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

Supporting Information

Largely conjugated planar acceptor and rotatable donors to construct AIEgens with large molar extinction coefficients for the detection of metal ions

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Experiment section:

Materials and instrumentation

Chemicals were purchased from Energy-Chemical, Sigma-Aldrich, J&K and used without further purification. Solvents and other common reagents were obtained from Sigma-Aldrich. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker ARX 500 MHz spectrometer. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were collected on a Bruker SolarixXR high-resolution mass spectrometer. Absorption spectra were measured on a SHIMADZU UV2600i spectrophotometer. Steady-state photoluminescence (PL) spectra were recorded on a HITACHI F-4700 spectrophotometer.

General procedures for the detection of Hg^{2+} and Cu^{2+}

Unless otherwise noted, all the spectral measurements were performed in water containing 1% DMF) according to the following procedure. The stock solutions (1.0 mM) of DTPEP or DTPAP were prepared in DMF. 40 μL stock solution was added to 2 mL double distilled water followed by addition of different volume of Hg^{2+} or Cu^{2+} solution. The obtained solution was transferred to a quartz cell with 1 cm optical length for measurements. In the meantime, the blank solution without Hg^{2+} or Cu^{2+} was also prepared and measured under the same conditions for comparison.

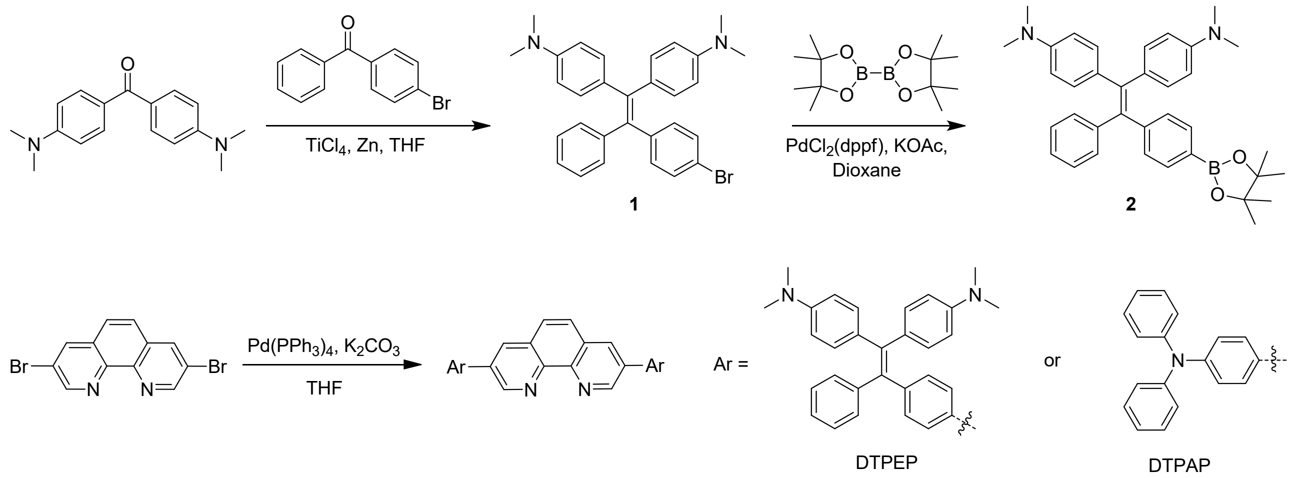
Determination of the detection limit

Based on the linear fitting in Figure 3D, 3E and 3F, the detection limit (C) is estimated as follows:

$$C = 3\sigma/B$$

Where σ is the standard deviation obtained from three individual fluorescent intensity ratio (I/I_0) of DTPEP or DTPAP (20 μM) without any metal ions and B is the slope obtained after linear fitting the titration curves within certain ranges.

Scheme S1. Synthetic route to DTPEP and DTPAP.



Figures and tables:

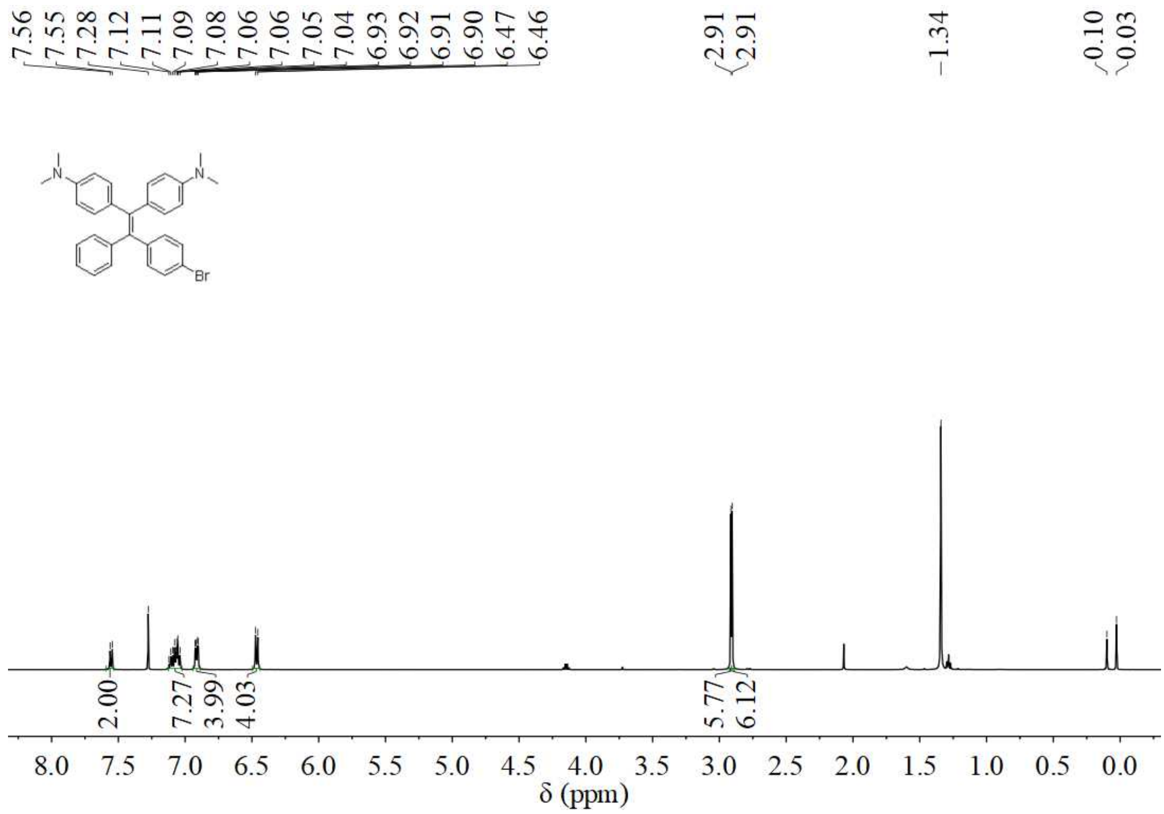


Figure S1. ^{1}H NMR spectrum of compound **1** in $CDCl_3$.

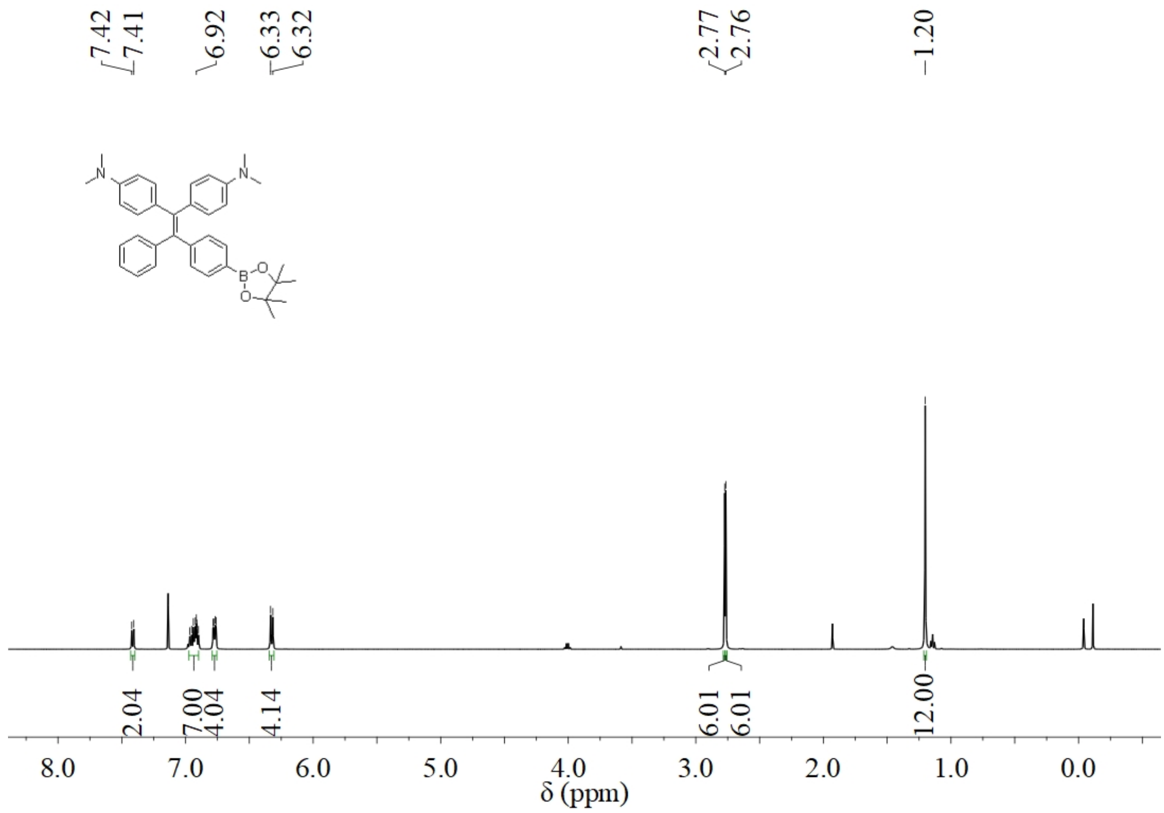


Figure S2. ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

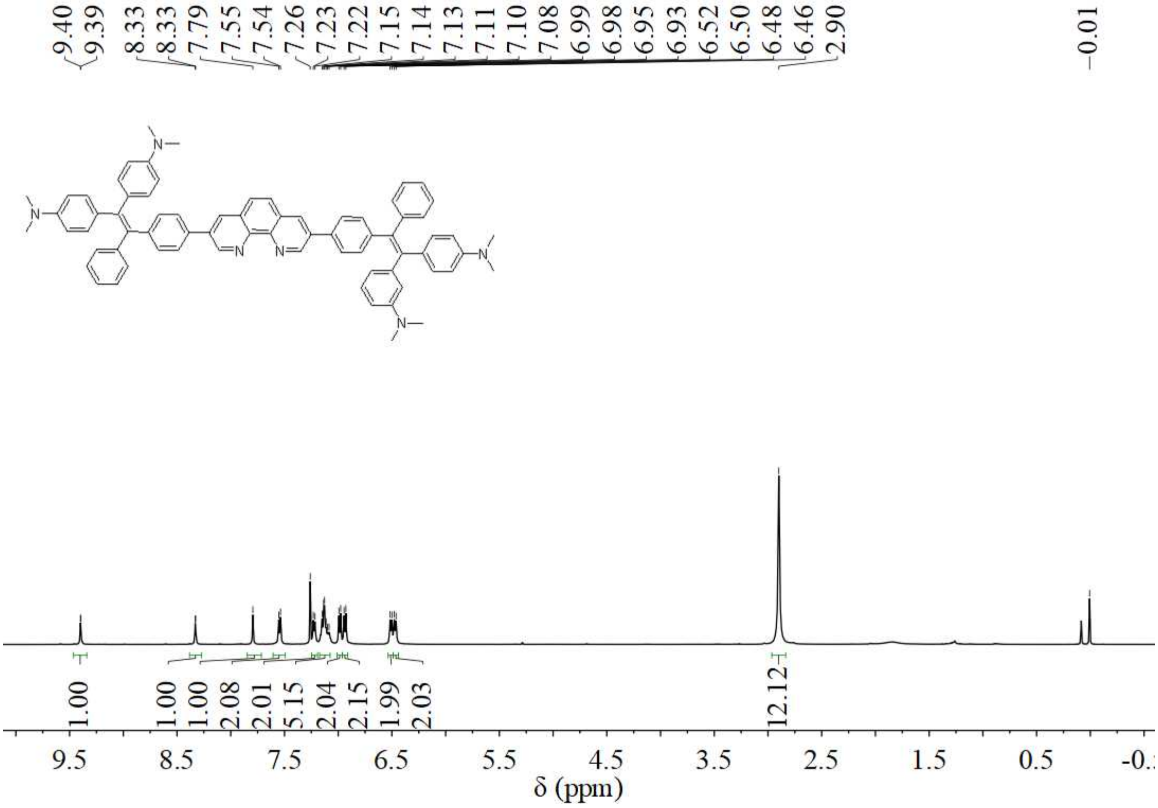


Figure S3. ^{1}H NMR spectrum of DTPEP in $CDCl_3$.

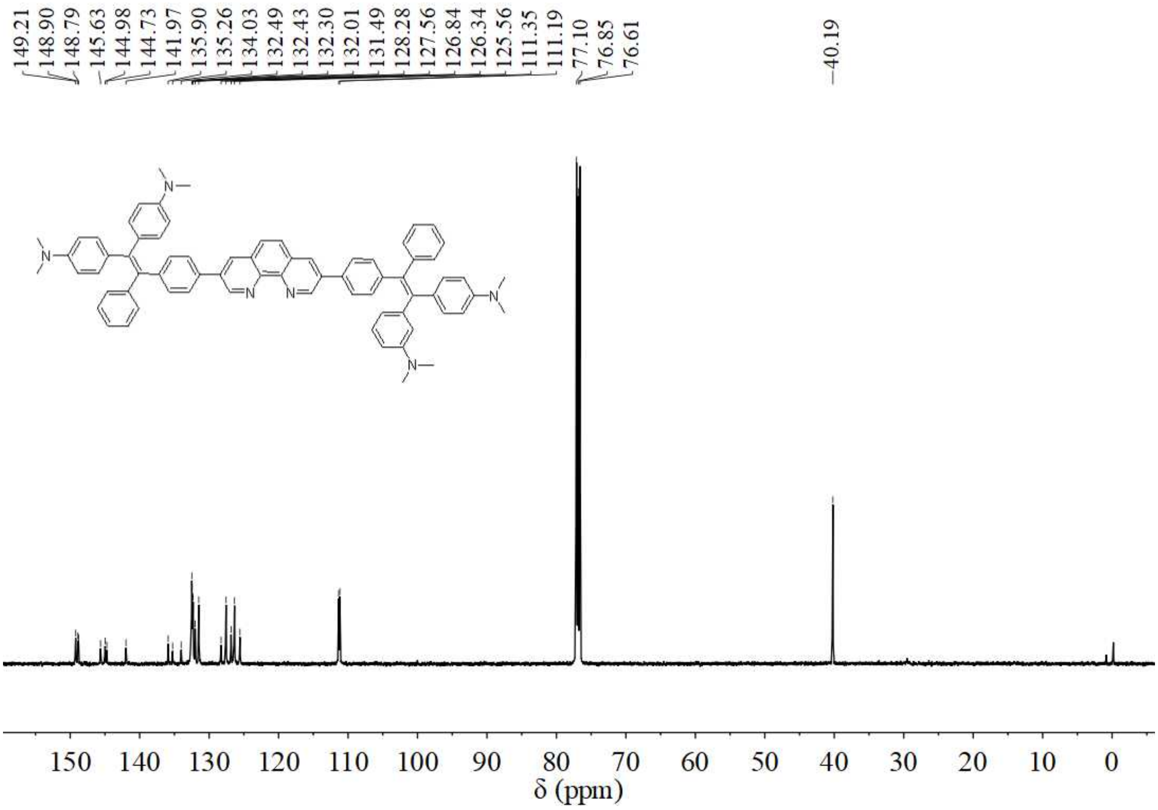


Figure S4. ^{13}C NMR spectrum of DTPEP in d_6-DMSO.

Formula Predictor Report

Printed at 2021/1/12 14:59:55

Formula Predictor Result	**C72 H64 N6**
Mass	1013.52593
Error Margin	5 ppm
DBE Range	Not Used
Electron Ions	Both configurations
HC Ratio	Not Used
Nitrogen Rule	Used

#	Score	Pred. (M)	Pred. m/z	Meas. m/z	Diff. (mDa)	Formulae (M)	Ion	Diff. (ppm)	Iso Score	DBE
4	31.20	1012.51925	1013.52652	1013.52593	-0.59	C72 H64 N6	[M+H]+	-0.582	23.83	44.0

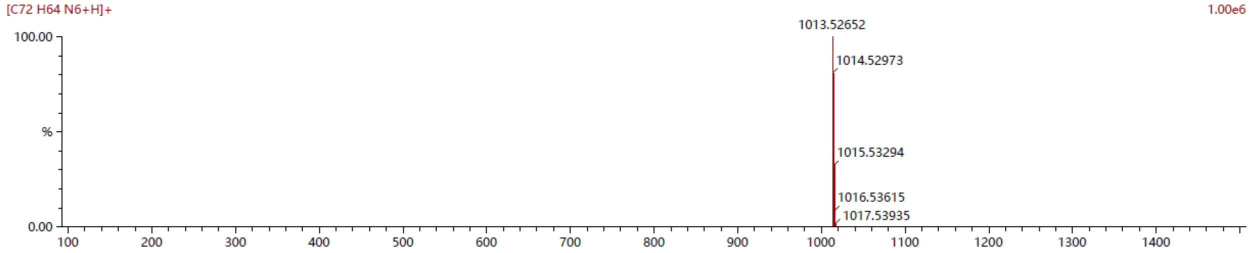


Figure S5. HRMS spectrum of DTPEP.

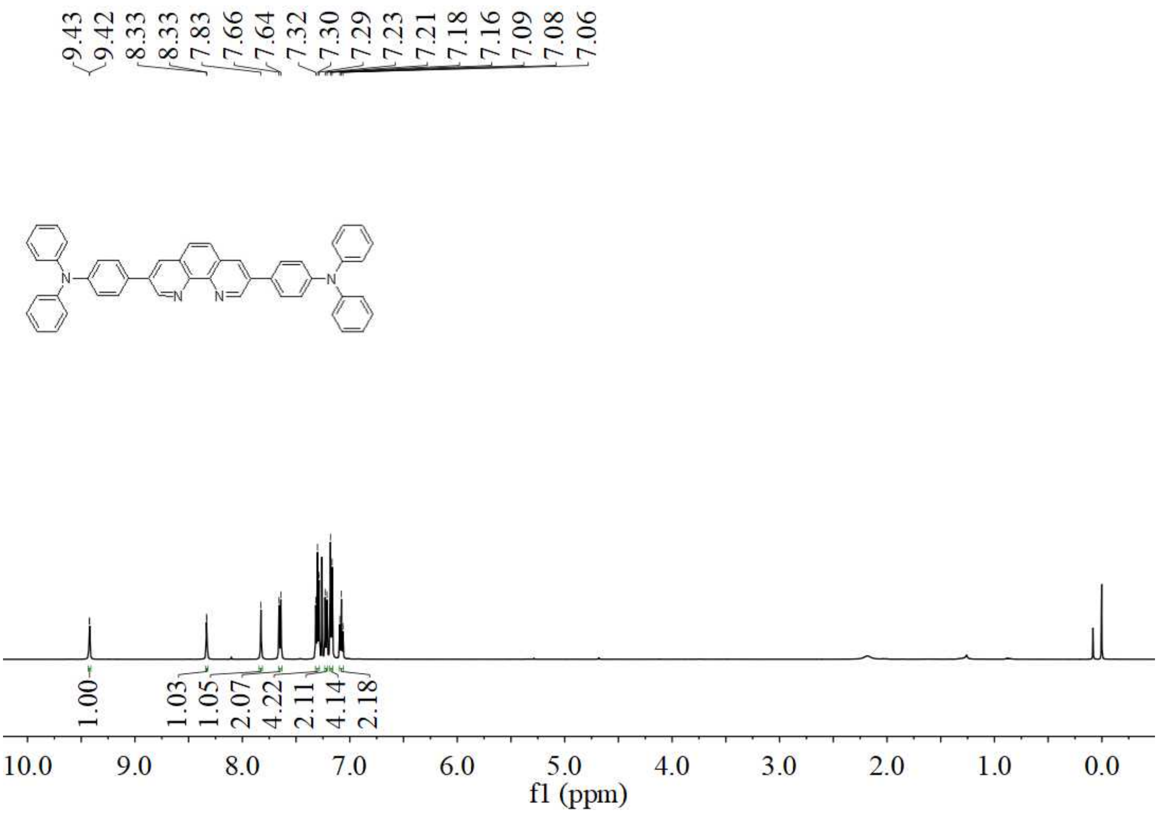


Figure S6. [1]H NMR spectrum of DTPAP in $CDCl_3$.

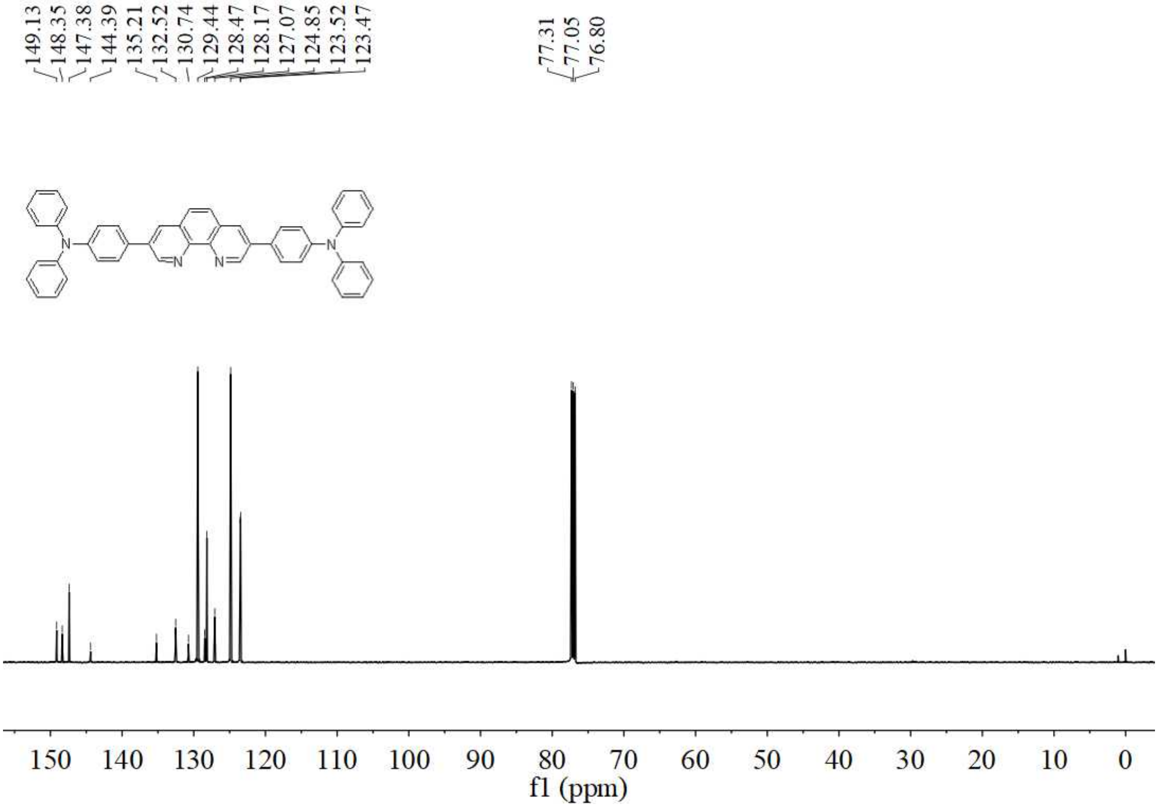


Figure S7. ^{13}C NMR spectrum of DTPAP in $CDCl_3$.

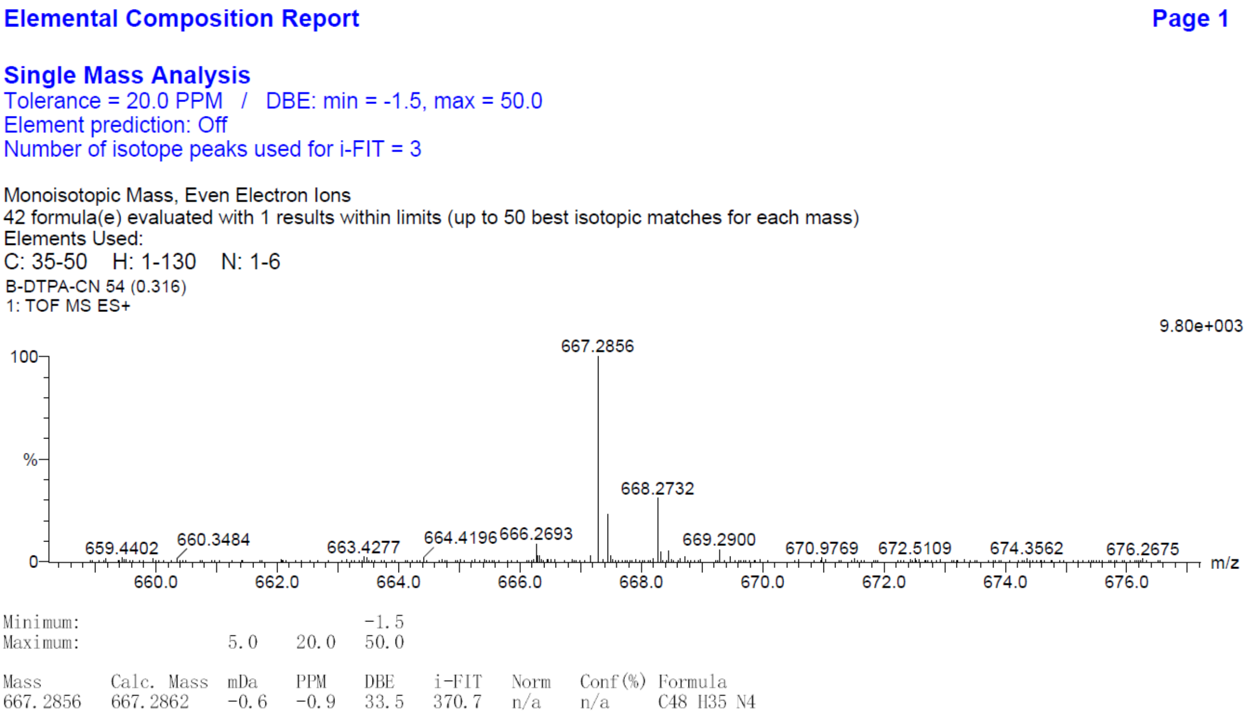


Figure S8. HRMS spectrum of DTPAP.

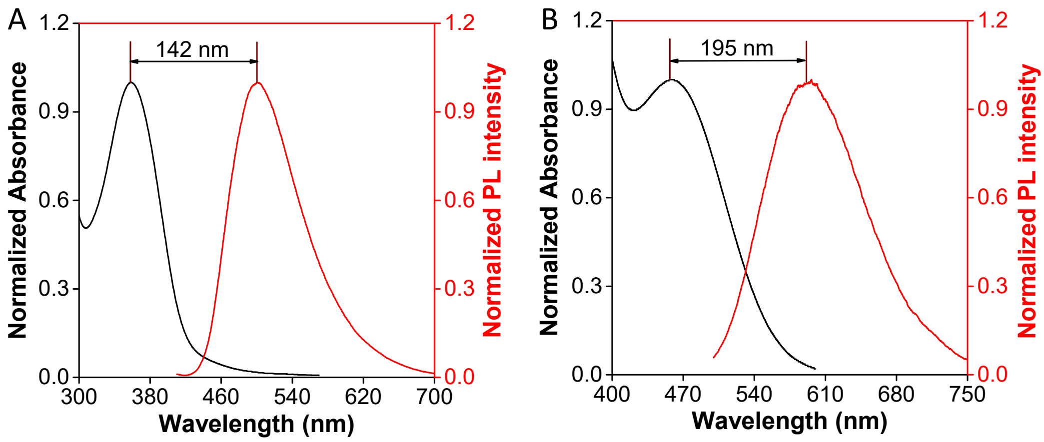


Figure S9. Normalized absorption and PL spectra of DTPAP (A) and DTPEP (B) in water with 1% DMF.

Table S1. The quantum yields of DTPAP and DTPEP.

Probe	λ_{ex} (nm)	Solution[a]	Aggregates[b]	Solid
DTPAP	395	84%	34%	4.5%
DTPEP	400	0.4%	2.7%	5.6%

[a]Data were measured in DMF solution.

[b]Data were measured in DMF/H_2O mixed solution with 90% H_2O fraction.

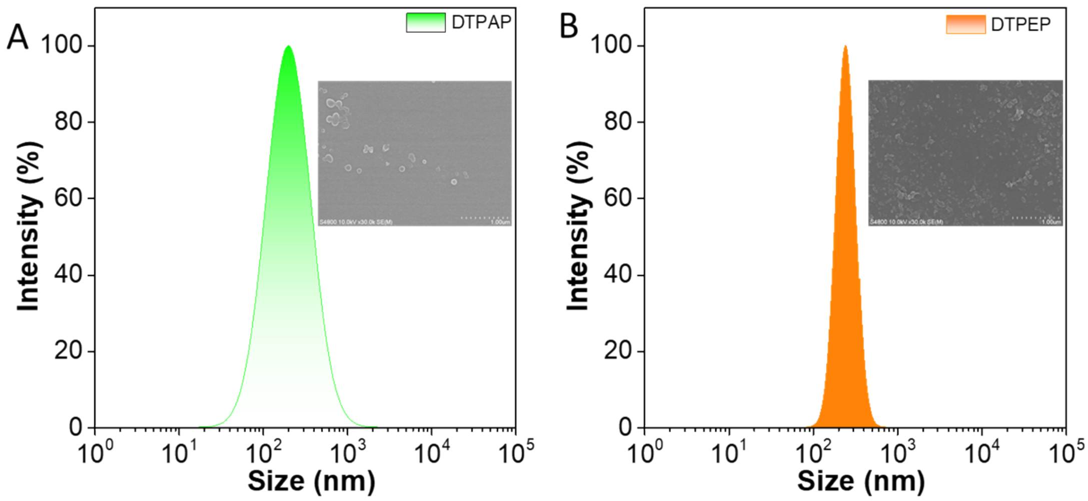


Figure S10. The DLS analysis of DTPAP (A) in DMF/H_2O solution with 10% DMF and DTPEP (B) in pure DMF. Insets show the corresponding SEM images.

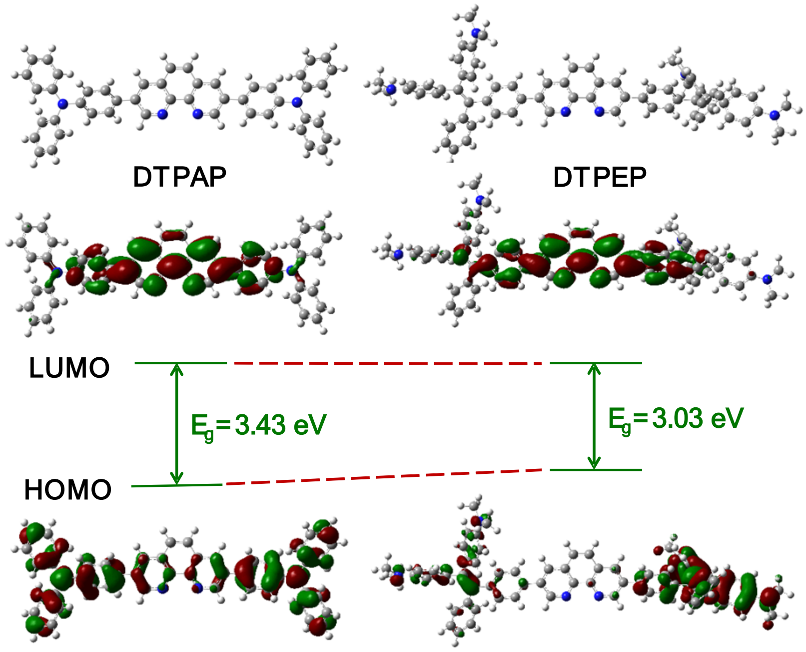


Figure S11. Optimized molecular structures and calculated HOMO and LUMO geometries for compound DTPEP and DTPAP.

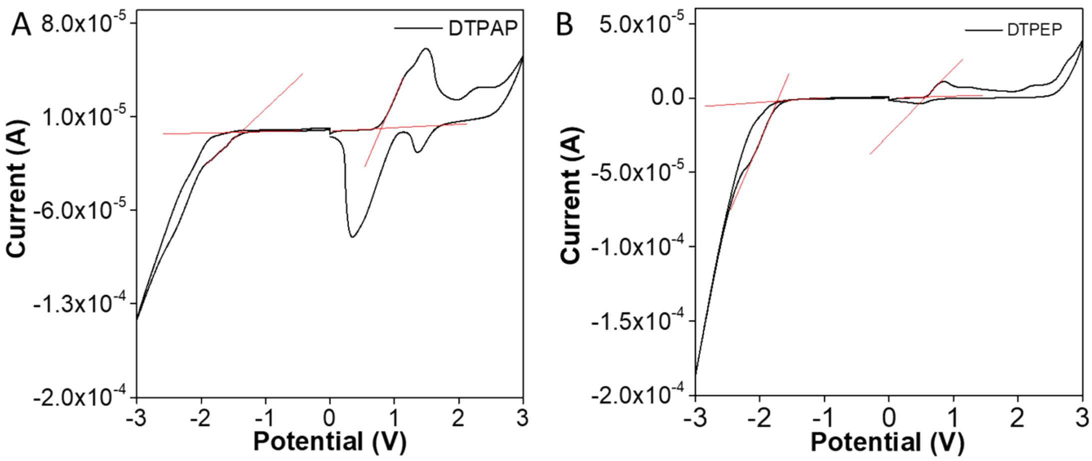


Figure S12. Cyclic voltammograms of 2 mM DTPAP (A) and DTPEP(B) measured in dichloromethane solution containing 0.1 M Bu_4NPF_6 as the supporting electrolyte at room temperature. Gold electrodes were used as a working electrode, and the scan rate was set at 50 $mV \cdot s^{-1}$.

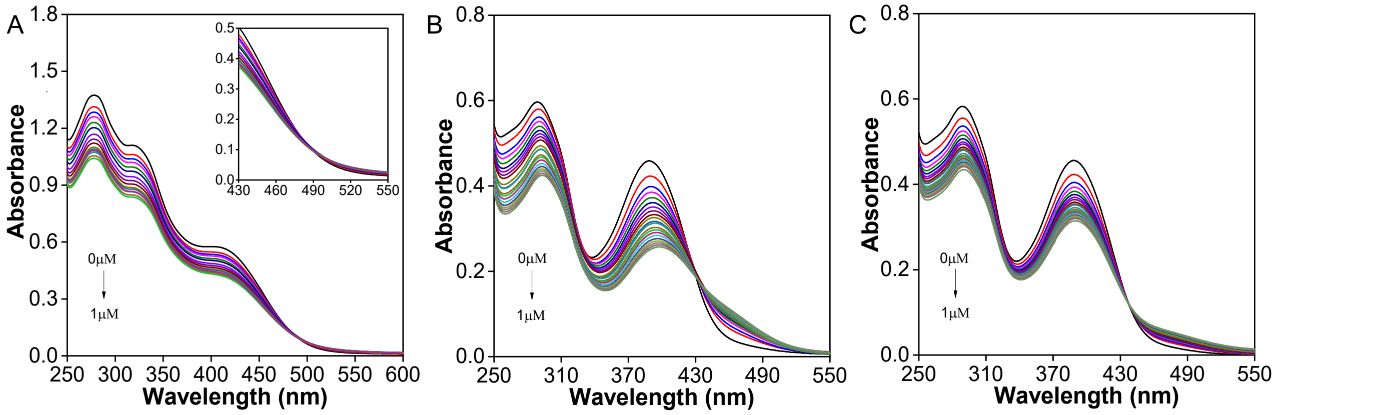


Figure S13. The UV-vis absorption spectra of DTPEP (A) and DTPAP (B and C) upon the addition of Hg^{2+} (A and B) or Cu^{2+} (C).

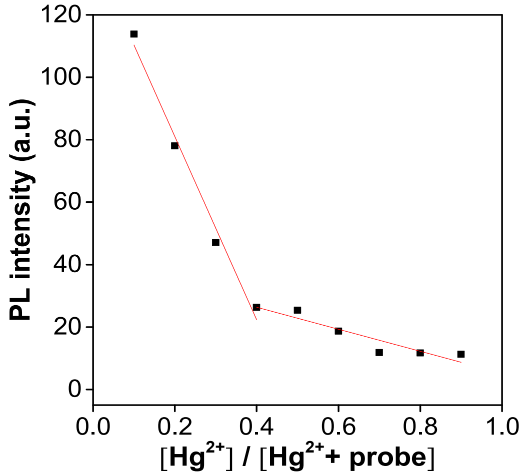


Figure S14. (A) The Job's plot between DTPEP probe and Hg^{2+}, with a total concentration of ($[Hg^{2+}]$ + [DTPAP]) = 5×10^{-6} mol L^{-1}.

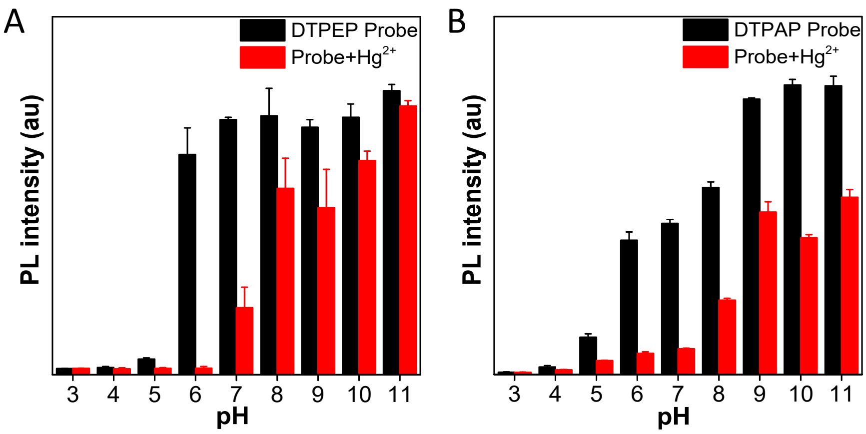


Figure S15. Fluorescence intensity of DTPEP (A) and DTPAP (B) (20.0 μM) in the presence and absence of Hg^{2+} (20.0 μM) under different pH environments (λ_{ex} = 395 nm).

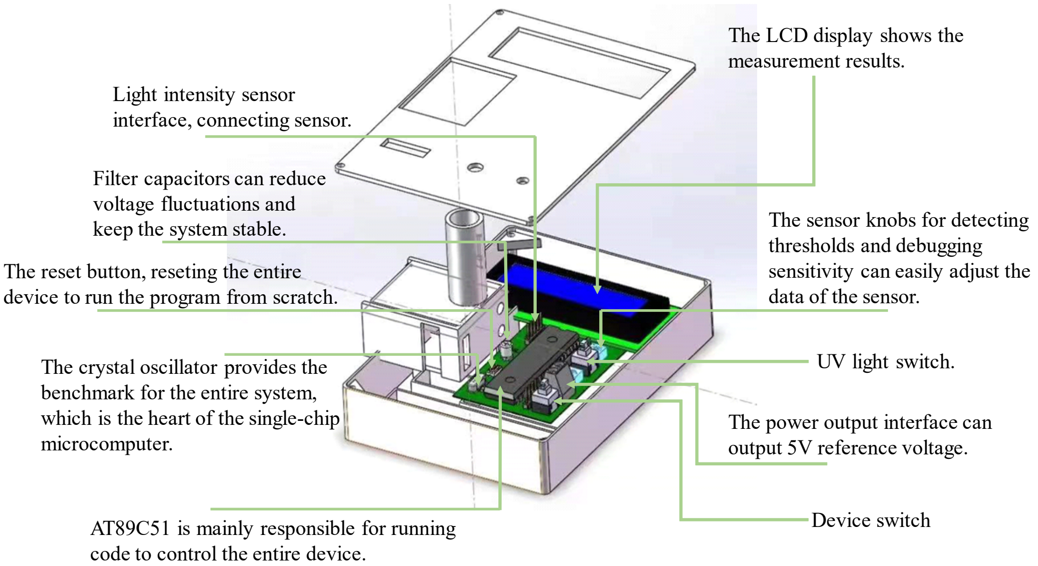
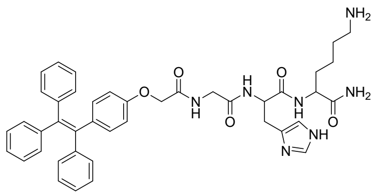
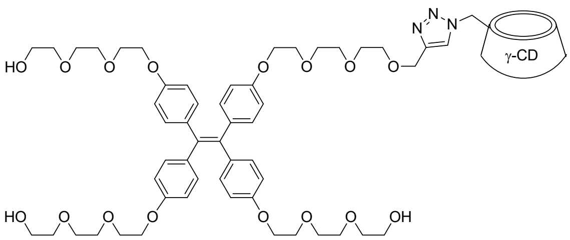
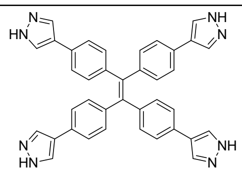
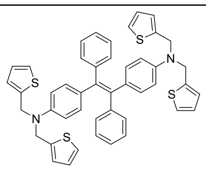
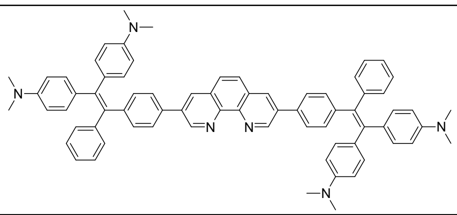


Figure S16. Structure of the portable device for detection of Hg^{2+} by using DTPEP.

Table S2. Comparison of DTPEP with some recently reported AIE-active fluorescent probes for Hg^{2+}.

AIEgen-based fluorescent probes	λ_{em} (nm)	LOD	Portable device	Ref
	< 500	28.6 nM	No	[1]
	488	1.8 μM	No	[2]
	525	60.7 nM	No	[3]
	550	10.5 nM	No	[4]
	575	18.7 nM	Yes	*This work*

References

[1] P. Wang, S. Xue, B. Chen, F. Liao, A novel peptide‑based fluorescent probe for highly selective detection of mercury (II) ions in real water samples and living cells based on aggregation‑induced emission effect, Anal. Bioanal. Chem. 414 (2022) 4717-4726.

[2] K.-R. Zhang, M. Hu, J. Luo, F. Ye, T.-T. Zhou, Y.-X. Yuan, M.-L. Gao, Y.-S. Zheng, *Pseudo* - crown ether having AIE and PET effects from a TPE-CD conjugate for highly selective detection of mercury ions, Chin. Chem. Lett. 33 (2022) 1505-1510.

[3] J. Wang, J. Tong, Z.-F. Wang, Q. Yuan, X.-Y. Wang, S.-Y. Yu, B. Z. Tang, Highly specific and selective fluorescent chemosensor for sensing of Hg(II) by NH-pyrazolate-functionalized AIEgens, Anal. Chim. Acta 1208 (2022) 339824.

[4] M. Selvaraj, K. Rajalakshmi, D.-H. Ahn, S.-J. Yoon, Y.-S. Nam, Y. Lee, Y. Xu, J.-W. Song, K.-B. Lee, Tetraphenylethene-based fluorescent probe with aggregation-induced emission behavior for Hg^{2+} detection and its application, Anal. Chim. Acta 1148 (2021) 238178.