Electronic Supplementary Information

Synthesis of covalently linked binuclear clamshell phthalocyanine by double-click reaction

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Experimental Section

General

All solvents were dried and distilled according to standard procedures. All of the reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica-gel plate (60F-254). Column chromatography was carried out on a column packed with silica gel 60N spherical neutral size 63-210 µm. ¹H NMR (200 MHz) spectra were taken on a Varian Gemini-200 spectrometer. Chemical shifts are expressed in ppm downfield from tetramethylsilane. Infrared (IR), UV-vis and steady-state fluorescence spectra were recorded on a JASCO FT/IR-200 Spectrometer, V-530 spectrometer and FP-6200 Fluorospectrometer, respectively. Quantum yields were calculated following the procedure mentioned before.¹ Fluorescence lifetimes were measured with a LaserStrobe Spectrofluorometer (Photon Technology International: http://www.pti-nj.com.) with 337 nm laser pulses from a nitrogen laser fiber-coupled to a lens-based T-formal sample compartment equipped with a stroboscopic detector. Mass spectra of MALDI-TOF were taken on a SHIMADZU Axima CFR plus. Reverse phase HPLC analyses were performed on a JASCO PU-2080 Plus using 4.6 x 250 mm Develosil ODS-HG-5 column and MD-2015 multiwavelength detector. Electrochemical experiments were carried out on a BAS 50W electrochemical analyzer (Bioanalytical Inc., West Lafayette, IN 47906, USA). Systems, Tetrabutylammonium hexafluorophosphate (TBAPF) was purchased from TCI and recrystallized from EtOH. The solvent THF (Kanto Chemical Co. Inc., tetrahydrofuran, dehydrated stabilizer free) was passed through Glass Contour Ultimate Solvent System. For CV and DPV, 3 mm

platinum was used as working electrode and platinium wire as counter electrode. Ag/AgNO₃ (0.01 M in MeCN/0.1 M TBAPF) was used as reference electrode separated by a vycor glass, and all potentials given relate to this electrode. The measurements were performed using a concentration of approximately 0.5 mM of the compounds. Zinc tri-*tert*-butyl-ethynylphthalocyaninate (2)² and 1,4-Bis(azidomethyl)benzene³ were previously synthesized.



Scheme S1 Synthesis of 1 from zinc tri-*tert*-butyl-ethynylphthalocyaninate $(2)^2$.

1,4-Bis(1-(tri-*tert*-butylphthalocyaninate zinc(II) yl)-1*H*-1,2,3-triazol-4-yl)benzene (1)

23-Ethynyl-2(3),9(10),16(17)-tri-*tert*-butylphthalocyaninate zinc (II) (114.7 mg, 0.1487 mmol), 1,3-Bis(azidomethyl)benzene (14.0 mg, 0.074 mmol) and CuI (2.4 mg, 0.0126 mmol) were heated in 0.8 mL of DMSO at 60 °C for 3 h. After cooling down to rt, the crude mixture was added with water and dil. HClaq and then filtered. The blue solids were washed with water, purified by silica gel column chromatography (hexane:dioxane=80:20 to 65:35), and finally washed with MeOH. Blue powder (102.2 mg, 80%).

 $C_{100}H_{88}N_{22}Zn_2 \\$

M.W.: 1728.70

¹H-NMR (THF-*d*₈, 200 MHz): δ 6.0-6.1 (brm, 4H), 8.6-9.6 (brm, 28H); IR (KBr): 692, 748, 763, 831, 899, 920, 1050, 1092, 1150, 1257, 1281, 1330, 1363, 1394, 1489, 1616,

2553, 2609, 2870, 2904, 2957 cm⁻¹; UV/Vis (0.5 x 10⁻⁵ M in CHCl₃): λ_{max} (log ϵ) = 349 (5.01), 681 (5.06) nm, (0.5 x 10⁻⁵ M in toluene): λ_{max} (log ϵ)= 348 (4.95), 684 (5.14) nm, Fluorescence (CHCl₃): λ_{em} = 687, 710 nm, Φ_{f} = 0.010, (toluene): λ_{em} = 685 nm, λ_{f} = 0.054.

MALDI-TOF MS (dithranol): m/z = 1726-1736 ([M+H⁺], isotopic pattern)



HPLC: (H₂O:MeCN:THF=4:16:80, 0.2 mL/min), t_R=13.6 min.





Figure S1 UV-Vis Spectra of 1 in toluene, $0.5 \ge 10^{-4}$ to $0.5 \ge 10^{-6}$ M (bold to thin lines). Dashed line: $1.0 \ge 10^{-4}$ M with 1 vol% of pyridine.



Figure S2 UV-Vis Spectra of **2** in toluene, $1.0 \ge 10^{-4}$ to $1.0 \ge 10^{-6}$ M (bold to thin lines). Dashed line: $1.0 \ge 10^{-4}$ M with 1 vol% of pyridine.



Figure S3 Steady-state fluorescence Spectra of **1** in toluene (Solid line) and 1 % of pyridine (dotted line).



Figure S4 Steady-state fluorescence Spectra of **2** in toluene (Solid line) and 1 % of pyridine (dotted line).

REFERENCES

- (1) J. Fu, X.-Y. Li, D. K. P. Ng, C. Wu, *Langmuir* 2002, 18, 3843.
- (2) E. M. Maya, P. Vázquez, T. Torres, Chem. Eur. J., 1999, 5, 2004.
- (3) J. R. Thomas, X. Liu, P. J. Hergenrother, J. Am. Chem. Soc. 2005, 127, 12434.