

Electronic Supplementary Information

A novel calix[4]arene-modified porphyrin-based dual-modal sensor for the specific detection of dopamine with excellent performance

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Contents

Fig. S1. Experimental isotopic pattern for the molecular ion of compound $H_2T[(C4AP)(Pyr)_3]P$ shown in the MALDI-TOF mass spectrum.

Fig. S2. Experimental isotopic pattern for the molecular ion of compound $H_2T[(IP)(Pyr)_3]P$ shown in the MALDI-TOF mass spectrum.

Fig. S3. 1H NMR spectrum of **1** in $CDCl_3$.

Fig. S4. ^{13}C NMR spectrum of **1** in $CDCl_3$.

Fig. S5. FT-IR spectrum of **1**(A) and **2**(B).

Fig. S6. TG/DSC curves of compound **1**.

Fig. S7. Fluorescence responses of 1×10^{-5} M THF solution of **2** with different concentrations of bio/medical molecules. (0 - 75 μM) ($\lambda_{ex_{max}} = 400$ nm).

Fig. S8. The electronic absorption spectra of DA (black line), DA quinone (red line), NE (blue line), and NEQ (green line).

Fig. S9. CVs from 0.1 mM APAP (A) and from 0.1mM DA in the present of 0.1 mM APAP (B) in 0.1 M PBS (pH = 7.3) at the film **1**/ITO (a), **2**/ITO (b) and bare ITO (c) electrodes.

Table S1. Thermal properties of **1**.

Table S2. Electronic absorption data for **1** and **2** in THF and the QLS films.

Experimental Section

Chemicals: Bis(triphenylphosphine) palladium(II) chloride ($\text{PdCl}_2(\text{PPh}_3)_2$) was purchased from TCI. Triethylamine and dichloromethane for section 3 were freshly distilled from CaH_2 under an atmosphere of nitrogen. Column chromatography was carried out on silica gel (200~300 mesh) with the indicated eluents. All other reagents and solvents were used as received. The compounds of calix[4]arene was prepared according to the literature methods.

Measurements: Electronic absorption spectra were recorded with a Hitachi U-3900 spectrophotometer. ^1H NMR spectrum was recorded on a Bruker DPX 400 spectrometer in CDCl_3 . Spectrum was referenced internally using the residual solvent resonance ($\delta = 7.26$ for ^1H NMR) relative to SiMe_4 . ^{13}C NMR spectrum was recorded on a Bruker DPX 400 spectrometer in CDCl_3 . AFM images were collected in air under ambient conditions using the tapping mode with a NanoscopeIII/Bioscope scanning probe microscope from Digital instruments. MALDI-TOF mass spectrum was taken on a Bruker BIFLEX III ultra-high-resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with alpha-cyano-4-hydroxycinnamic acid as matrix. IR spectra were recorded as KBr pellets using a Bruker Tensor 37 spectrometer with 2 cm^{-1} resolution. Thermogravimetry/differential scanning calorimetry (TG-DSC)

measurements were carried out with TA-SDT650. Fluorescent measurement was carried out with F-7000 spectrophotometer.

Synthesis of H₂T[(IP)(Pyr)₃]P (2): In scheme 1, Iodobenzaldehyde (1.16 g; 5 mmol) and pyrene-1-carboxaldehyde (4.6 g; 20 mmol) were stirred and refluxed in propionic acid (200 ml) for 0.5 h, and then pyrrole (1.34 g; 20 mmol) was added. The mixture was stirred at 140°C for 0.5 h, then MeOH was added and stay overnight below 0°C. The crude product was purified by column chromatography to afford H₂T[(IP)(Pyr)₃]P in 10% yield(CHCl₃: petroleum ether = 7:3). MALDI-TOF MS: an isotopic cluster peaking at m/z 1112, calcd for H₂T[(IP)(Pyr)₃]P, [M]⁺,1113.07.

Synthesis of propinyl-calix[4]arene: In scheme 2, Calix[4]arene (3.10 g; 4.78 mmol) and potash (0.57 g; 4.12 mmol) were stirred and refluxed in acetonitrile (50ml) for 1 h, and then propargyl bromide (80 wt% solution in toluene, 0.82 g; 6.89 mmol) was added. The mixture was stirred at 57°C for 18 h, and the crude product was purified by column chromatography (CHCl₃:n-hexane = 3:1) to afford propinyl-calix[4]arene in 20% yield.¹MALDI-TOF MS: an isotopic cluster peaking at m/z 686, calcd for propinyl-calix[4]arene, [M]⁺, 686.98.

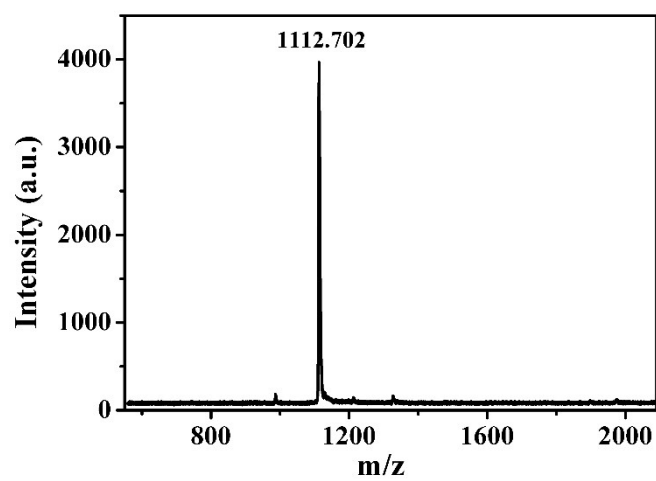


Fig. S1. Experimental isotopic pattern for the molecular ion of compound $\text{H}_2\text{T}[(\text{IP})(\text{Pyr})_3]\text{P}$ shown in the MALDI-TOF mass spectrum.

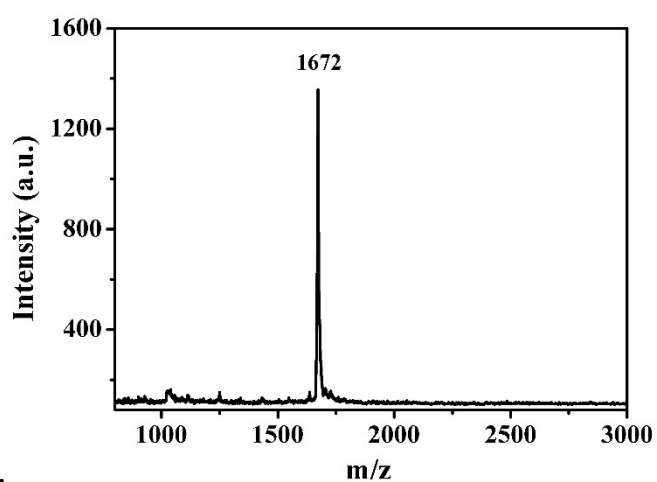


Fig. S2. Experimental isotopic pattern for the molecular ion of compound $\text{H}_2\text{T}[(\text{C4AP})(\text{Pyr})_3]\text{P}$ shown in the MALDI-TOF mass spectrum.

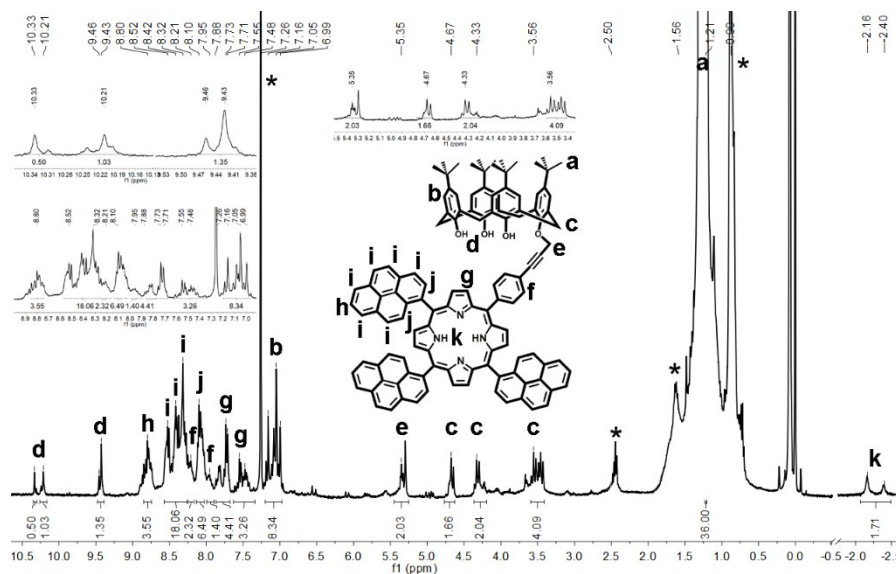


Fig. S3. ¹H NMR spectrum of **1** in CDCl₃. The signals due to residue solvents (CHCl₃, H₂O, trimethylamine and petroleum ether) are denoted as *. (The insets are the signals in the range of 3.4–5.4, 7.0–8.9 and 9.3–10.3 ppm).

¹H NMR (400 MHz, Toluene-D₈, 343K) for **1**, δ: -2.40, -2.16 (s, 2, Hk), 1.21 (s, 36, Ha), 3.56, 4.33, 4.67 (s, 8, Hc), 5.35 (s, 2, He), 6.99, 7.05, 7.16(s, 8, Hb), 7.48, 7.55, 7.71, 7.73 (m, 8, Hg), 7.95, 8.21 (d, 4, Hf), 8.10 (m, 6, Hj), 8.32, 8.38, 8.42 (m, 18, Hi), 8.52 (m, 3, Hh), 9.43, 10.21, 10.33 (m, 3, Hd).

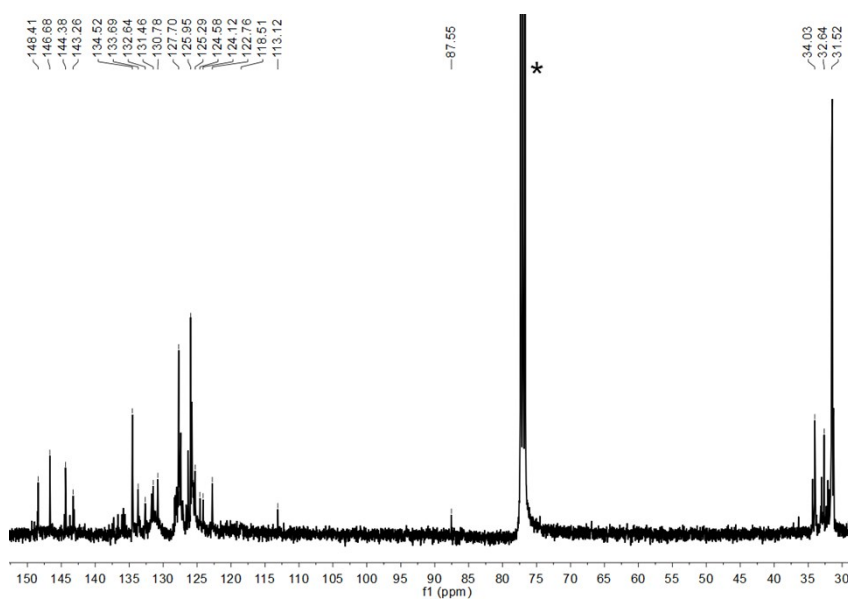


Fig. S4. ^{13}C NMR spectrum of **1** in CDCl_3 . The signals due to residue solvents of CHCl_3 , is denoted as $*$. ^{13}H NMR (CHCl_3 , 400 MHz, δ/ppm): 148.41, 146.68, 144.38, 143.26, 134.52, 133.69, 132.64, 131.46, 130.78, 127.70, 125.95, 125.29, 124.58, 124.12, 122.76, 118.51, 113.12, 87.55, 34.03, 32.64, 31.52.

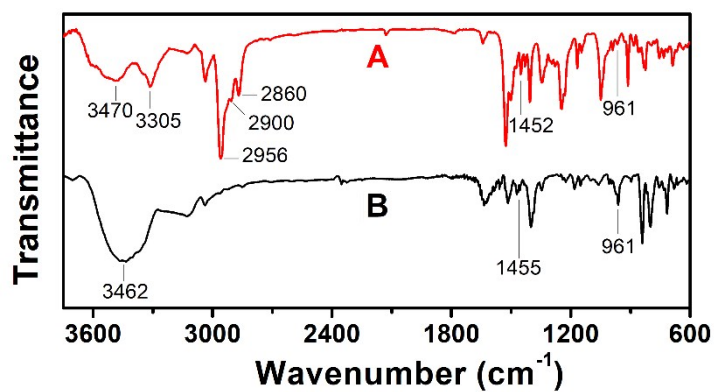


Fig. S5. FT-IR spectrum of **1**(A) and **2**(B).

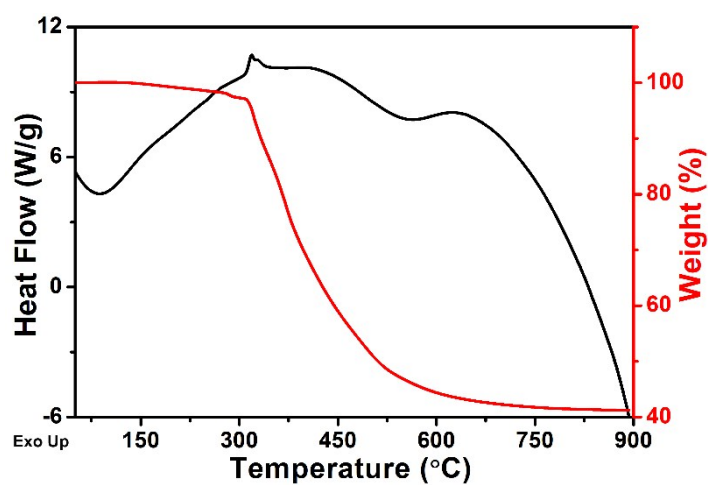


Fig. S6. TG/DSC curves of compound **1**.

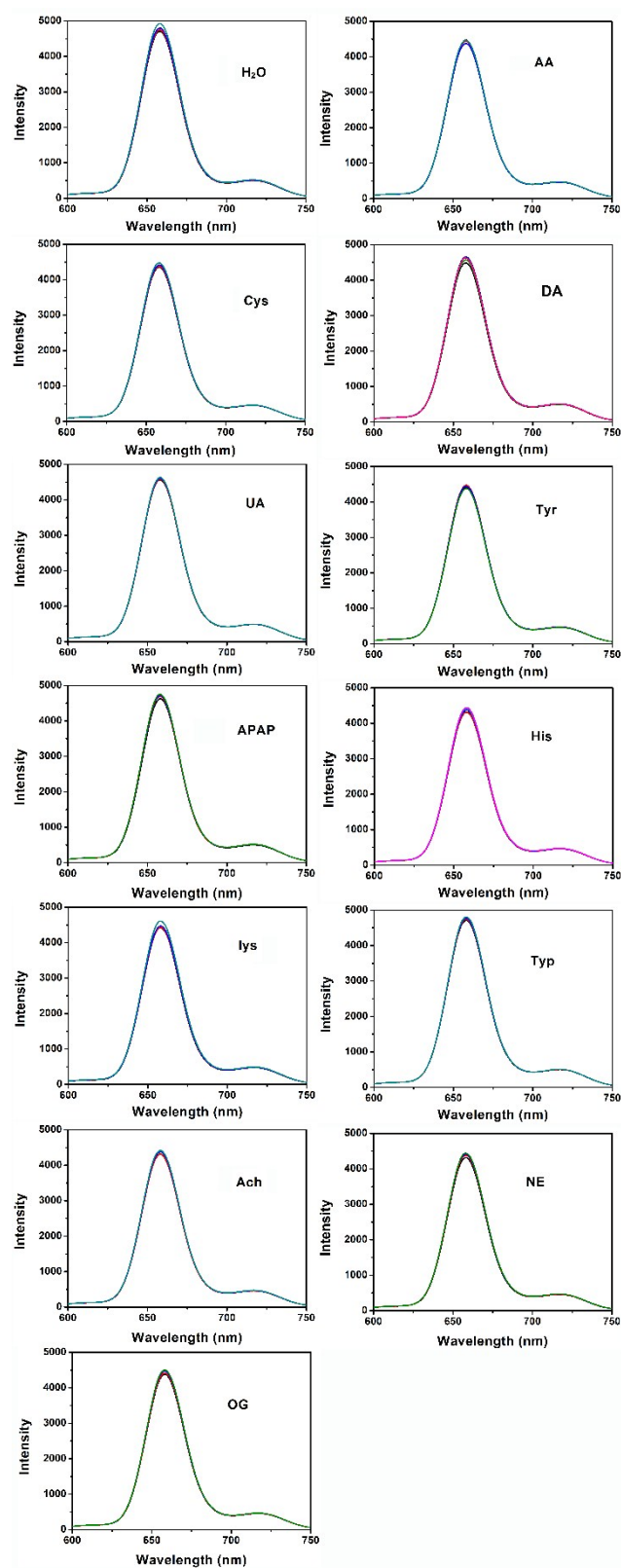


Fig. S7. Fluorescence responses of 1×10^{-5} M THF solution of **2** with different concentrations of bio/medical molecules. (0 - 50 μ M) ($\lambda_{ex_{max}} = 400$ nm).

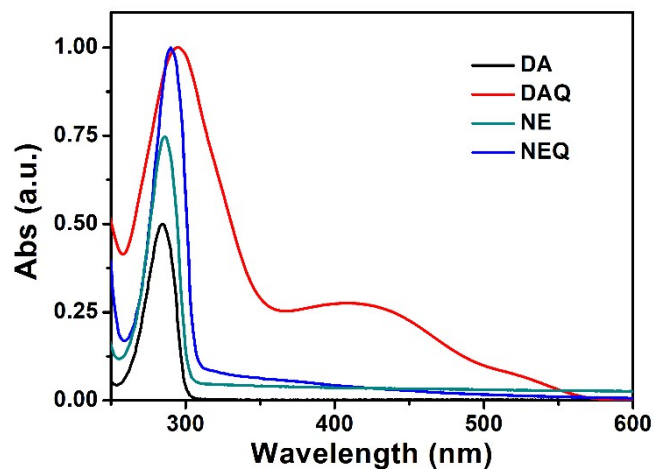


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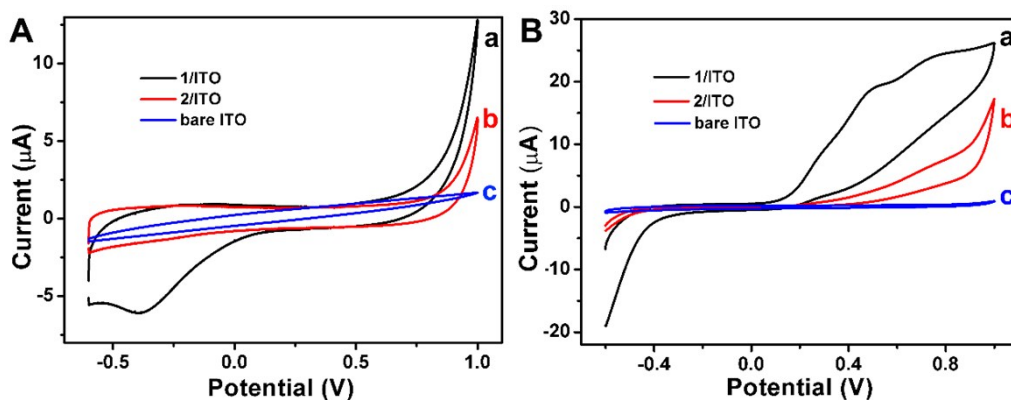


Fig. S9. CVs from 0.1 mM APAP (A) and from 0.1mM DA in the present of 0.1 mM APAP (B) in 0.1 M PBS (pH 7.3) at the film 1/ITO (a), 2/ITO (b) and bare ITO (c) electrodes.

Table S1. Thermal properties of **1**.

T_m (°C)	T_{onset} (°C) (1 step)	T_{onset} (°C) (2 step)	T_{max} (°C) (2step)	Residueb /%
557.6	272.8	313.4	328.5	41

Table S2. Electronic absorption data for **1** and **2** in THF and the QLS films.

Compounds	Solution (nm)	Film (nm)
1	427, 518, 553, 591, 649	436, 524, 559, 595, 649
2	430, 519, 555, 592, 651	442, 525, 560, 596, 654

Reference

- [1] M. J. Chetcuti, A. M. J. Devoille, A. Othman, R. Souane, P. Thuéry and J. Vicens *Dalton Trans.*, 2009, 2999-3008.