Electronic Supplementary Information (ESI)

Two hexaazatriphenylene-pyrene based Hg^{2+} fluorescent chemosensors applicable to test paper detection

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Experimental

1. Materials and general methods

All the starting reagents and chemicals were purchased from commercial sources and used as received. Intermediates 2,7-di-tert-butylpyrene-4,5,9,10-tetraone, 2,7-di-tert-butylpyrene-4,5-dione and 2,3,8,9-tetraphenylpyrazino[2,3-f]quinoxaline-5,6-diamine were prepared according to literature procedures.[1-3] The solvents used for fluorescence measurements were purified by standard procedures. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker 300 MHz NMR spectrometer. High-resolution mass spectra were measured on an IonSpec 7.0T FT-ICR mass spectrometer. IR spectra were recorded on a TENSOR 27 OPUS Fourier transform infrared (FT-IR) spectrometer (Bruker) in the range of 4000−400 cm^{-1} using KBr disks dispersed with sample powders. Elemental analyses (C, H, and N) were tested using a Perkin-Elmer 240C analyzer. Fluorescence spectra were measured at room temperature on a Varian Cary Eclipse fluorescence spectrometer. UV-vis absorption spectra were recorded by a Shimadzu UV-2450 UV-vis spectrophotometer.

*2. Characterization data of compound **1***

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.67 (s, 18H), 7.46 (s, 24H), 7.92 (q, 8H), 7.99 (q, 8H), 8.76 (d, 2H), 10.07 (d, 2H). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) 31.98, 36.65, 128.50, 128.64, 129.85, 130.34, 138.27, 138.33, 139.36, 139.72, 141.28, 141.79, 152.46, 153.50, 154.35. MS-ESI calcd. for $C_{92}H_{63}N_{12}$ $[M + H]^+$ 1336.5, found 1336.5. Anal. Calcd. for $C_{92}H_{64}N_{12}$•$2H_2O$: C, 80.56; H, 5.58; N, 12.25%; Found: C, 80.41; H, 5.47; N, 12.14%. IR (KBr, cm^{-1}): 3132, 2917, 2849, 1586, 1472, 1369, 1247, 788, 594, 548.

*3. Characterization data of compound **2***

^{1}H NMR (300 MHz, CD_3Cl): δ (ppm) 1.75 (s, 18H), 7.46 (m, 12H), 7.93 (m, 4H), 8.05 (m, 6H), 8.38 (s, 2H), 10.03 (s, 2H). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) 32.73, 36.55, 122.01, 124.66, 127.40, 128.48, 128.62, 129.68, 130.38, 131.24, 138.58, 139.38, 139.86, 140.68, 144.25, 149.70, 153.41, 153.87. MS-ESI calcd. for $C_{58}H_{45}N_6$ $[M + H]^+$ 825.4, found 825.8; calcd. for $C_{116}H_{89}N_{12}$ $[2M + H]^+$ 1650.7, found 1649.4. Anal. Calcd. for $C_{58}H_{44}N_6 \cdot 3H_2O$: C, 79.25; H, 5.73; N, 9.56%; Found: C, 79.14; H, 5.76; N, 9.18%. IR (KBr, cm^{-1}): 3441, 3056, 2951, 1586, 1473, 1370, 905, 741, 695, 594.

Table S1 The Hg^{2+} responsive chemosensors reported in recent years (2012-2014)

Entry	Chromophore	Detection limit (nM)	Ref.
1	pyrene-hexaazatriphenylene	2.8 for **1** 3.1 for **2**	This work
2	acridinedione	2	4
3	anthracene and pyrene	2−4	5
4	rhodamine	3	6
5	rhodamine B	5.9	7
6	pyrene	22	8
7	phenanthroimidazole	25	9
8	BODIPY	27	10
9	1-aminoanthraquinone	50	11
10	rhodamine B and hexaphenylbenzene	50−100	12
11	dansyl	50−250	13
12	pyrene	74	14
13	7-methoxycoumarin	200−315	15
14	BODIPY	226	16
15	naphthalene	230	17
16	pyrene	510−2400	18
17	10-ethylphenothiazine	906	19
18	Tetraphenylethene and benzothiazolium	1000	20
19	quinazoline	1500	21
20	nitrobenzoxadiazole	1500	22
21	anthracene and oxyquinoline	3200	23
22	BODIPY	10000	24
23	BODIPY	15000	25
24	BODIPY	Not given	26

Table S2 The energies of the frontier orbitals of compound **1** and **2**

Compound	HOMO (eV)	LUMO (eV)	LUMO – HOMO (eV)
1	–5.663	–2.281	3.383
2	–5.462	-2.187	3.274

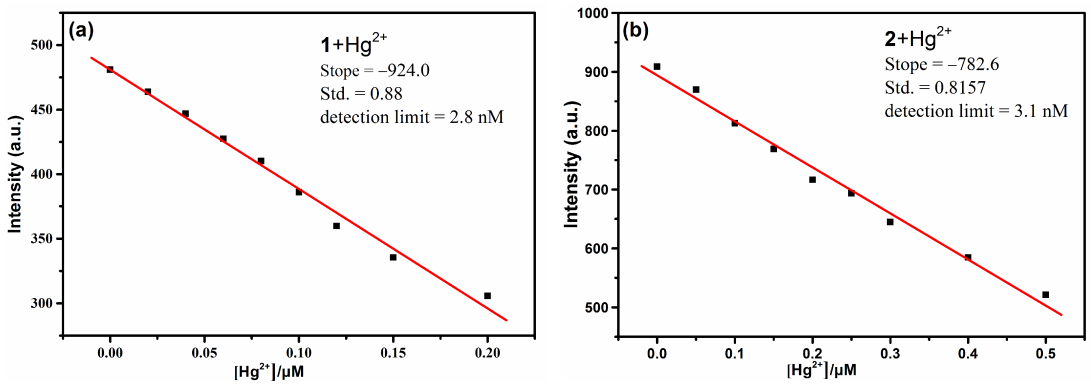

Fig. S1 Linear emission intensity change of (a) **1** and (b) **2** as a function of Hg^{2+} concentration. λ_{em} is 459 nm for **1** and 529 nm for **2**.

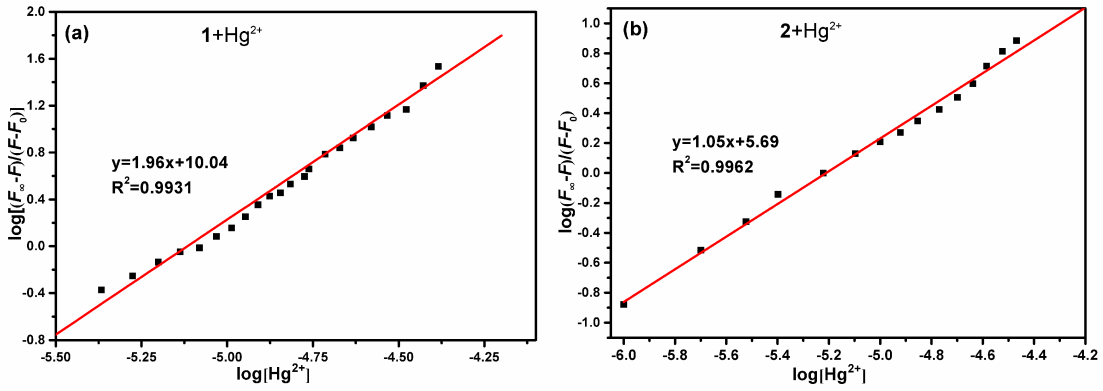

Fig. S2 The linear fitting of fluorescence intensity change with $\log[(F_\infty - F)/(F - F_0)] = n\log[Hg^{2+}] + \log\beta$. n is the complex-ratio of **1** or **2** to Hg^{2+}, β is the stability constant of the formed complex, F_0, F and F_∞ are the fluorescence intensities of the solution of **1** or **2** after the addition of none, a given amount and excess amount of Hg^{2+}, respectively. (a) [**1**] = 10 μM, λ_{em} = 459 nm. (b) [**2**] = 10 μM, λ_{em} = 529 nm.

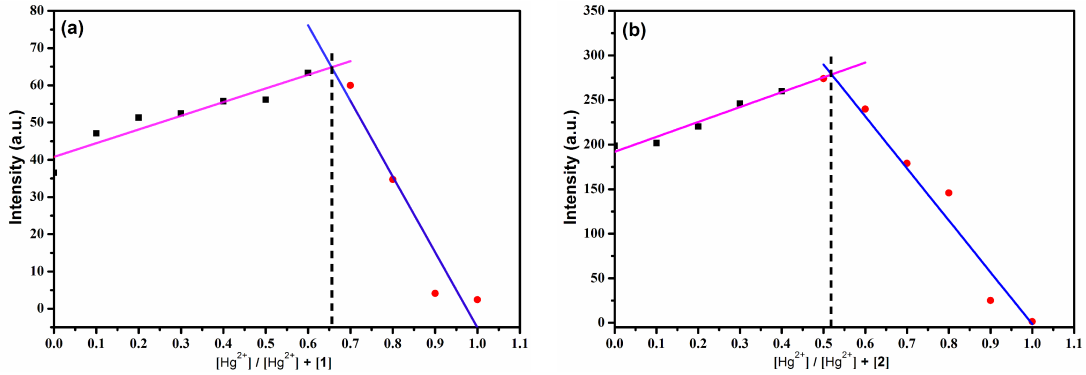

Fig. S3 Job's plots of (a) **1** and (b) **2** to Hg^{2+} in CH_3CN-H_2O (v/v = 9/1) media obtained by fluorescence measurements.

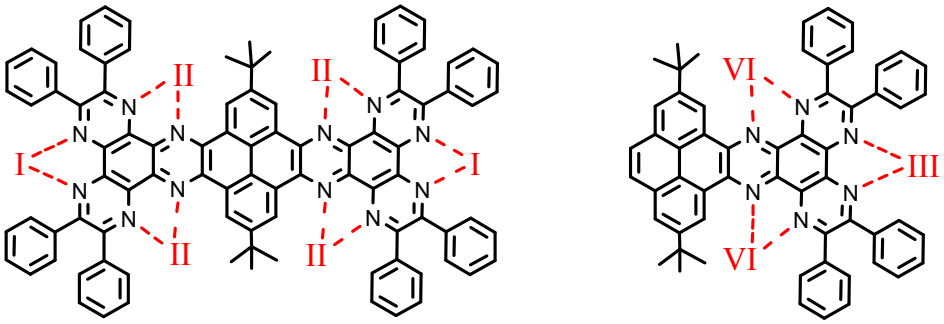

Fig. S4 Possible binding sites of compounds **1** and **2**.

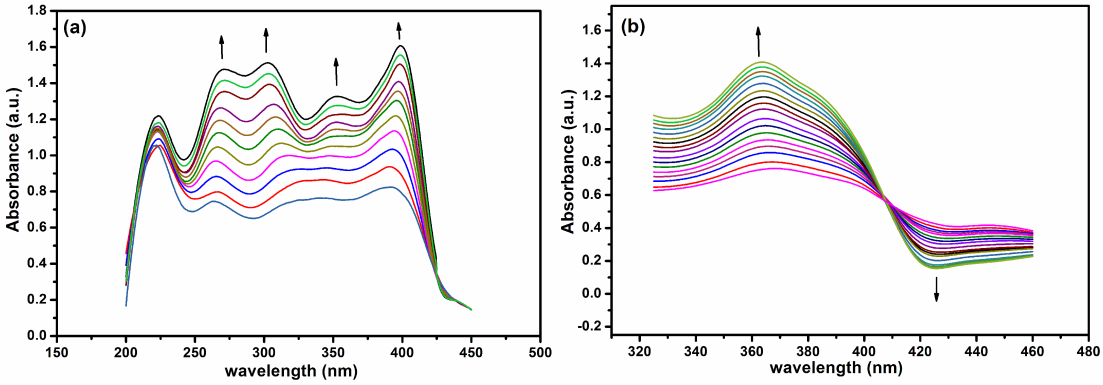

Fig. S5 Absorption spectra of (a) **1** (50 μM) and (b) **2** (50 μM) in CH_3CN-H_2O (v/v = 9/1) media upon the addition of Hg^{2+} (0−220 μM for **1** and 0−500 μM for **2**).

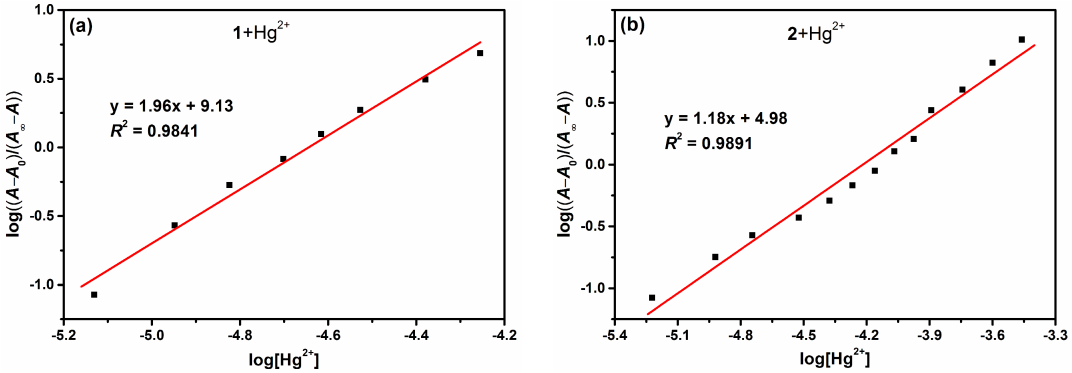

Fig. S6 The linear fitting of absorbance change with $\log[(A_\infty - A)/(A - A_0)] = n\log[Hg^{2+}] + \log\beta$. n is the complex-ratio of **1** or **2** to Hg^{2+}, β is the stability constant of the formed complex, A_0, A and A_∞ are the absorbances of the solution of **1** or **2** after the addition of none, a given amount and excess amount of Hg^{2+}, respectively. (a) [**1**] = 50 μM, λ = 399 nm. (b) [**2**] = 50 μM, λ = 364 nm.

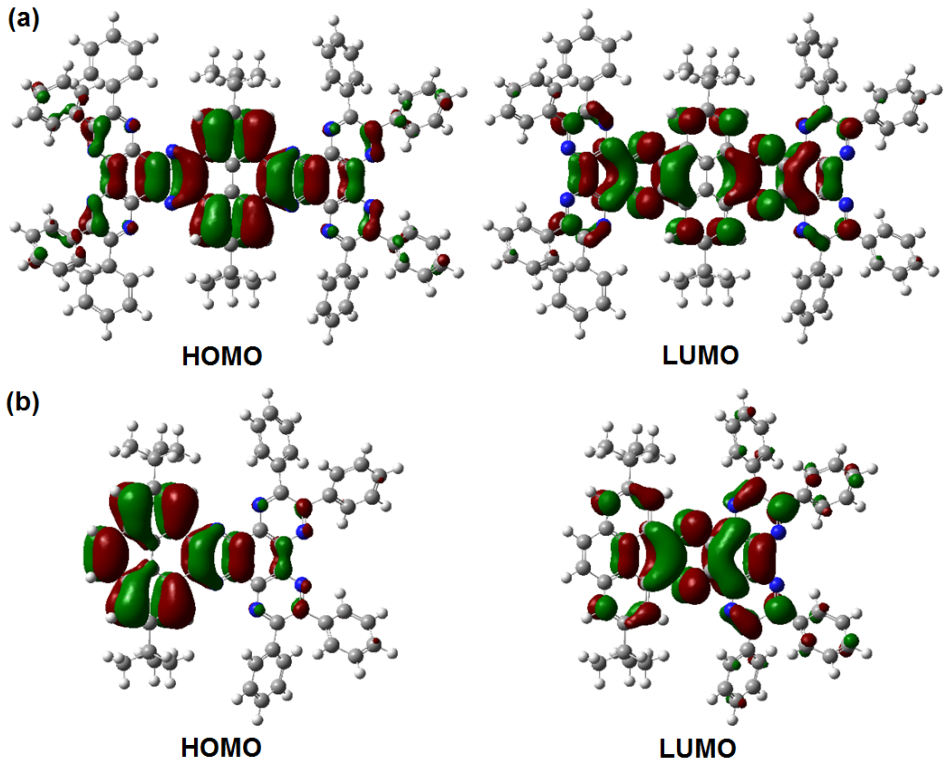

Fig. S7 Interfacial plots of the HOMO and LUMO of compunds (a) **1** and (b) **2**. The molecular configurations of these compounds were optimized at B3LYP/6-31G(d) level previously. Gray, white and blue atoms of the molecular frameworks indicate the C, H and N atoms, respectively. Red and green parts on the interfacial plots refer to the different phases of the molecular wave functions, for which the isovalue is 0.02 au.

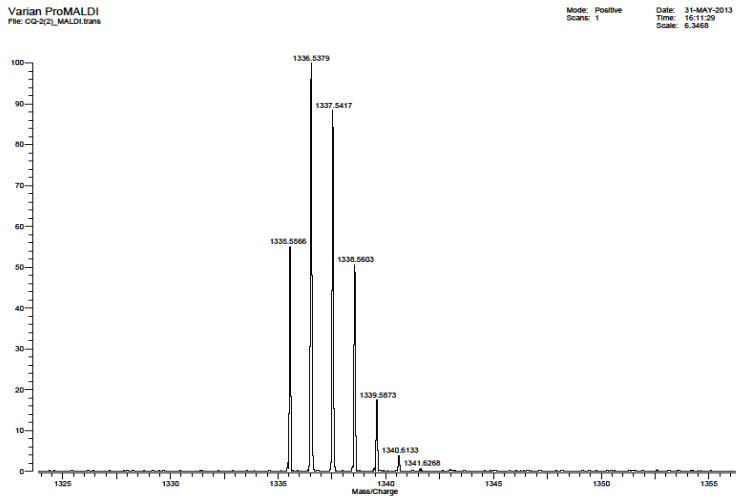

Fig. S8 ESI-MS spectrum of compound **1**.

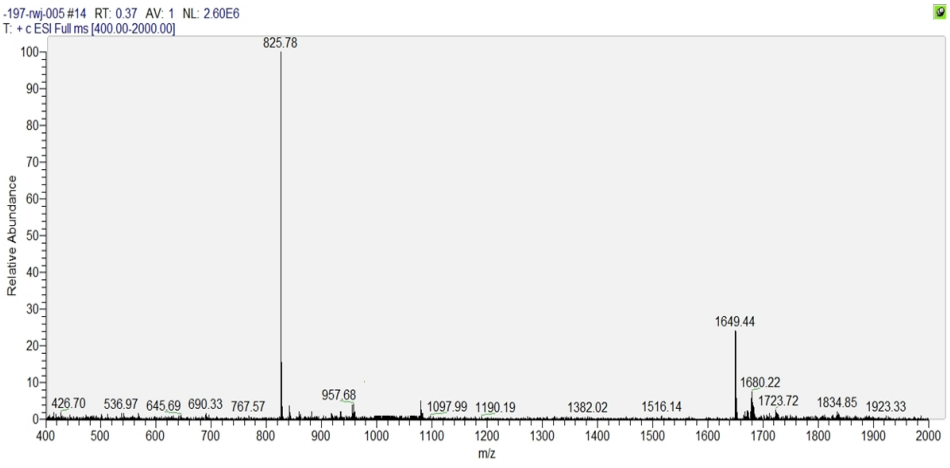

Fig. S9 ESI-MS spectrum of compound **2**.

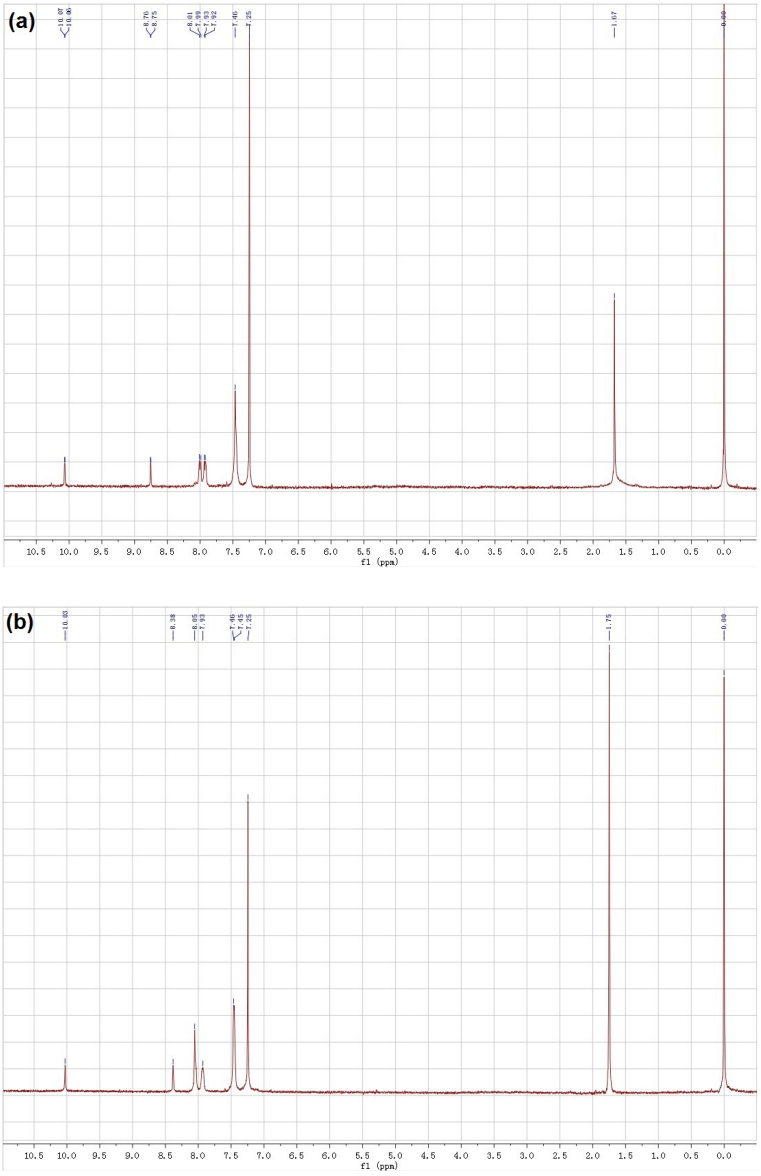

Fig. S10 The ^{1}H NMR spectra of (a) **1** and (b) **2**.

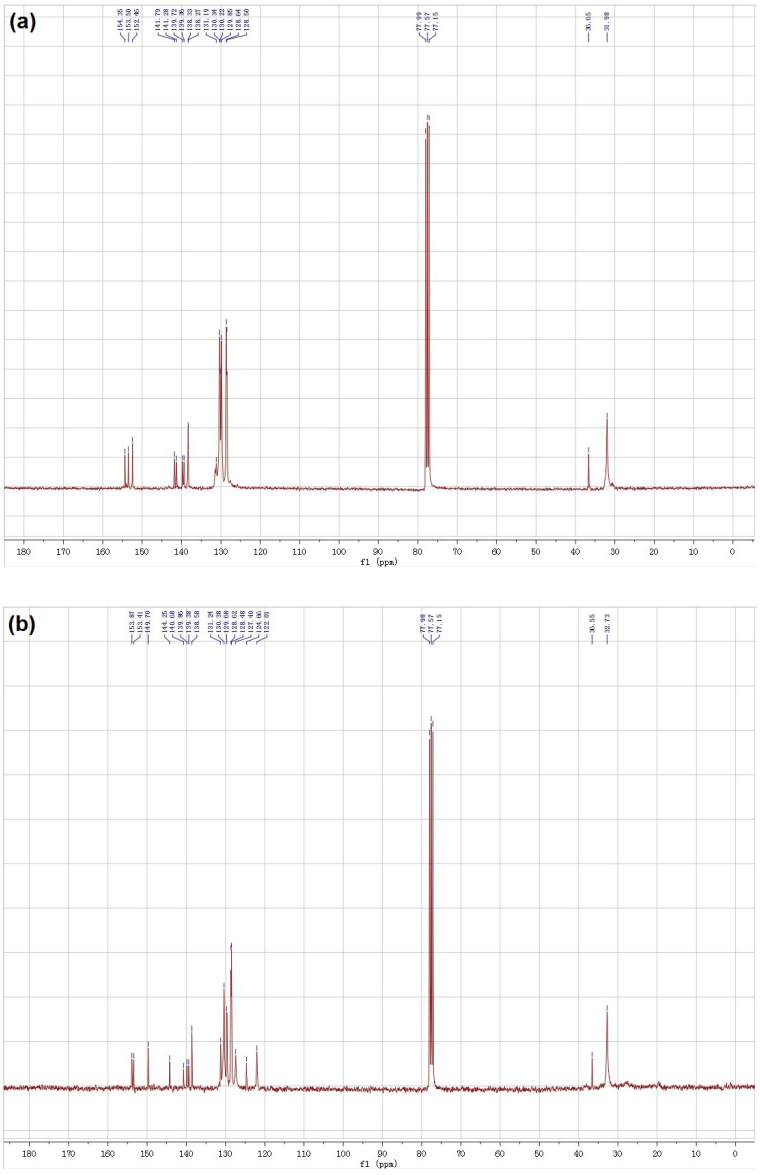

Fig. S11 The ^{13}C NMR spectra of (a) **1** and (b) **2**.

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