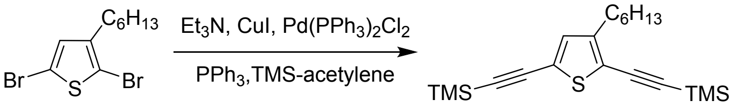
Electronic supplementary information (ESI)

1. Supporting Experimental

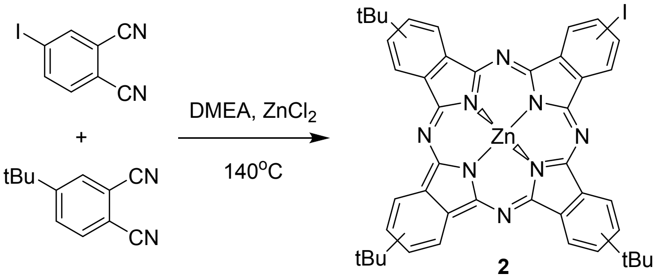
1.1. Synthesis

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), PPh_3 (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, $Pd(PPh_3)_2Cl_2$ (0.10 g, 0.14 mmol) was added and the mixture was heated overnight at 50 ^{o}C. The reaction mixture was poured into brine and extracted with chloroform. The organic layer was washed with brine several times and dried over $NaSO_4$. 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. ^{1}H NMR (400MHz, $CDCl_{3,}$): 0.27 (18H, s, CH_3-Si), 0.90 (3H, t, CH3-), 1.28 (6H, m, -CH2-), 1.56 (2H, m, -CH2-), 2.66 (2H, t, -CH2-thiopene), 6.93 (1H, s, thiophene-H).



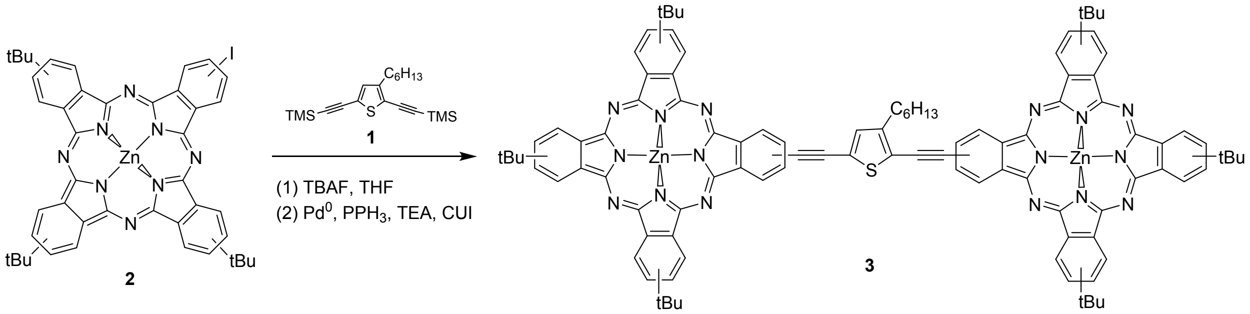
1

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 $ZnCl_2$ (0.100 g, 0.72 mmol). The mixture was concentrated under reduced pressure. The blue solid was subsequently extracted with CH_2Cl_2 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)+.



2

Pc-thiophene-Pc triad (3). To a stirred solution of **1** [S1] (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**) [S2] (20 mg, 0.023 mmol), CuI (catalytic amount), PPh_3 (3 mg, 0.011 mmol), $Pd(PPh_3)_2Cl_2$ (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_2Cl_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_2CH_2 $CH_2CH_2CH_3$)]; 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),[S2, S3] 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

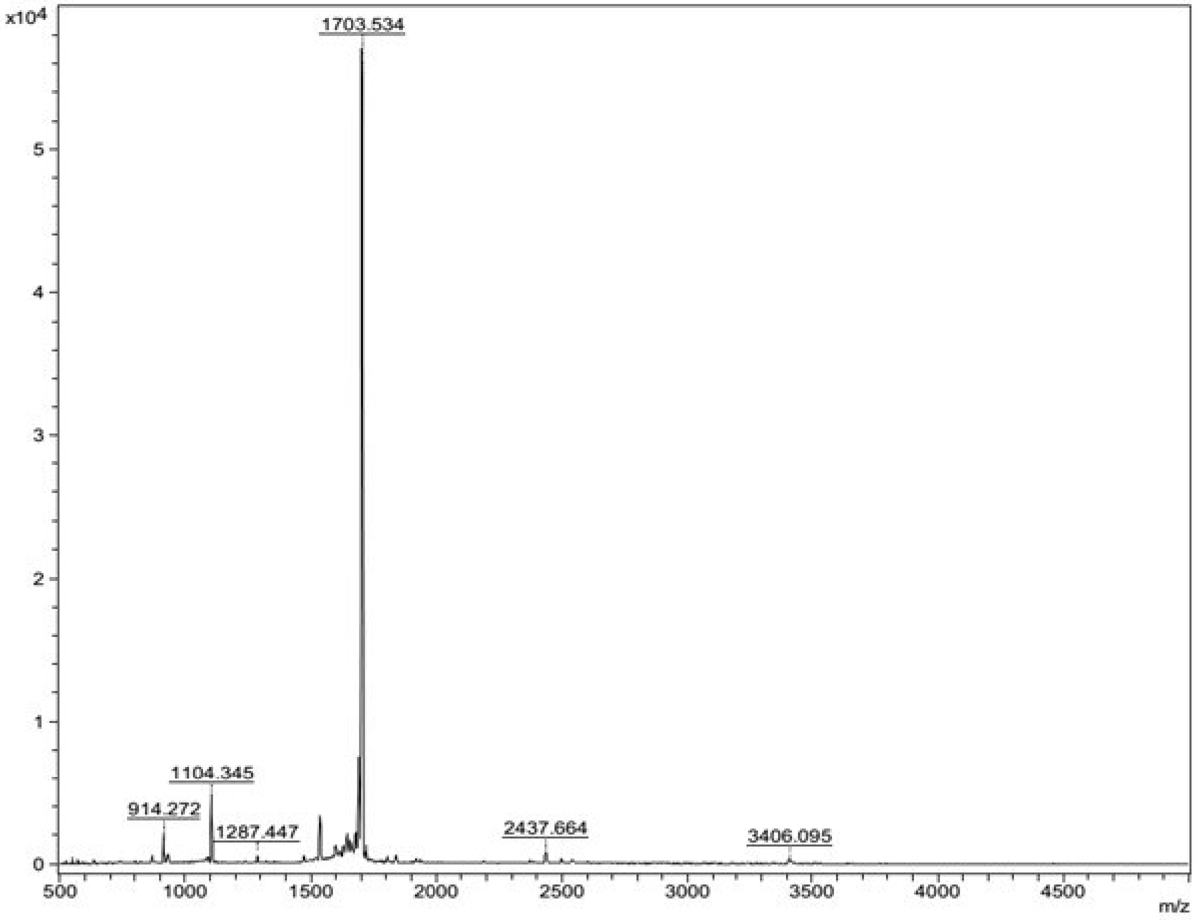


Fig. S1. Mass spectrum of Pc-triad **3**.

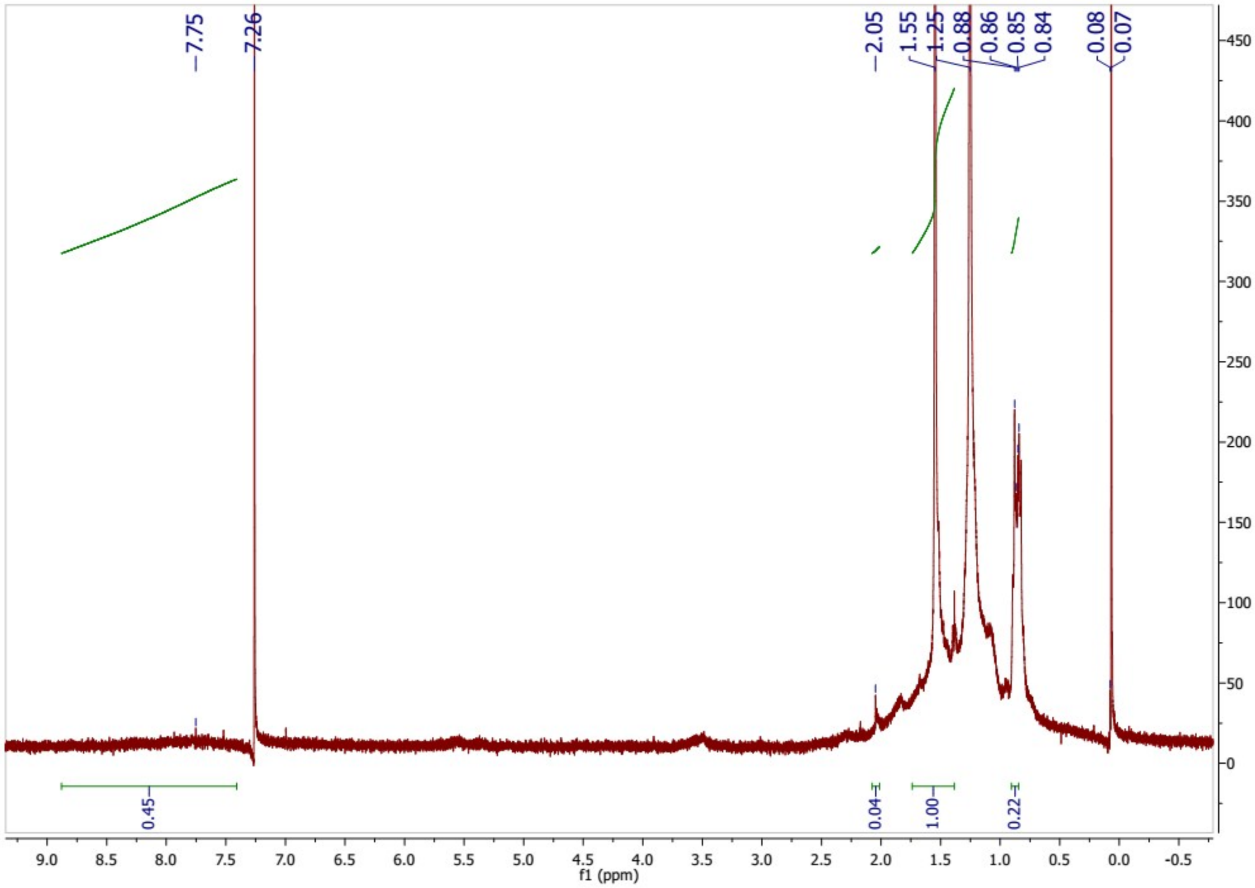


Fig. S2. ^{1}H NMR spectrum of Pc-triad **3**.

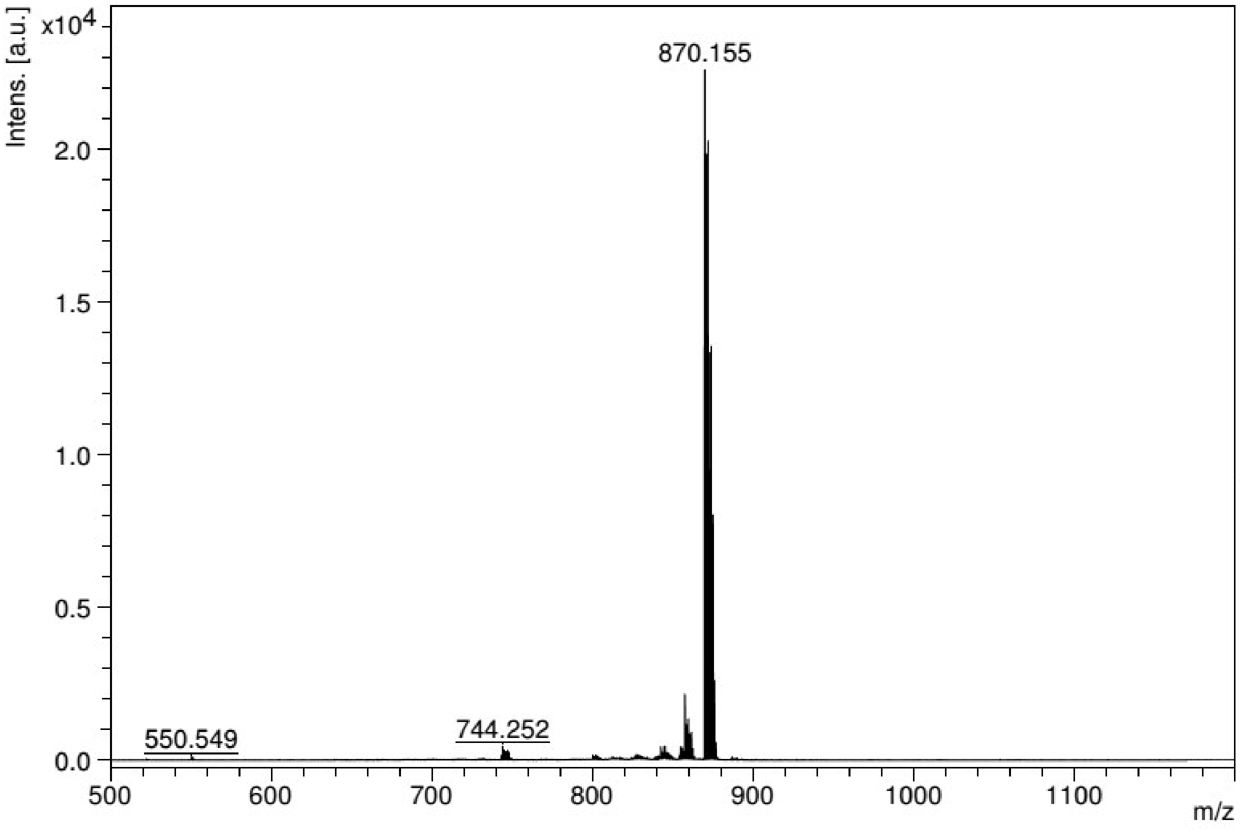


Fig. S3. Mass spectrum of spectrum of **2**.

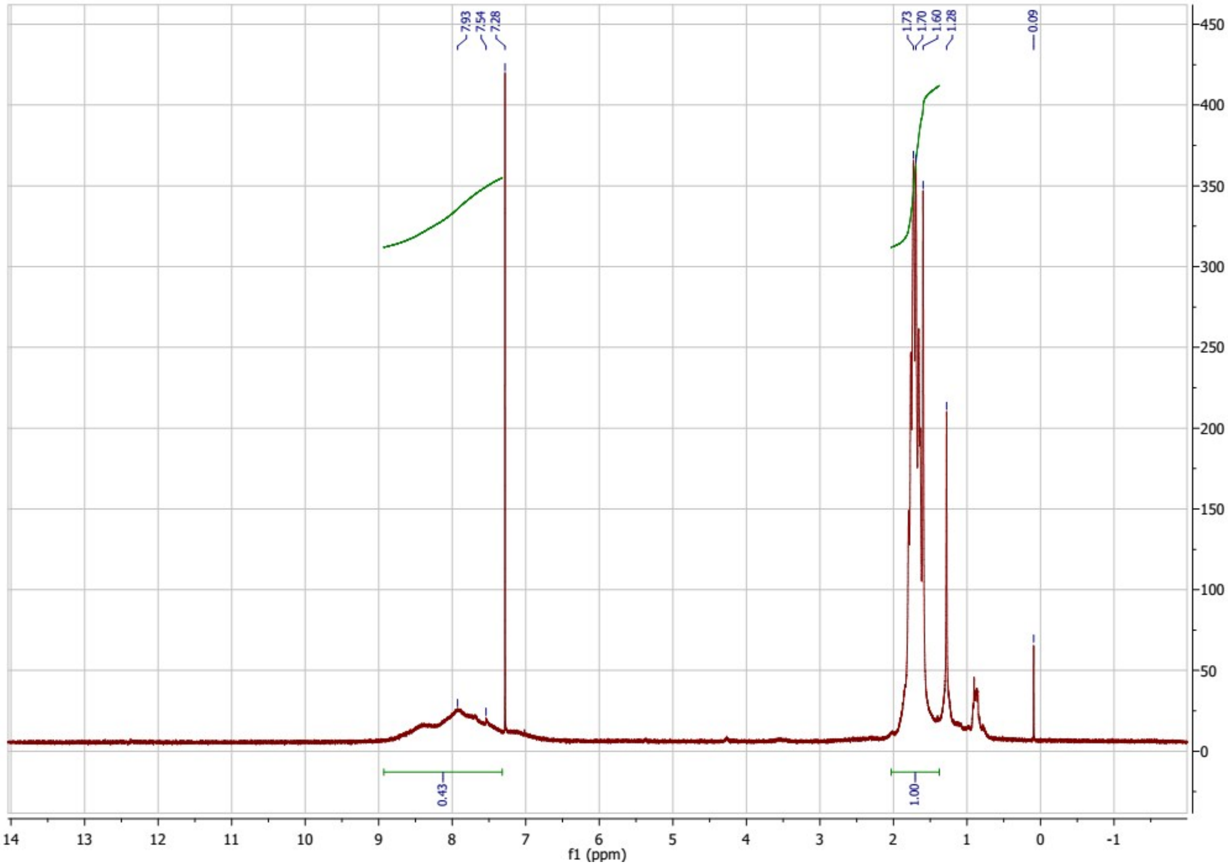


Fig. S4. ^{1}H NMR spectrum of **2**.

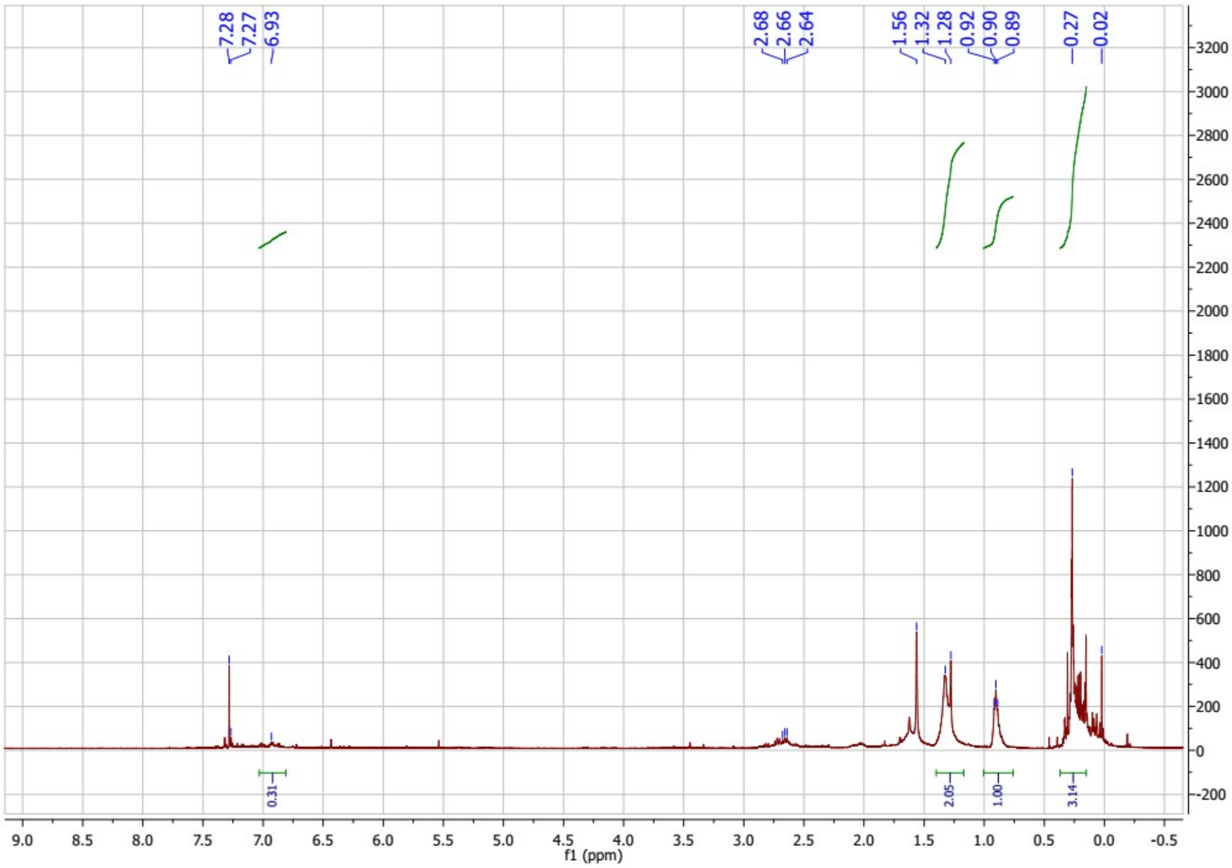


Fig. S5. ^{1}H NMR spectrum of **1**.

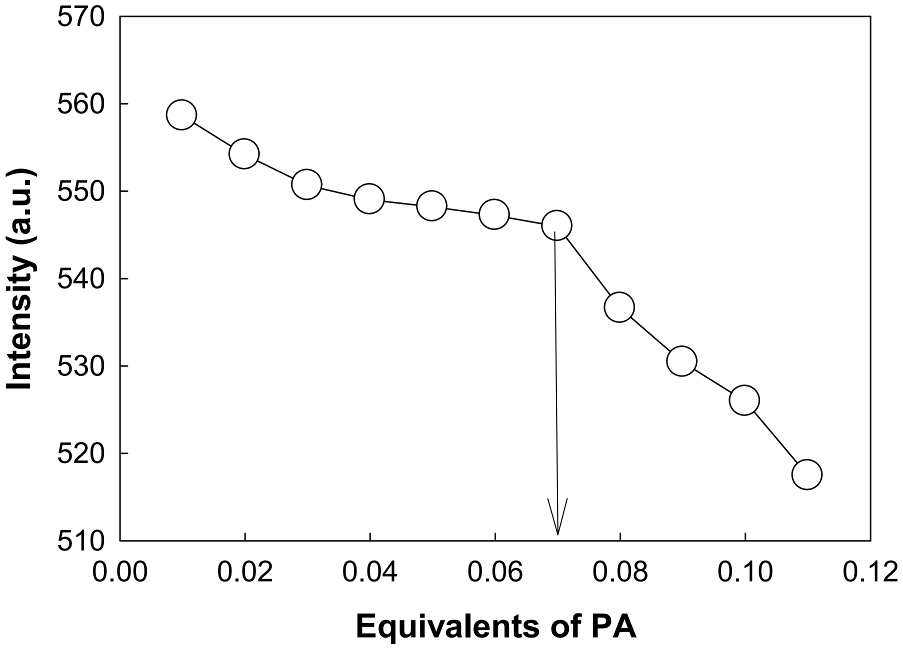


Fig. S6. Fluorescence intensity of **3** at 694 nm as a function of PA concentration.

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: [S4]

$$DL = C_L \times C_T$$

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

Thus, detection limit for PA is calculated:

$$D_L = 10 \times 10^{-6}\ \mathrm{M} \times 0.07\ \text{equiv.} = 7.0 \times 10^{-7}\ \mathrm{M}$$

Reference

[S1] M. Toba, T. Nakashima and T. Kawai, *Macromolecules*, 2009, **42**, 8068.

[S2] E. M. Maya, P VaAzquez and T. Torres, *Chem. Eur. J.*, 1999, **7**, 2004.

[S3] R. O. Ogbodu, E. Antunes and T. Nyokong, *Dalton Trans.*, 2013, **42**, 10769; T. Onodera and T. Akitsu, *Polyhedron*, 2013, **59**, 107.

[S4] J. X. Liu, H. Chen, Z. Lin and J. M. Lin, *Anal. Chem.*, 2010, **82**, 7380; H. Y. Du, G. He, T. H. Liu, L. P. Ding and Y. Fang, *J. Photoch. Photobio. A*, 2011, **217**, 356.