxide at 60 °C. \*denotes the solvent impurity.



**Fig. S14.** Molecular structure of **3** in side-view (a) and top-view (b) with all the hydrogen atoms omitted for clarity. [Eu red, N blue, and C off-white].



Fig. S15. Electronic absorption spectra of 2 (solid line), 4 (short dashed line), and  $[Lu(Pc)_2][TBA]$  (dashed line) in DMSO.



Fig. S16. The negative shielding space in (a)  $H_2Hp$  and (b)  $H_2Pc$  with the isovalue of 0.7 a.u.



**Fig. S17.** The negative shielding space in (a)  $Lu[H(Hp)_2]$  and (b) Lu[H(Pc)(Hp)] with the isovalue of 0.7 a.u.



Fig. S18. The contour map of shielding space in top-view and bottom-view.



**Fig. S19.** IR spectra of 1-4 as well as  $H_2Hp$  in the region of 400-4000 cm<sup>-1</sup> with 2 cm<sup>-1</sup> resolution.



Figure S20. The N-H tautomers for Lu[H(Pc)(Hp)].



**Figure S21.** The schematic representation of the reason for one pyridine moiety is significantly tilted away from the metal in Eu[H(Pc)(Hp)].



**Fig. S22.** Frontier molecular orbitals of  $Lu[H(Hp)_2]$  with the corresponding orbitals of Hp.



**Fig. S23.** Frontier molecular orbitals of Lu[H(Pc)(Hp)] with the corresponding orbitals of Hp and Pc.



**Fig. S24.** Electron transition manner of Lu[H(Hp)<sub>2</sub>].



Fig. S25. The experimental and simulated electronic absorption spectra for 2 and 4.



Fig. S26. Electron transition manner of Lu[H(Pc)(Hp)].



Fig. S27. The induced current ring calculated by AICD program.

	Table S1.         H NMR data (0) 101         1-4.					
	Acidic proton	Рс-а-Н	Рс-β-Н	pyridine	benzene α-H	benzene β-H
1ª	15.84 (1H, s)	8. (8H	79 I, b)	11.99(1H, br) 11.41(1H, br) 11.18(1H, br) 10.85(1H, br) 10.77(1H, br) 9.83(1H, br)	7.99(2H, br) 5.94(1H, br) 5.66(1H, br)	7.38(1H, br) 7.22(1H, br) 6.26(2H, br)
2 <sup>a</sup>	10.84 (1H, s)	9.23(2H, d) 8.85(1H, d) 8.73(1H, d) 8.05(4H, m)	9.18(2H, t) 8.81(2H, t) 8.05(4H, m)	7.40(2H, m) 6.21(2H, d) 6.17(1H, d) 6.01(1H, d)	7.45(1H, d) 7.24(1H, d) 7.09(1H, d) 7.05(1H, d)	7.73(1H, t) 7.66(1H, t) 7.45(2H, m)
3 <sup>b</sup>				10.98(4H, t) 9.76(8H, b)	6.80(8H, b)	6.52(8H, b)
<b>4</b> <sup>b</sup>				7.20(4H, t) 6.16(8H, b)	7.34(8H, b)	7.30(8H, b)

**Table S1.** <sup>1</sup>H NMR data ( $\delta$ ) for **1-4**.

[a] Recorded in  $[D_8]$ THF at 25 °C. [b] Recorded in  $[D_6]$ DMSO with adding 1.0 equiv tetrabutylammonium hydroxide at 60 °C.

Compound	1	3
formula	C <sub>60</sub> H <sub>38</sub> EuN <sub>16</sub> O <sub>2</sub>	C <sub>53</sub> H <sub>32</sub> EuN <sub>16</sub> O
fw	1167.02	1060.91
crystal system	monoclinic	monoclinic
space group	$P2_{1}/c$	$P2_{1}/c$
a	9.4769(2)	9.2221(2)
b	24.0061(4)	20.0308(3)
С	21.6073(3)	22.9016(4)
α	90.00	90.00
β	100.792(2)	99.274(2)
γ	90.00	90.00
V	4828.79(15)	4175.22(13)
Ζ	4	4
$\theta$ range (deg)	3.68-62.49	2.95-62.50
$F_{\text{calcd}}(\text{g/cm}^3)$	1.605	1.688
$\mu(\text{mm}^{-1})$	9.841	11.291
F(000)	2356	2132
$R_1 (I > 2\theta)$	0.0386	0.0338
$R_{w2}$ (I>2 $\theta$ )	0.0997	0.0877
$R_{w2}$ for all	0.1038	0.0915
$GOF$ on $F^2$	1.020	1.022
CCDC number	1480590	1532414

 Table S2. Crystal data and structure refinements for compounds 1 and 3.

compound			$\lambda_{max}/nm$	$n (\log \varepsilon)$		
1	330(4.85)	350(4.83)		562(3.87)	630(4.25)	688(4.74)
2	326(4.85)	352(4.86)	426(4.43)	566(4.06)	680(4.51)	704(4.55)
3		362(4.88)	398(4.74)			
4		362(4.86)	398(4.74)			
H <sub>2</sub> Pc <sup>a</sup>	343(4.73)				656(5.08)	692(5.17)
$H_2Hp$	351(4.30)					
[Eu(Pc) <sub>2</sub> ][TBA]	335(4.99)				628(4.92)	675(4.87)

**Table S3.** Electronic absorption data of 1-4 as well as  $[Eu(Pc)_2][TBA]$  and  $H_2Hp$  in DMSO with  $H_2Pc$  in toluene.

**Table S4**. Light induced electron tranfering direction (LIETD, isovalue:  $1.0 \times 10^{-3} e au^{-3}$ ) and light harvesting efficiency (LHE) for Lu[H(Hp)<sub>2</sub>]. Electron densities move from the green area to the red area.

Wavelength:	Transitions:
(Exp.) 630 nm	HOMO $\rightarrow$ LUMO+1 (75%)
(Calc.) 636 nm	HOMO-1 $\rightarrow$ LUMO (25%)
<b>LHE</b> : 0.4%	
LIETD:	
Rearrangement in Hp	
Wavelength:	Transitions:
(Exp.) 574 nm	HOMO-1 $\rightarrow$ LUMO (75%)
(Exp.) 574 nm (Calc.) 573 nm	HOMO-1 $\rightarrow$ LUMO (75%) HOMO $\rightarrow$ LUMO+1 (25%)
(Exp.) 574 nm (Calc.) 573 nm LHE: 6%	HOMO-1 $\rightarrow$ LUMO (75%) HOMO $\rightarrow$ LUMO+1 (25%)
(Exp.) 574 nm (Calc.) 573 nm LHE: 6% LIETD:	HOMO-1 $\rightarrow$ LUMO (75%) HOMO $\rightarrow$ LUMO+1 (25%)
(Exp.) 574 nm (Calc.) 573 nm LHE: 6% LIETD: Rearrangement in Hp	HOMO-1 $\rightarrow$ LUMO (75%) HOMO $\rightarrow$ LUMO+1 (25%)
(Exp.) 574 nm (Calc.) 573 nm LHE: 6% LIETD: Rearrangement in Hp	HOMO-1 → LUMO (75%) HOMO→ LUMO+1 (25%)
(Exp.) 574 nm (Calc.) 573 nm LHE: 6% LIETD: Rearrangement in Hp	HOMO-1 → LUMO (75%) HOMO→ LUMO+1 (25%)

Wavelength:	Transitions:
(Exp.) 517 nm	HOMO $\rightarrow$ LUMO+3 (67%)
(Calc.) 501 nm	HOMO-1 $\rightarrow$ LUMO+2 (31%)
LHE: 1%	
<b>LIETD</b> : Rearrangement in Hp	
Wavelength:	Transitions:
(Exp.) 433 nm	HOMO-1 $\rightarrow$ LUMO+2 (56%)
(Calc.) 437 nm	HOMO $\rightarrow$ LUMO+3 (20%)
LHE: 33%	HOMO-2 $\rightarrow$ LUMO (17%)
LIETD:	HOMO-3 $\rightarrow$ LUMO+1 (3%)
Rearrangement in Hp	

Wavelength:	Transitions:
(Exp.) 406 nm	HOMO-2 $\rightarrow$ LUMO (71%)
(Calc.) 409 nm	HOMO-3 $\rightarrow$ LUMO+1 (7%)
LHE: 30%	HOMO $\rightarrow$ LUMO+3 (7%)
LIETD:	HOMO-1 $\rightarrow$ LUMO+2 (4%)
Rearrangement in Hp	HOMO-4 $\rightarrow$ LUMO (4%)
	HOMO-6 $\rightarrow$ LUMO (3%)
Wavelength:	Transitions:
(Exp.) 406 nm	HOMO-2 $\rightarrow$ LUMO+1 (82%)
(Calc.) 400 nm	HOMO-6 $\rightarrow$ LUMO+1 (4%)
LHE: 28%	HOMO-1 $\rightarrow$ LUMO+3 (4%)
LIETD	
	$HOMO-5 \rightarrow LUMO(3\%)$
Rearrangement in Hp	HOMO-5 → LUMO (3%) HOMO-7 → LUMO (3%)

Wavelength:	Transitions:
(Exp.) 363 nm	HOMO-5 $\rightarrow$ LUMO (33%)
(Calc.) 359 nm	HOMO-3 $\rightarrow$ LUMO (17%)
LHE: 20%	HOMO-4 $\rightarrow$ LUMO+1 (15%)
LIETD:	HOMO $\rightarrow$ LUMO+4 (10%)
Rearrangement in Hp	HOMO-6 $\rightarrow$ LUMO+1 (9%)
Wavelength:	Transitions:
Wavelength: (Exp.) 363 nm	Transitions: HOMO-6 $\rightarrow$ LUMO+1 (37%)
Wavelength: (Exp.) 363 nm (Calc.) 349 nm	Transitions: HOMO-6 $\rightarrow$ LUMO+1 (37%) HOMO-3 $\rightarrow$ LUMO (14%)
Wavelength: (Exp.) 363 nm (Calc.) 349 nm LHE: 62%	Transitions: HOMO-6 $\rightarrow$ LUMO+1 (37%) HOMO-3 $\rightarrow$ LUMO (14%) HOMO-5 $\rightarrow$ LUMO (12%)
Wavelength: (Exp.) 363 nm (Calc.) 349 nm LHE: 62% LIETD:	Transitions: HOMO-6 $\rightarrow$ LUMO+1 (37%) HOMO-3 $\rightarrow$ LUMO (14%) HOMO-5 $\rightarrow$ LUMO (12%) HOMO-1 $\rightarrow$ LUMO+5 (11%)
Wavelength: (Exp.) 363 nm (Calc.) 349 nm LHE: 62% LIETD: Rearrangement in Hp	Transitions: HOMO-6 $\rightarrow$ LUMO+1 (37%) HOMO-3 $\rightarrow$ LUMO (14%) HOMO-5 $\rightarrow$ LUMO (12%) HOMO-1 $\rightarrow$ LUMO+5 (11%) HOMO-7 $\rightarrow$ LUMO (6%)

Wavelength:	Transitions:
(Exp.) 363 nm	HOMO-3 $\rightarrow$ LUMO+1 (20%)
(Calc.) 348 nm	HOMO-5 $\rightarrow$ LUMO+1 (20%)
<b>LHE</b> : 41%	HOMO-11 $\rightarrow$ LUMO (12%)
LIETD:	HOMO-6 $\rightarrow$ LUMO (10%)
Rearrangement in Hp	HOMO-1 $\rightarrow$ LUMO+4 (9%)
	HOMO-7 $\rightarrow$ LUMO+1 (8%)
Wavelength:	Transitions:
Wavelength: (Exp.) 329 nm	Transitions: HOMO-7 $\rightarrow$ LUMO+1 (70%)
Wavelength: (Exp.) 329 nm (Calc.) 334 nm	Transitions: HOMO-7 $\rightarrow$ LUMO+1 (70%) HOMO-5 $\rightarrow$ LUMO+1 (8%)
Wavelength: (Exp.) 329 nm (Calc.) 334 nm LHE: 20%	Transitions: HOMO-7 $\rightarrow$ LUMO+1 (70%) HOMO-5 $\rightarrow$ LUMO+1 (8%) HOMO-6 $\rightarrow$ LUMO (6%)
Wavelength:         (Exp.) 329 nm         (Calc.) 334 nm         LHE: 20%         LIETD:	Transitions: HOMO-7 $\rightarrow$ LUMO+1 (70%) HOMO-5 $\rightarrow$ LUMO+1 (8%) HOMO-6 $\rightarrow$ LUMO (6%) HOMO-11 $\rightarrow$ LUMO (6%)
Wavelength: (Exp.) 329 nm (Calc.) 334 nm LHE: 20% LIETD: Rearrangement in Hp	Transitions: HOMO-7 $\rightarrow$ LUMO+1 (70%) HOMO-5 $\rightarrow$ LUMO+1 (8%) HOMO-6 $\rightarrow$ LUMO (6%) HOMO-11 $\rightarrow$ LUMO (6%) HOMO-12 $\rightarrow$ LUMO+1 (4%)

**Table S5**. Light induced electron tranfering direction (LIETD, isovalue:  $1.0 \times 10^{-3} e au^{-3}$ ) and light harvesting efficiency (LHE) for Lu[H(Hp)(Pc)]. Electron densities move from the green area to the red area.

Wavelength:	Transitions:
(Exp.) 760 nm	HOMO $\rightarrow$ LUMO (79%)
(Calc.) 701 nm	HOMO $\rightarrow$ LUMO+2 (19%)
LHE: 18%	
LIETD:	
Rearrangement in Pc	
$Pc \rightarrow Hp$	
Wavelength:	Transitions:
Wavelength: (Exp.) 707 nm	Transitions: HOMO $\rightarrow$ LUMO+2 (93%)
Wavelength: (Exp.) 707 nm (Calc.) 634 nm	Transitions: HOMO $\rightarrow$ LUMO+2 (93%) HOMO-4 $\rightarrow$ LUMO (4%)
Wavelength: (Exp.) 707 nm (Calc.) 634 nm LHE: 39%	Transitions: HOMO $\rightarrow$ LUMO+2 (93%) HOMO-4 $\rightarrow$ LUMO (4%)
Wavelength: (Exp.) 707 nm (Calc.) 634 nm LHE: 39% LIETD:	Transitions: HOMO $\rightarrow$ LUMO+2 (93%) HOMO-4 $\rightarrow$ LUMO (4%)
Wavelength: (Exp.) 707 nm (Calc.) 634 nm LHE: 39% LIETD: Rearrangement in Pc	Transitions: HOMO $\rightarrow$ LUMO+2 (93%) HOMO-4 $\rightarrow$ LUMO (4%)

Wavelength:	Transitions:
(Exp.) 673 nm	HOMO $\rightarrow$ LUMO+2 (79%)
(Calc.) 586 nm	HOMO $\rightarrow$ LUMO (17%)
LHE: 33%	HOMO-4 $\rightarrow$ LUMO+1 (3%)
LIETD:	
$Pc \rightarrow Hp$	
Wavelength:	Transitions:
(Exp.) 572 nm	HOMO $\rightarrow$ LUMO+3 (100%)
(Calc.) 526 nm	
LHE: 4%	
LIETD:	
$Pc \rightarrow Hp$	

Wavelength:	Transitions:
(Exp.) 429 nm	HOMO-1 $\rightarrow$ LUMO+3 (72%)
(Calc.) 444 nm	HOMO-3 $\rightarrow$ LUMO (21%)
LHE: 32%	
LIETD:	
Rearrangement in Hp	
$Hp \rightarrow Pc$	
Wavelength:	Transitions:
(Exp.) 355 nm	HOMO-5 $\rightarrow$ LUMO+2 (41%)
(Calc.) 347 nm	HOMO-2 $\rightarrow$ LUMO+2 (23%)
LHE: 49%	HOMO $\rightarrow$ LUMO+9 (14%)
LIETD:	HOMO-4 $\rightarrow$ LUMO+1 (5%)
Rearrangement in Hp	

