**SUPPLEMENTARY INFORMATION**

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# Target-selective degradation of proteins by porphyrins upon visible photo-irradiation

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**Porphyrin derivatives.**

All porphyrin derivatives used in the present study were purchased from Tokyo Chemical Industry Co., LTD. The list of the compound is shown as Fig. 1.

**Ptotein photo-degradation**.

Human estrogen receptor-α (hER-α), bovine serum albumin (BSA) and hen egg lysozyme (Lyso) were purchased from Sigma Co. B-100A (UVP Inc., 365 nm, 100 W) and I-Sunsun (Wacom Sunray Lamp, 75 W xenon lamp) were used as a UV lamp and a visible lamp, respectively, for the photo-irradiation. All the protein cleavage experiments were performed with each protein (1.5 μM) in a volume of 10 μL containing 20% acetonitrile in 50 mM Tris-HCl buffer (pH 8.0) at 25 °C for 2 h under irradiation of the UV lamp placed at 10 cm from the mixture. The protein-sample levels

were varied as indicated in the figure captions.

**Electrophoresis.**

SDS/polyacrylamide gel electrophoresis (SDS-PAGE) experiments were performed as reported.[1] After addition of a 4.8 μL solution containing SDS (5%, wt/vol), glycerol (27%, vol/vol), DTT (0.5%, wt/vol) and bromophenol blue (0.007%, wt/vol) to the photoirradiated samples. Gels (8% for BSA and 12% for hER-α and Lyso) were run by applying 110 V for 1.5 h for BSA or 2.5 h for hER-α and Lyso. The gels were stained with SYPRO Ruby Protein Gel Stain (Bio-Rad Lab. Inc.) for 3 h, destained in acetic acid (7%, vol/vol) and methanol (10%, vol/vol) for 0.5 h, and then washed with water. The gels were scanned with a Molecular Imager FX (Bio-Rad Lab. Inc.) and images were processed using Adobe Photoshop software. Molecular weight markers were used in each gel for calibration.

References.

1 H. Schägger and G. von Jagow, *Anal. Biochem*., 1987, **166**, 368.

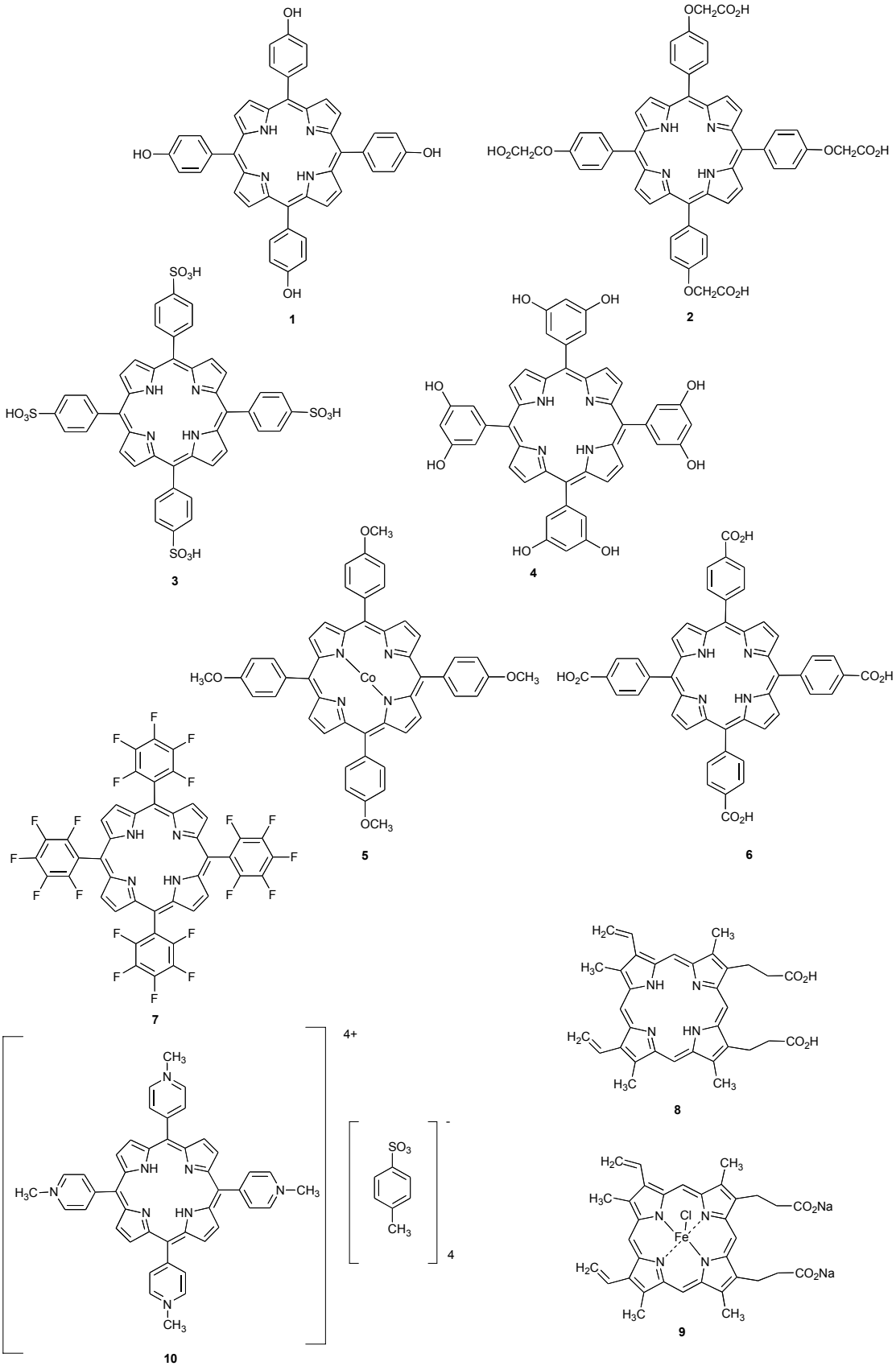


**Fig. 1** Porphyrin derivatives.

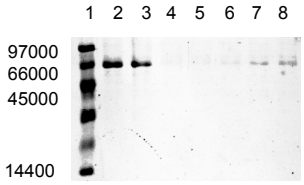


**Fig. 2** Inhibition of photo-degradation of hER-α using **1** in the presence of 17α-ethynylestradiol. hER-α (1.5 μM) was incubated with **1** (15 nM) in the presence or absence of 17α-ethynylestradiol in 20% acetonitrile/Tris-HCl buffer (pH 7.0, 50 mM) at 25°C for 2 h while irradiating with a visible wavelength lamp (diffuse sunlight, 75 W) placed 10 cm from the sample. The products were analyzed by tricine-SDS-PAGE. Lane 1, size markers; lane 2, hER-α alone; lane 3, hER-α with visible wavelength irradiation; lane 4, hER-α + **1** with irradiation; lanes 5-8, hER-α + **1** + 17α-ethynylestradiol (concentrations 15, 150, 1500 and 15000 nM, respectively) with visible wavelength irradiation.

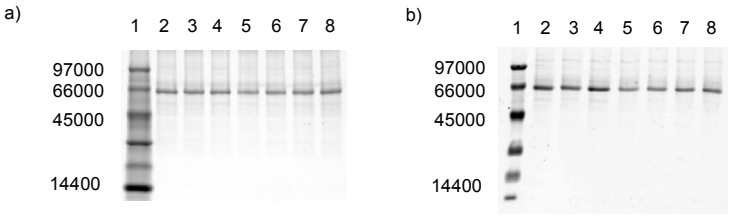


**Fig. 3** Photo-degradations of hER-α using **2** and **4** under visible wavelength irradiation. hER-α (1.5 μM) was incubated with **2** or **4** in 20% acetonitrile/Tris-HCl buffer (pH 7.0, 50 mM) at 25°C for 2 h while irradiating with a visible wavelength lamp (diffuse sunlight, 75 W) placed 10 cm from the sample. The products were analyzed by tricine-SDS-PAGE. Gels a) and b) represent **2** and **4**, respectively: lane 1, size markers; lane 2, hER-α alone; lane 3, hER-α with visible wavelength irradiation; lane 4, hER-α + each compound (15 nM) without irradiation; lanes 5-8, hER-α + each compound (concentrations 15, 5.0, 1.5 and 0.5 nM, respectively) with visible wavelength irradiation.

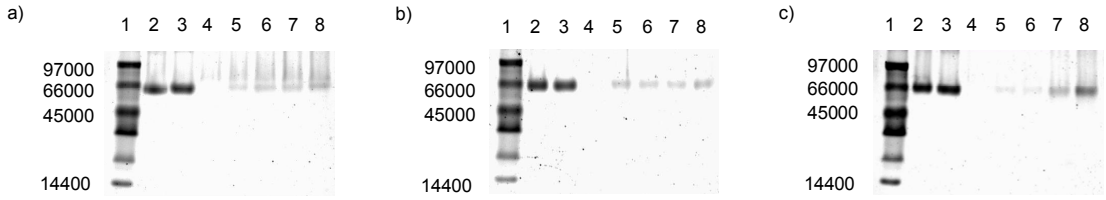


**Fig. 4** Inhibition of photo-degradations of BSA using **1** in the presence of several scavengers. BSA (1.5 μM) was incubated with **1** in 20% acetonitrile/Tris-HCl buffer (pH 7.0, 50 mM) at 25 °C for 2 h under irradiation from a VIS lamp (diffuse sunlight, 75 W) placed 10 cm from the sample, and the products were analyzed by tricine-SDS-PAGE. Gels a), b) and c) represent EtOH, KI and histidine, respectively: lane 1, size marker; lane 2, BSA alone; lane 3, BSA + each scavenger (5000 μM) with visible irradiation; lane 4, BSA + **1** (15 μM) without irradiation; lanes 5-8, BSA + **1** (15 μM) + each scavenger (concentrations 5, 50, 500 and 5000 μM, respectively) with visible irradiation.