Electronic supplementary information (ESI)

1. Supporting Experimental

1.1. Synthesis

2,5-Bis-trimethylsilylethynyl-3-hexylthiophene (1). A mixture of 2,5-dibromo-3-hexylthiophene (1.0 g, 3.066 mmol), trimethylsilylacetylene (0.7 g, 7.0 mmol), CuI (0.035 g, 0.18 mmol), PPh₃ (0.11 g, 0.37 mmol), and triethylamine (10 mL) was stirred in 5 mL of anhydrous THF. After bubbling with N₂ for 20 min, Pd(PPh₃)₂Cl₂ (0.10 g, 0.14 mmol) was added and the mixture was heated overnight at 50 °C. The reaction mixture was poured into brine and extracted with chloroform. The organic layer was washed with brine several times and dried over NaSO₄. After the removal of the solvent, the crude product was purified with alumina column chromatography using hexane as an eluent to yield intermediate 1 as colorless oil. ¹H NMR (400MHz, CDCl₃): 0.27 (18H, s, CH₃-Si), 0.90 (3H, t, CH₃-), 1.28 (6H, m, -CH2-), 1.56 (2H, m, -CH2-), 2.66 (2H, t, -CH2-thiophene), 6.93 (1H, s, thiophene-H).

Tri-tert-butyl-iodophthalocyaninato zinc(II) (2). A mixture of 4-tert-butylphthalonitrile (0.4 g, 2.17 mmol) and 4-iodophthalonitrile (0.183 g, 0.72 mmol) was refluxed in DMAE (1.5mL) under nitrogen for 15h in the presence of ZnCl₂ (0.100 g, 0.72 mmol). The mixture was concentrated under reduced pressure. The blue solid was subsequently extracted with CH₂Cl₂ and then washed with water. The corresponding tri-tert-butyl iodophthalocyaninato zinc(II) (2) was taken out of tetra-tert-butyl phthalocyaninato zinc(II), di-tert-butyl-diiodophthalocyaninato zinc(II), and tert-
butyl-triiodophthalocyaninato zinc(II) by chromatography (silica gel, hexane/dioxane 4:1). The compound was then washed with hot MeOH after chromatography. $^1$H NMR (400MHz, CDCl$_3$): 8.7-7.5 (br, ArH), 1.7-1.6 [br, C(CH$_3$)$_3$]; MALDI: 870.155 (M$^+$).

**Pc-thiophene-Pc triad (3).** To a stirred solution of 1 $^1$S$_1$ (8 mg, 0.02 mmol) in dry THF (1 mL) was added a solution of 1 M tetrabutylammonium fluoride (TBAF) (6.5 mg, 0.024 mmol) under a nitrogen atmosphere, which was accompanied by an immediate color change to dark brown. After the completion of the reaction, tri-tert-butyl-iodophthalocyaninato zinc(II) ($^2$S$_2$) (20 mg, 0.023 mmol), CuI (catalytic amount), PPh$_3$ (3 mg, 0.011 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (1.5 mg, 0.0022 mmol) and triethylamine (4 mL) were added and the mixture was then refluxed at 70 °C under a N$_2$ atmosphere for 1 day. After the completion of the reaction, the mixture was concentrated under reduced pressure. The green solid was extracted with CH$_2$Cl$_2$ and then washed with water. The corresponding Pc-triad 3 was purified by chromatography (silica gel, hexane/dioxane 4:1). $^1$H NMR (400MHz, CDCl$_3$): 7.75 (br, ArH), 2.04 [s, CH$_2$], 1.6 [br, C(CH$_3$)$_3$], 0.85 (br, CH$_2$CH$_2$ CH$_2$CH$_2$CH$_3$)]; We could not obtained good quality of $^1$H NMR of Pc-triad 3 from broadening and overlap of the aromatic signals, which may be attributed to either extended conjugation or the existence of more than one isomers (from the position of t-Bu),$^2$S$_2$, $^3$S$_3$ however, a single peak in MALDI data indicating the purity of Pc-triad 3, MALDI: 1703.534 (M$^+$).
1.2. Property characterization

The synthesis of compounds was characterized using MALDI-TOF measurements, with α-Cyano-4-hydroxy cinnamic acid as matrix (Korea Basic Science Institute, KBSI). The UV and photoluminescence emission spectra were obtained from Lambda 7 spectrometer (Perkin Elmer) and LS-45 spectrofluorophotometer (Perkin Elmer), respectively, with a cuvette of 1 cm path-length. SEM images were analyzed using a FE-SEM apparatus (JEOL Scanning Microscope JSM-6700F). FT-IR spectra were collected by an Avatar 370 FT-IR spectrometer, after the samples were vacuum-dried for a week. XPS measurements were performed on an ESCALAB 250 XPS system (Thermo Fisher Scientific/U.K., KBSI) with Al Kα radiation (1486.6 eV) as the X-ray source.
2. Supporting Data

Fig. S1. Mass spectrum of Pc-triad 3.
Fig. S2. $^1$H NMR spectrum of Pc-triad 3.
Fig. S3. Mass spectrum of spectrum of 2.
Fig. S4. $^1$H NMR spectrum of 2.
Fig. S5. $^1$H NMR spectrum of 1.
Fig. S6. Fluorescence intensity of 3 at 694 nm as a function of PA concentration.

Determination of the detection limit was carried out by fluorescence titration of compound 3 with PA and then fluorescence intensity as a function of PA was plotted. From the graph, the concentration of PA, at which there was a sharp change in the fluorescence intensity was multiplied with the concentration of 3.

Equation used for calculating detection limit (DL) is given as follows: 54

\[ DL = C_L \times C_T \]

Where, \( C_L \) = Conc. of Ligand; \( C_T \) = Conc. of Titrant at which change observed.

Thus, detection limit for PA is calculated:

\[ D_L = 10 \times 10^{-6} \text{ M} \times 0.07 \text{ equiv.} = 7.0 \times 10^{-7} \text{ M} \]
Reference


