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

Supporting Information

A copillar[5]arene-based fluorescent “on-off-on” sensor is applied in sequential recognition of iron cation and fluoride anion

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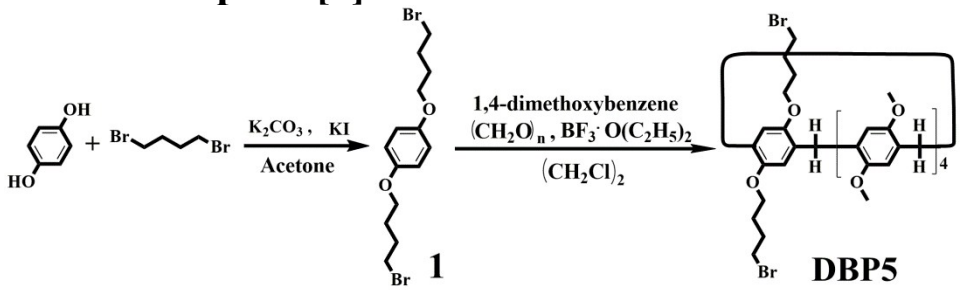
1. Synthesis of copillar[5]arene DBP5



Scheme S1 Synthesis of copillar[5]arene **DBP5.**

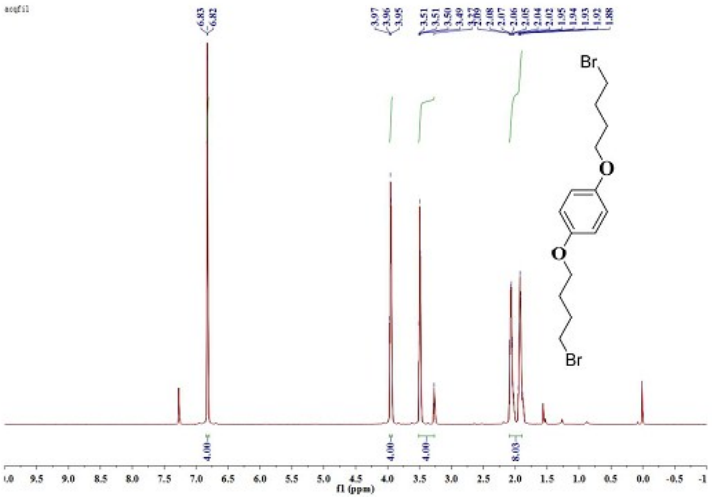


Fig. S1 ^{1}H NMR spectra (600 MHz, $CDCl_3$) of 1,4–bis (4–bromobutoxyl) benzene **1**.

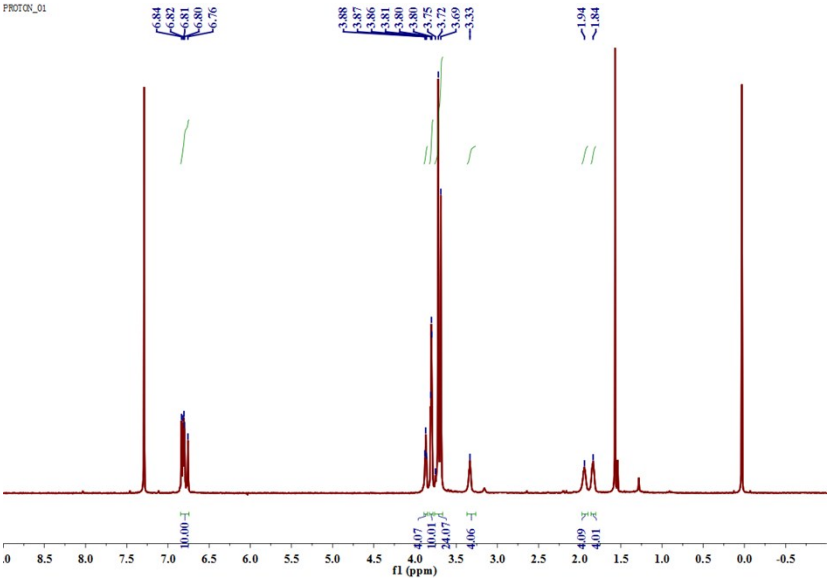


Fig. S2 ^{1}H NMR spectra(600 MHz, $CDCl_3$) of a copillar[5]arene **DBP5**.

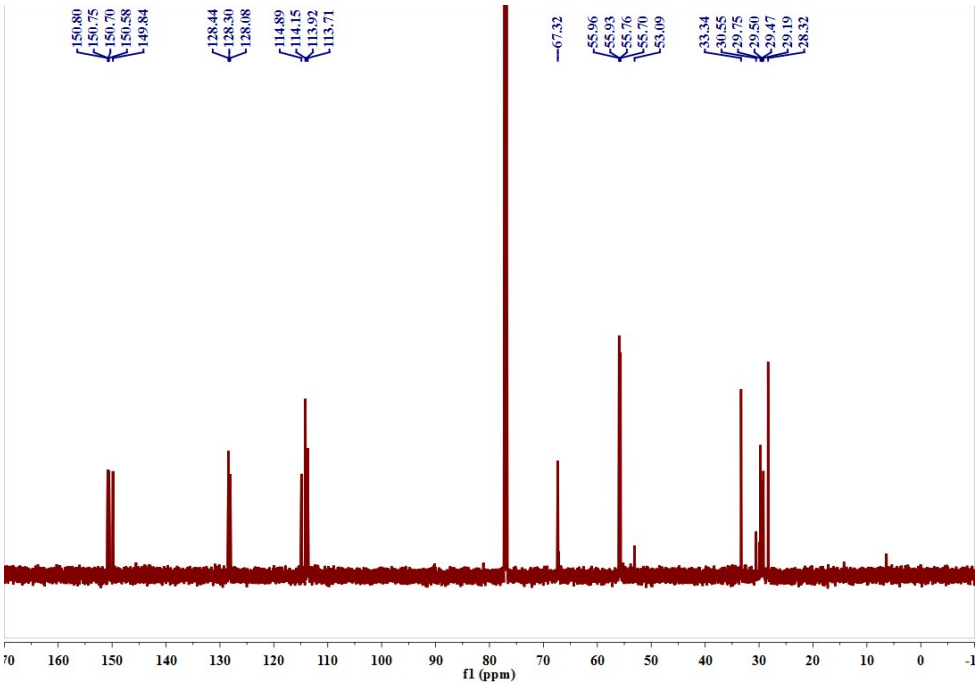


Fig. S3 ^{13}C NMR spectra(151 MHz, $CDCl_3$) of a copillar[5]arene **DBP5**.

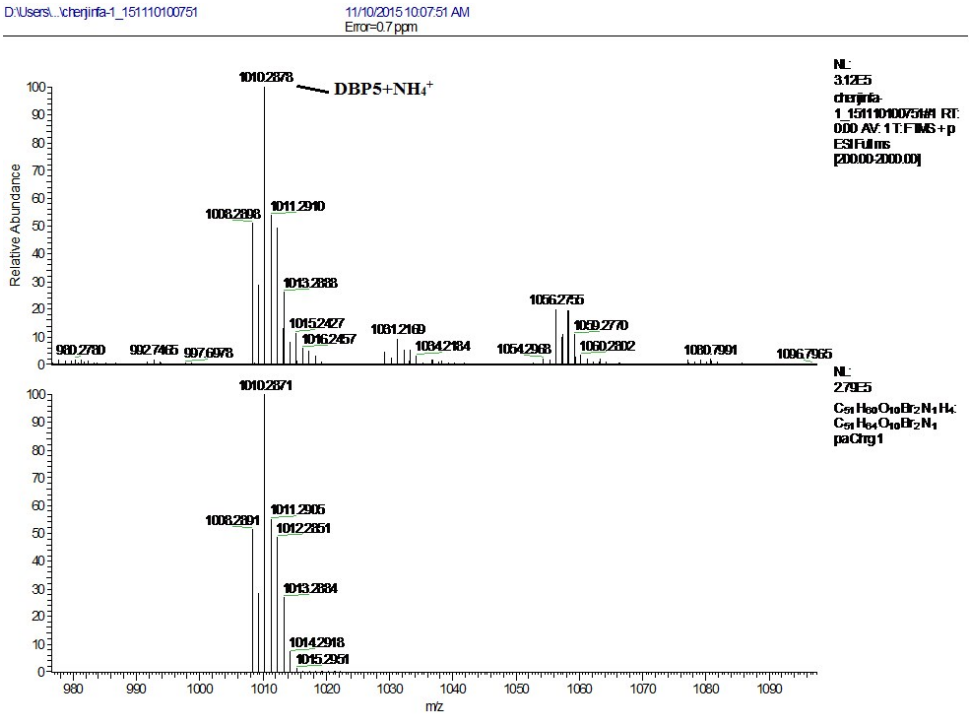


Fig. S4 High resolution mass data of a copillar[5]arene **DBP5**.

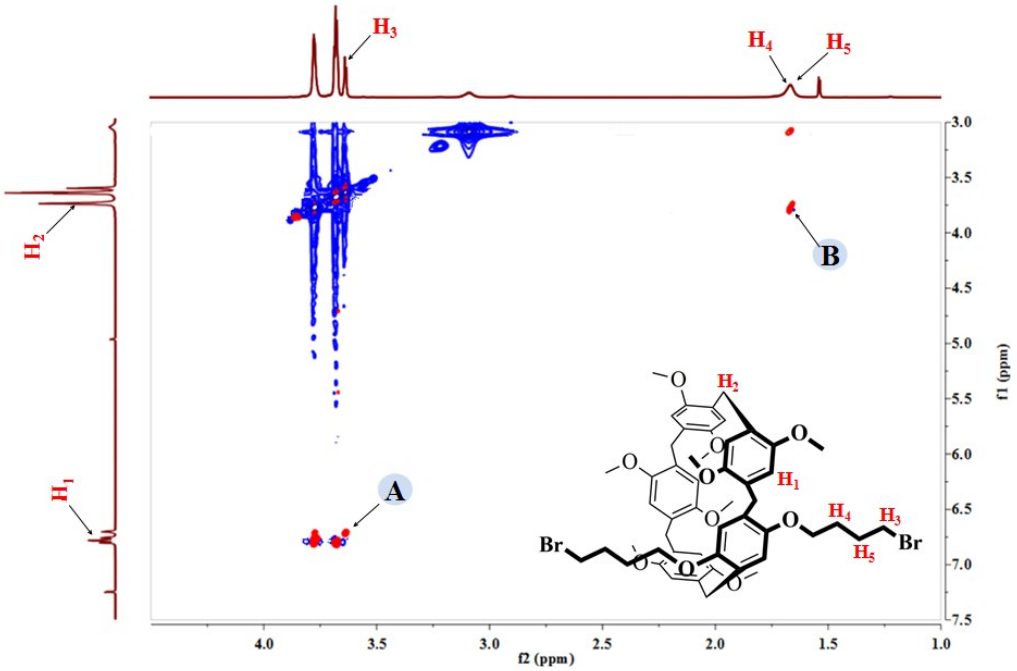


Fig. S5 The 2D NOESY spectrum of (600 MHz, CDCl3, 298 K) of **DBP5** at 50.0 mM.

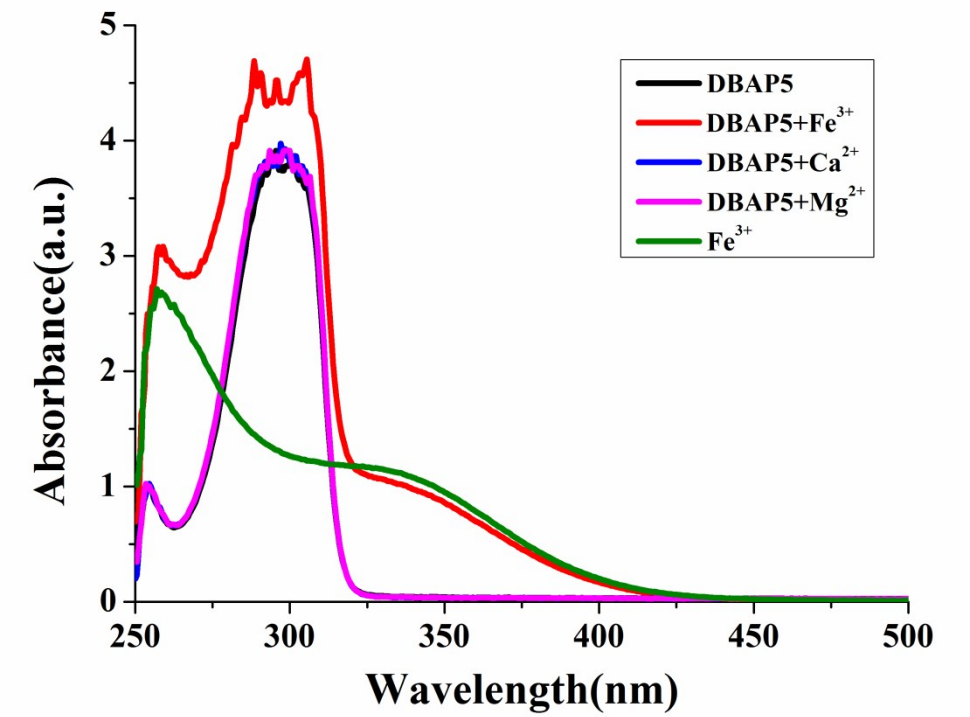


Fig. S6 Absorbance spectra of **DBP5**, **DBP5**+Fe^{3+}, **DBP5**+Ca^{2+}, **DBP5**+Mg^{2+} and Fe^{3+} in H_2O/DMSO (1 : 9 , v/v).

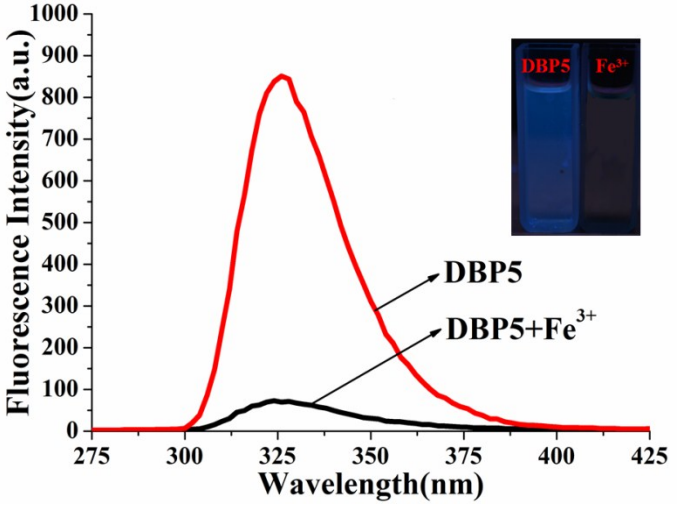


Fig. S7 Fluorescence spectral response of **DBP5** (2×10^{-4} M) in H_2O/DMSO (1 : 9 , v/v) solution upon addition of 2 equiv. of Fe^{3+} (λ_{ex} = 295 nm). Inset: photograph of **DBP5** (2×10^{-4} M) upon addition of 2 equiv. of Fe^{3+}, which was taken under a UV−lamp (365 nm).

Determination of the detection limit

We use the 3δ way to figure out the detection limit. The process of the analysis as follows.

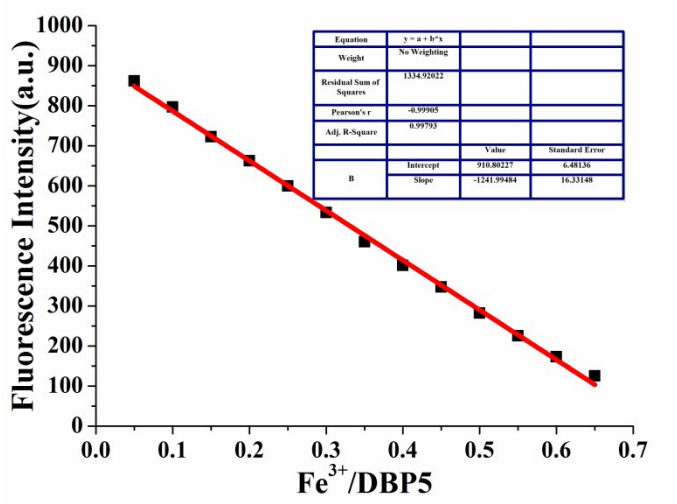


Fig. S8 The photograph of the linear range.

Linear Equation: Y=−1241.99484X+910.80227 R^2=0.9979

S=1241.99×10^6

$$\delta=\sqrt{\frac{\sum(x_i-\bar{x})^2}{n-1}}=6.82(n=30)$$

K=3

LOD =K×δ/S= 1.65×10^{-8}M

Table S1 The detection limits of various analytical techniques about Fe^{3+}.

Analytical techniques	The detection limits	Ref.
Spectrophotometry	1.8×10^{-6} mol/L (0.1 mg/L)	[S1]
Atomic absorption spectroscopy	10^{-7} mol/L	[S2]
Voltammetry	7.7×10^{-9} mol/L	[S3]
Electrophoresis	8.9×10^{-6} mol/L (0.5 mg/L)	[S4]

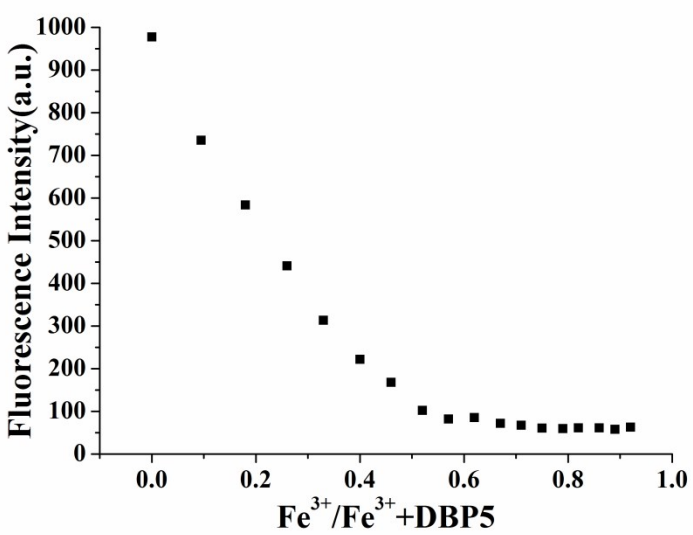


Fig. S9 The Job's plot examined between Fe^{3+} and **DBP5**, indicating the 1 : 1 stoichiometry, which was carried out by fluorescence spectra (λ_{ex} = 295 nm).

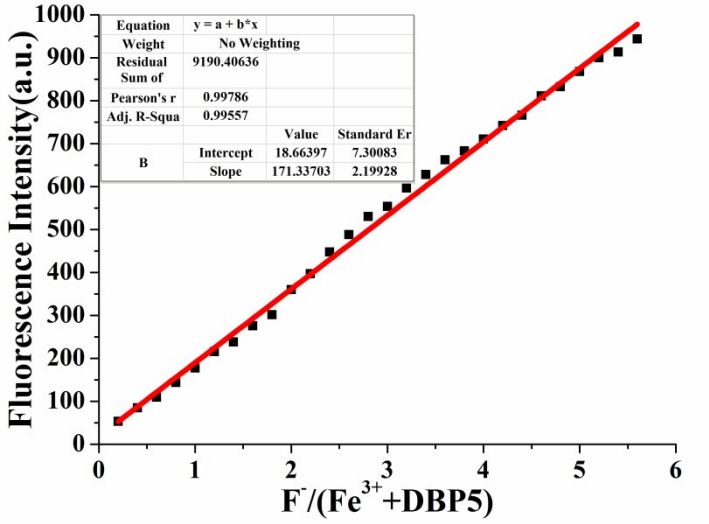


Fig. S10 The photograph of the linear range.

Linear Equation: Y=171.33703X+18.66397 R^2=0.99557

S=171.34×10^6

$$\delta = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}} = 3.68(n = 30)$$

K=3

LOD =K×δ/S= 6.44 ×10^{-8}M

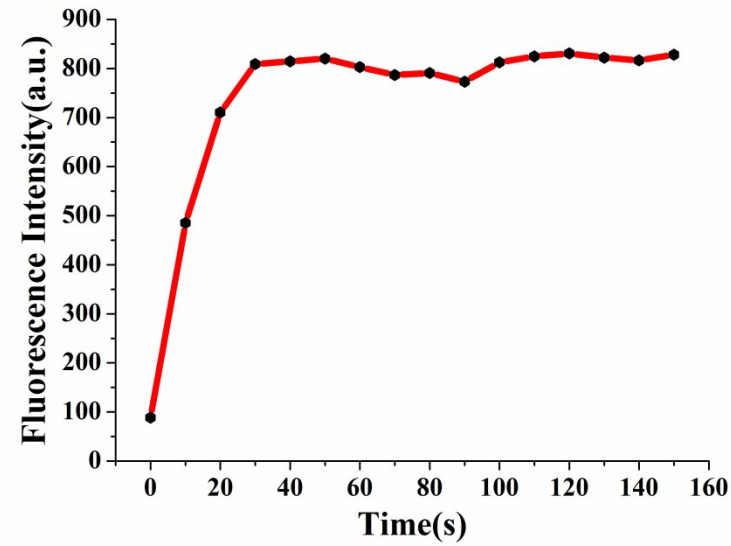


Fig. S11 Time-dependent of **DBP5**−Fe^{3+} (2×10^{-4} M) upon addition of F^- (1×10^{-3} M) in H_2O/DMSO (1 : 9 , v/v) with a plot of the fluorescence intensity that is estimated as the peak height at 330 nm.

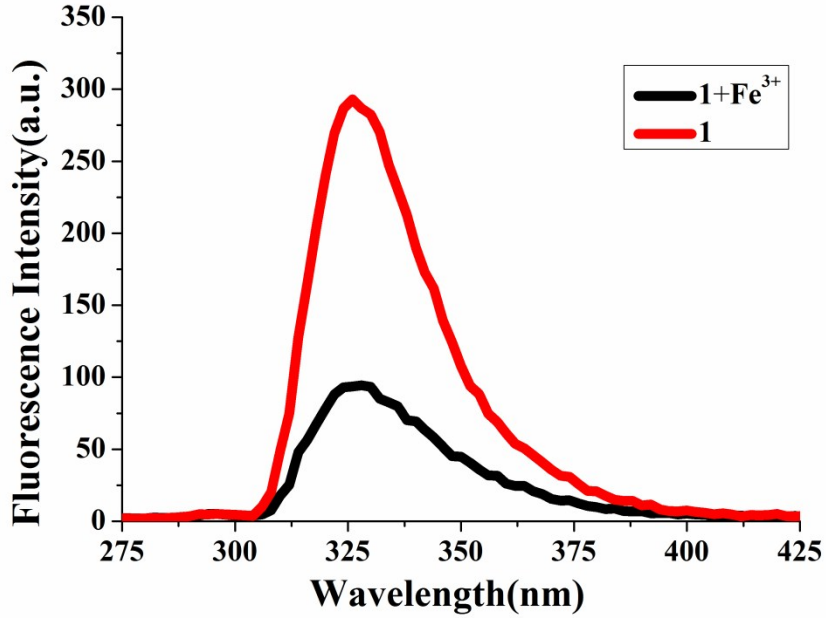


Fig. S12 Fluorescence spectral response of **1** (2×10^{-4} M) in H_2O/DMSO (1 : 9 , v/v) upon addition of 2 equiv. of Fe^{3+} (λ_{ex} = 295 nm).

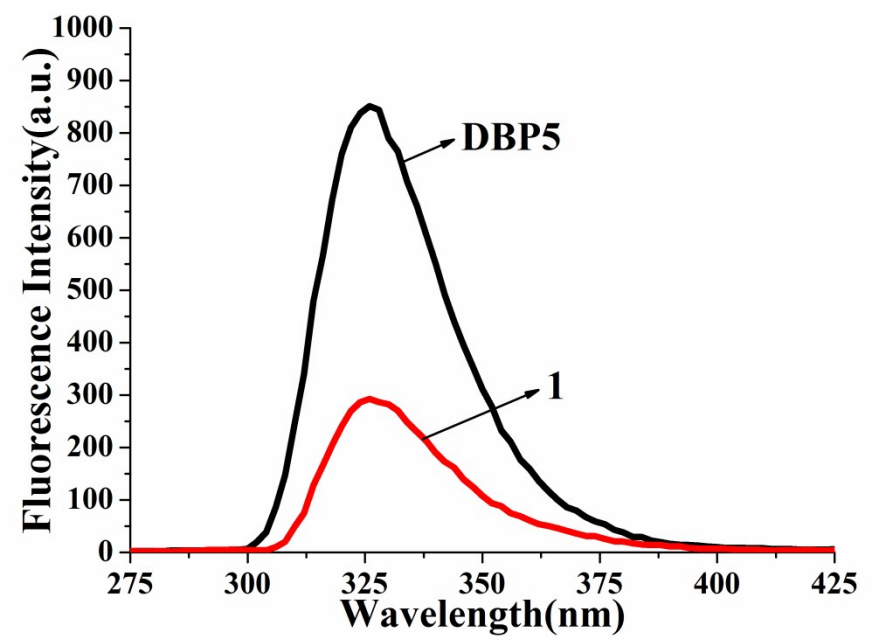


Fig. S13 Fluorescence spectral response of **1** (2×10^{-4} M) and **DBP5** (2×10^{-4} M) in H_2O/DMSO (1 : 9 , v/v) , λ_{ex} = 295 nm.

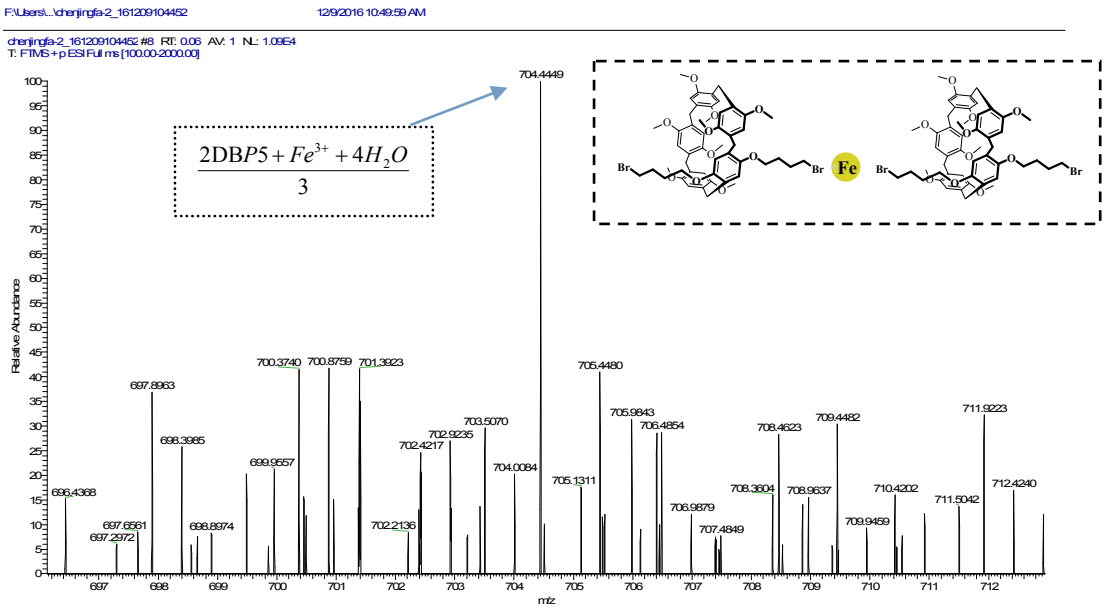


Fig. S14 High resolution mass data of complex 2**DBP5**·**Fe**$^{3+}$.

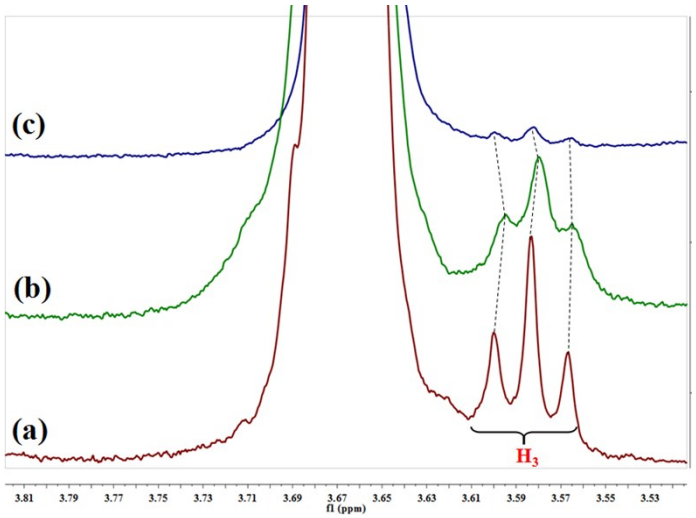


Fig. S15 Partial ^{1}H NMR spectra (600 MHz, 298 K) of (a) 5.0 mM DBP5; (b) 5.0 mM DBP5 and 10 mM Fe^{3+}; (c) 5.0 mM DBP5, 10 mM Fe^{3+} and 25 mM F^{-}.

Table S2 X-ray crystal data of **DBP5**

chemical formula	$C_{51}H_{60}Br_2O_{10}$
Chemical formula weight	992.81
Crystal system	triclinic
Space group	P-1
Cell length a	11.8851(10)
Cell length b	12.1025(10)
Cell length c	21.0450(13)
Volume	2566.6(3)
Z	2
Temperature	294.44(10) K
Crystal color	clear dark yellow
Crystal F 000	1032
Crystal density	1.285
Special details	Solvent masking has been carried out
Radiation wavelength	0.71073 Å
Measurement device	four-circle diffractometer
Measurement device type	SuperNova, Dual, Cu at zero, Eos
Measurement method	\w scans
Computing cell refinement	CrysAlisPro, Agilent Technologies, Version 1.171.37.35 (release 13-08-2014 CrysAlis171 .NET) (compiled Aug 13 2014,18:06:01)

Computing data collection	CrysAlisPro, Agilent Technologies, Version 1.171.37.35 (release 13-08-2014 CrysAlis171 .NET) (compiled Aug 13 2014,18:06:01)
Structure refinement	ShelXL (Sheldrick, 2015)

References:

[S1] L. V. Mulaudzi, J. F. van Staden and R. I. Stefan, *Anal. Chim. Acta*, 2002, **467**, 35.

[S2] A. Ohashi, H. Ito, C. Kanai, H. Imura and K. Ohashi, *Talanta*, 2005, **65**, 525.

[S3] A. Bobrowski, K. Nowak and J. Zarebski, *Anal. Bioanal. Chem.*, 2005, **382**, 1691.

[S4] C. Ortega, S. Cerutti, R. A. Olsina, L. D. Martínez and M. F. Silav, *J. Pharm. Biomed. Anal.*, 2004, **36**, 721.

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