Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary material for:

Amphiphilic Unsymmetrically-Substituted Porphyrin Zinc Derivatives：Synthesis, Aggregation Behavior in the Self-Assemblied Films and NO_2 Sensing Properties

Yanling Wu,[a] Pan Ma,[c] Shanshan Liu[a] and Yanli Chen[a,b*]

[a] Shandong Provincial Key Laboratory of Fluorine Chemistry and Chemical Materials, School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, China

[b] School of Science, China University of Petroleum (East China), Qingdao 266580, China.

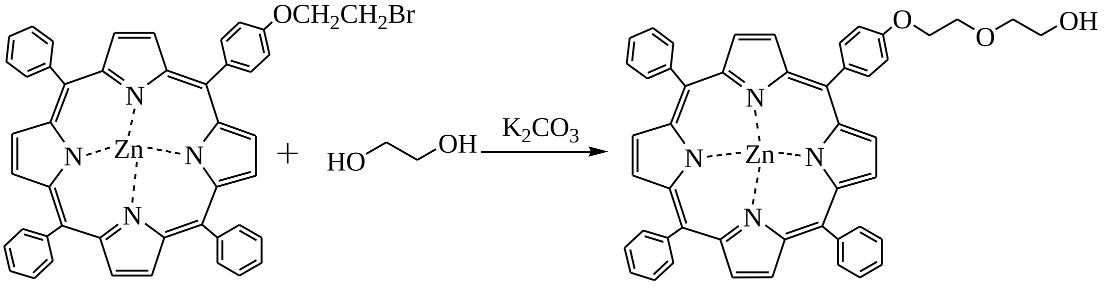
[c] Jinan Academy of Agricultural Sciences, Jinan 250316, China

1. Experimental section

1.1 Measurements

NMR spectra were recorded with Bruker Avance 300 spectrometer at 298 K using partially deuterated solvents as internal standards. Chemical shifts (δ) are denoted in ppm. Electrochemical measurement was carried out with a CHI760D voltammetric analyzer. The cell comprised inlets for a glassy carbon disk working electrode of 3.0 mm indiameter and a silverwire counter electrode. The reference electrode was Ag/Ag^+ (0.01 mol dm^{-3}), which was connected to the solution by a Luggin capillary, whose tip was placed close to the working electrode. It was corrected for junction potentials by being referenced internally to the ferrocenium/ferrocene (Fe^+/Fe) couple [$E_{1/2}(Fe^+/Fe)$=0.50 V *vs*. SCE]. Typically, a 0.1 mol dm^{-3} solution of $[Bu_4N][ClO_4]$ in CH_2Cl_2 containing 0.5 mmol dm^{-3} of sample was purged with nitrogen for 5 min, then the voltammogram was recorded at ambient temperature. Electronic absorption spectra were recorded on a Hitachi U-4100 spectophotometer. X-ray diffraction experiment was carried out on a Brucker D8 FOCUS X-ray diffractometer. AFM images were collected under ambient conditions using the tapping mode with a NanoscopeIII/Bioscope scanning probe microscope from Digital instruments.

1.2 Synthesis of 5-(Benzo-(4-(2-(2-hydroxy)ethoxy)ethoxy))-10,15,20-triphenylporphyrinato zinc complex [ZnT($OC_2H_4OC_2H_4OH$)PP] (1)

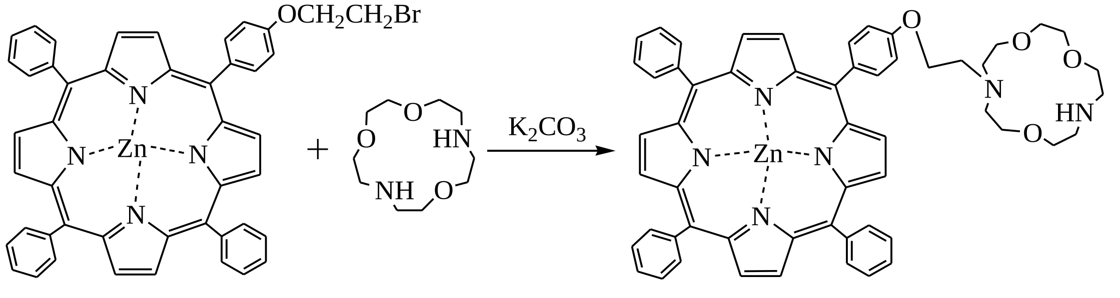


(**a**) **1**

Scheme S1 Synthesis of [ZnT($OC_2H_4OC_2H_4OH$)PP] (**1**)

A mixture of (**a**) (0.1 g, 0.125 mmol), ethanediol (7.75 mg, 0.125 mol) and K_2CO_3 in dry DMF(100 mL) was heated to 155℃ for 4 h under N_2 atmosphere. After being cooled to room temperature, a mixture containing distilled water and toluene were added to it. The resulting mixture was extracted into the toluene repeatedly. The volatiles were evaporated in *vacuo* and the residue was chromatographed on a silica gel column using $CHCl_3$ as eluent. A purple band containing 5-(Benzo-(4-(2-(2-hydroxy)ethoxy)ethoxy))-10,15,20-triphenylporphyrinato zinc complex [ZnT($OC_2H_4OC_2H_4OH$)PP] (**1**) was eluted first. Then $CHCl_3$-methanol (100:1) developed a second purple band which was collected and rotary evaporated. Repeated chromatography followed by recrystallization from $CHCl_3$ and MeOH gave pure target compound [ZnT($OC_2H_4OC_2H_4OH$)PP] (**1**) as dark-purple powder (40 mg, 60%). UV-vis [λ_{max}(nm)]: $CHCl_3$, 420, 548, 587. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.07 (8H, bpy$^+$), 7.28-8.24 (19H, phenyl), 5.04 (2H, OCH_2), 4.67-4.68 (2H, OCH_2CH_2), 1.28 (2H, $OCH_2CH_2OCH_2$), 0.80-0.90 (2H, $OCH_2CH_2OCH_2CH_2$) ppm. MALDI-TOF MS: an isotopic cluster peaking at m/z 782, calcd for [ZnT($OC_2H_4OC_2H_4OH$)PP] (**1**).

1.3 Synthesis of 5-(Benzo-(4-(2-(4,10-N,N-15-Crown-5)ethoxy))-10,15,20-triphenylporphyrinato zinc complex [ZnT(OC_2H_4NN15C5)PP] (2)



(**b**) **2**

Scheme S2 Synthesis of [ZnT(OC_2H_4NN15C5)PP] (**2**)

A mixture of (**a**) (0.1 g, 0.125 mmol), 1,4,10-trioxa-7,13-diazacyclopentadecane (0.028 g, 0.125 mol) and K_2CO_3 in dry DMF(100 mL) was heated to 155℃ for 4 h under N_2 atmosphere. After being cooled to room temperature, a mixture containing distilled water and toluene were added to it. The resulting mixture was extracted into the toluene repeatedly. The volatiles were evaporated in *vacuo* and the residue was chromatographed on a silica gel column using $CHCl_3$ as eluent. A purple band containing 5-(Benzo-(4-(2-(4,10-N,N-15-Crown-5)ethoxy))-10,15,20-triphenylporphyrinato zinc complex [ZnT(OC_2H_4NN15C5)PP] (**2**) was eluted first. Then $CHCl_3$-methanol (100:1) developed a second purple band which was collected and rotary evaporated. Repeated chromatography followed by recrystallization from $CHCl_3$ and MeOH gave pure target compound [ZnT(OC_2H_4NN15C5)PP] (**2**) as dark-purple powder (30 mg, 40%). UV-vis [λ_{max}(nm)]: $CHCl_3$, 421, 553, 602.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.92 (8H, bpy$^+$), 7.28-8.25 (18H, phenyl), 5.55 (1H, $CH_2CH_2OCH_2CH_2OCH_2$), 0.43 (2H, OCH_2CH_2), 1.16-4.19 (20H, $CH_2CH_2OCH_2CH_2OCH_2CH_2NH$) ppm. MALDI-TOF MS: an isotopic cluster peaking at m/z 940, calcd for [ZnT(OC_2H_4NN15C5)PP] (**2**).

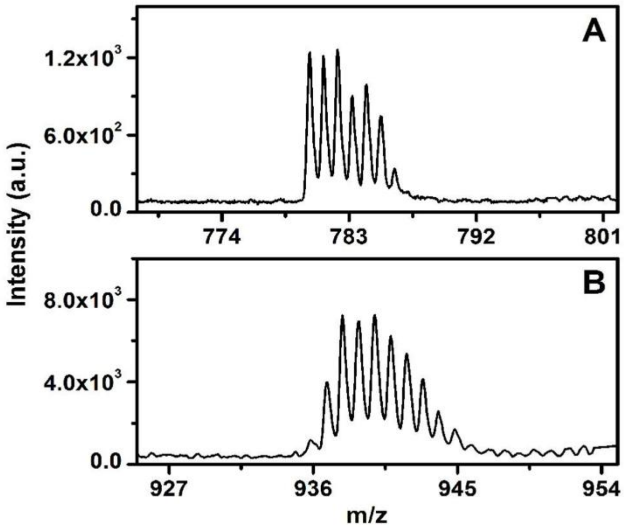


Fig. S1 Experimental isotopic pattern for the molecular ion of **1** (A) and **2** (B) shown in the MALDI–TOF mass spectrum.

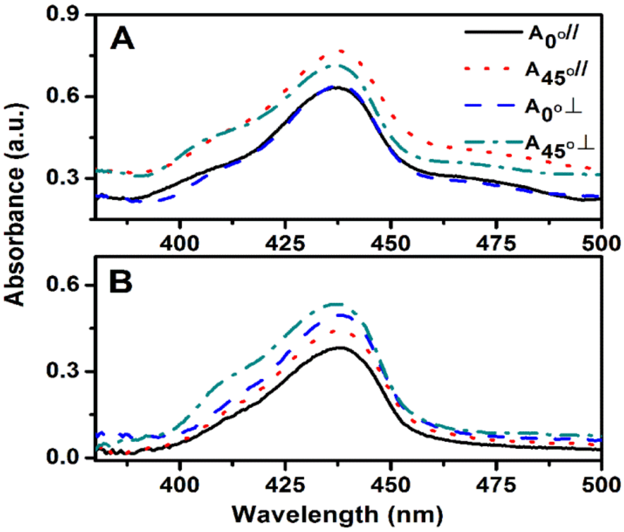


Fig. S2 Polarized UV-vis spectra of compounds **1**-**2** (A-B) QLS films. 0 and 45° represent the angle between the light and the normal of the substrate, respectively, while “A∥ and A⊥” represent the absorbance for light polarized with the electric vector parallel and perpendicular to the dipping direction.

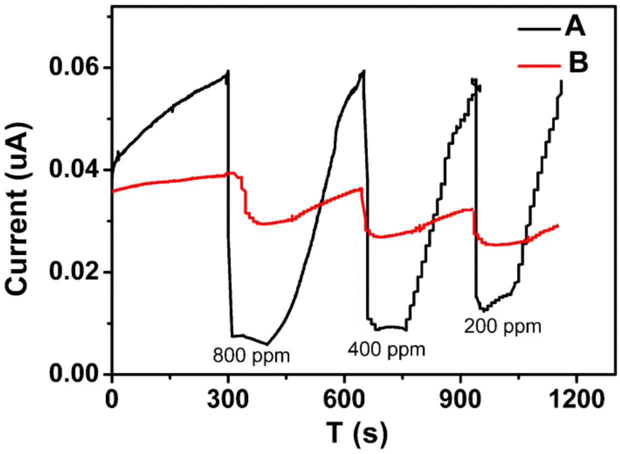
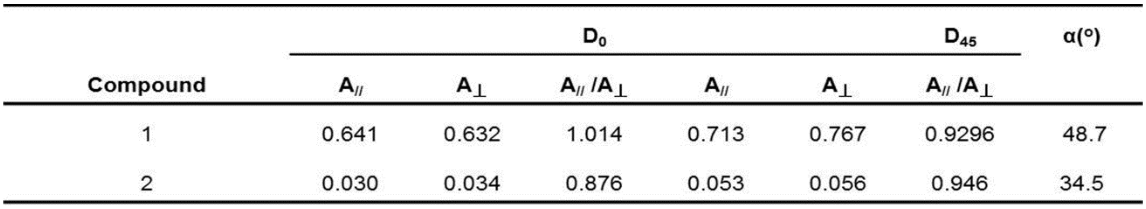


Fig. S3 The time-dependent current plots of the QLS films of **1** (A) and **2** (B) exposed to the different concentrations of NO_2 ranging from 800, 400 to 200 ppm in ambient air, respectively.

Table S1 The orientation angle of the porphyrin ring determined from polarized UV–vis absorbance of the QLS films of compounds **1**-**2**.



	D_0			D_{45}			α(°)
Compound	$A_{//}$	$A_{\perp}$	$A_{//}$ /$A_{\perp}$	$A_{//}$	$A_{\perp}$	$A_{//}$ /$A_{\perp}$	
1	0.641	0.632	1.014	0.713	0.767	0.9296	48.7
2	0.030	0.034	0.876	0.053	0.056	0.946	34.5