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ARTICLE TYPE

Hg^{2+}-induced deprotonation of anthracene based chemosensor: Set Reset flip-flop at the molecular level using Hg^{2+} and I^- ions

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A highly selective, simple, cost-effective anthracene-based chemosensor (**1**) has been developed. It exhibits Hg^{2+}-selective "on-off" fluorescence quenching behavior, wherein, Hg^{2+} induces deprotonation of imidazole NH which is rationalized by ^1H NMR titrations. The system exhibits fluorescence color change from fluorescent bluish-green to blue with high selectivity and sensitivity over other metal ions. The *in situ* generated deprotonated species of **1** with Hg^{2+} can recognize I^- ions via fluorescence enhancement. The present sensing system is successfully applied for the detection of Hg^{2+} ions in real samples. Chemosensor **1** can also mimic the functioning of set/rest flip-flop with chemical inputs from Hg^{2+} and I^- ions.

Introduction

Over the past few decades, there is mounting interest for synthesis of structurally simple receptors that can effectively signal binding phenomenon of the cationic[1-3] and anionic[4-5] guest species in terms of sensitivity and selectively. Due to the non-biodegradability of heavy metals in water, they have caused widespread water endangerment and other serious health problems[6]. Mercury is one of the most prevalent toxic metals as it can cause serious health problems such as brain damage, kidney failure and various cognitive and motion disorders[7] even at very low concentration[8-9]. The minamata disease cause by methylmercury accumulation resulted in disastrous effects in Minamata Bay in Japan in 1953[10]. One of the most stable inorganic forms of mercury is the solvated mercury, which is highly toxic due to its good water solubility[11]. The bacteria present in the marine environment convert inorganic mercury into neurotoxic methylmercury which accumulates through food chain[12]. A Key source of human revelation is mercury in contaminated natural water, and therefore, it is of great necessity to explore rapid, cost-effective and selective methods for detecting mercury in aqueous media.

On the other hand, iodide is very important microelement for humans because it plays an essential role in biological activities, such as thyroid function, neurological activity, cell growth and brain functions[13-15]. Excess or deficiency of iodide could lead to thyroid diseases. The World Health Organization (WHO) data shows that iodide deficiency disorders are a significant public health problem in many countries[16]. Iodide content in urine has been widely used as a marker for status assessment of iodide deficiency disorder. The elemental iodine has been frequently used in many areas of chemistry for synthesizing important compounds / intermediates such as drugs, dyes and molecular electronics[17]. Thus, the development of analytical methodology for the determination of trace levels of iodide ion is of significant research interest. However, due to iodide's large anionic radius, low charge density, and low hydrogen-bonding ability, iodide sensing probes are less commonly known[18-20]. Thus, keeping in view the role of mercury and iodide ions in day to day life, the detection of both Hg^{2+} and I^- is very important for human health and environmental protection. Amongst different types of chemosensors, fluorescent method is very useful due to its operational simplicity, high selectivity, sensitivity, rapidity, and nondestructive methodology[21-24].

In the present study, we have designed and synthesized anthracene appended chemosensor **1** for the selective recognition of Hg^{2+} in CH_3CN:H_2O (9:1, v/v) using fluorogenic turn-off modes. This can be attributed to the perturbation of excimer band of anthracene due to Hg^{2+} induced deprotonation of the imidazole –NH, resulting in the enhanced spin-orbit coupling associated with the heavy atom effect of the complexed Hg^{2+}. Furthermore, the deprotonated species of **1** generated in situ with Hg^{2+} can be used as a platform for recognition of I^- ions via fluorescence enhancement. Thus, chemosensor **1** behaves like a fluorescence sensor for both cationic and anionic species, based on a different approach to that of a chemosensing ensemble. The analytical applications of **1** were also tested for the detection of Hg^{2+} in real water samples.

Earlier literature reports of deprotonation caused by metal ions has been quite generously used for developing alkali and alkaline earth metal ion sensors in phenolic chromophores[25-29] but probably due to less acidic nature of NH, its deprotonation in the design of metal ion sensors has been scarcely investigated[30-32].

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† Electronic Supplementary Information (ESI) available:

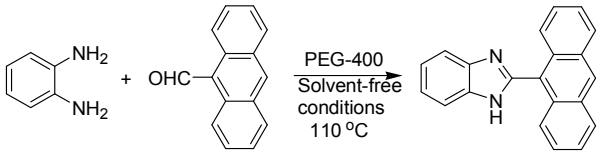
Since, in case of metal ion sensors, the anion thus formed on deprotonation of NH is more stabilized by cation– anion electrostatic interactions than in case of anion sensors, it is expected to provide wider scope in developing metal ion sensors.

Based on the fluorescence behavior of **1** with Hg^{2+} and I^- ions, set/reset flip-flop has been designed. It is a binary sequential logic circuit that can be used for information storage. It can be constructed from a pair of cross-coupled NOR logic gates. Sequential circuits are essential for the realization of memory devices capable of storing information and operating through feedback loops, where one of the outputs of the device functions as an input and is memorized as a "memory element"[33].

Results and discussion

Synthesis of chemosensor 1

The synthesis of chemosensor **1** is depicted in scheme1. Chemosensor **1** was synthesized by the refluxing 9-anthraldehyde with phenylenediamine in PEG-400 under solvent-less conditions at 110 °C[34].



Scheme-1. Synthesis of chemosensor **1**

The chemosensor **1** has been obtained with quantitative yield and characterized by several techniques such as IR, ^1H NMR, ^{13}C NMR and mass spectra. The spectral investigations gave consistent data for the structure of **1**.

Binding studies with Hg^{2+}

With an objective to evaluate the potential use of probe **1** as chemosensor, we have investigated its interaction with various metal ions using perchlorate as a counter anion using fluorescence and NMR spectroscopy. Among the competitive metal ions such as Na^+, K^+, Mg^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+} and Cd^{2+} tested in 9:1 (v/v) aqueous acetonitrile (pH 7.0 HEPES buffer), only Hg^{2+} responds to chemosensor **1** (Fig. S1).

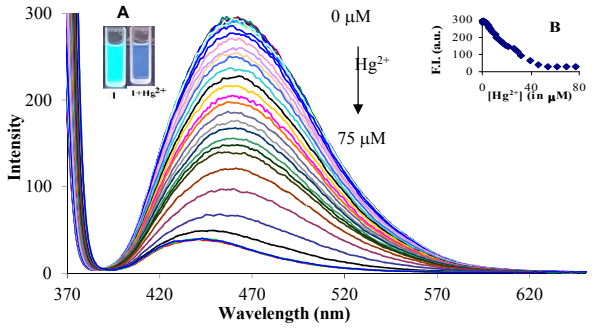


Fig. 1 Fluorescence response of chemosensor **1** (1.5 μM) on addition of Hg^{2+} ions (0-75 μM) in CH_3CN-buffer solution (9:1, v/v, pH 7.0); λ_{ex} 365 nm. Inset A: fluorescence color change before and after the addition of Hg^{2+} ions. Inset B: Change in the fluorescence intensity of **1** as a function of Hg^{2+} ion concentration.

In the fluorescence spectrum, chemosensor **1** (1.5 μM) exhibits an intense characteristic excimer emission band of anthracene moiety at 463 nm with a stoke's shift of 98 nm, when excited at 365 nm (Fig. 1). The dimer peak corresponding to $2x[M+1]^+$ in mass spectra (Fig. S2) also support to the excimer formation in chemosensor **1**. Upon addition of Hg^{2+} ions, the emission gradually decreases, which we attribute to the perturbation of excimer band due to formation of **1**-Hg^{2+}-**1** structure as shown in figure 2[35]. ^1H NMR spectroscopy and Job's plot results support this assumption.

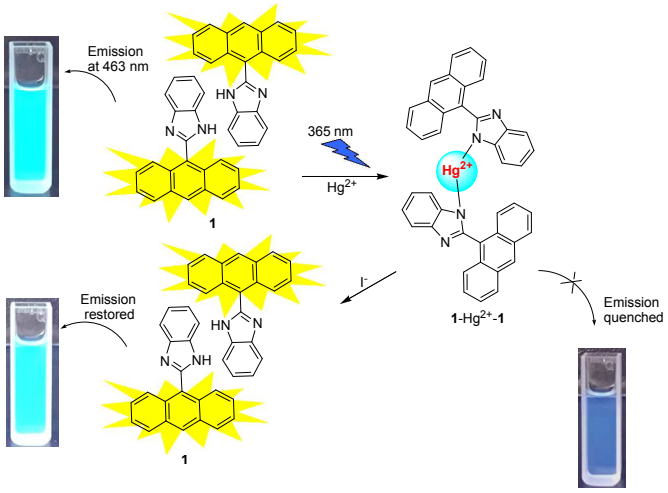


Fig. 2 Schematic illustration of the formation of **1**-Hg^{2+}-**1** complex and subsequent fluorescent turn-on sensing for I^- in CH_3CN-buffer solution (9:1, v/v, pH 7.0). Photographs were taken under a hand-held 365 nm UV lamp.

The fluorescence quenching observed at 463 nm with addition of Hg^{2+} ions is accompanied with a change in the color of the fluorescence from bluish-green to blue (inset A, Fig. 1). The emission intensity of chemosensor **1** decreases as a function of the Hg^{2+} ion concentration, as shown in inset B of figure 1. The quenching response of **1** on addition of Hg^{2+} ions occurs due to the deprotonation of the imidazole –NH by Hg^{2+} addition which disrupts the excimer band resulting in the enhanced spin-orbit coupling associated with the heavy atom effect of the complexed Hg^{2+} ions[36].

The limit of detection (LOD) and limit of quantification (LOQ) are calculated from fluorescence titrations. Linear regression graph of titrations was used to calculate standard deviation and slope of linear response.

$LOD = 3\sigma s^{-1}$

$LOQ = 10\sigma s^{-1}$

where σ = standard deviation of response and s = slope of the calibration curve.

So, to calculate limit of detection, standard deviation is divided by slope of line followed by multiply it with 3[37]. The detection limit and limit of quantification is reasonably estimated to be 2.45 μM and 7.43 μM. The linear concentration range for the determination of Hg^{2+} by this sensor is 2.1–70 μM.

The competition metal binding assay has been conducted in order to scrutinize the solution behavior of chemosensor **1** with various metal ions. For this, different solutions of chemosensor **1** with 30 eq. of Hg^{2+} mixed with excess of different metal ions (100 equiv.) are prepared. It has been observed that the

interference of other surveyed metal ions was negligible or moderately low in sensing of Hg^{2+} with chemosensor **1**. These results indicate that chemosensor **1** shows a worthy sensitivity and selectivity towards the Hg^{2+} over other competitive metal ions (Fig. S3).

The chemosensing properties are, in general, highly dependent on the pH of the system, therefore, the influence of pH on **1** has been evaluated in 9:1 (v/v) aqueous acetonitrile. The fluorescence intensity of **1** at 463 nm remains by and large unaffected between pH 6.7-11 (Fig. S4). Significantly, on moving beyond the pH range 6.7-11, the fluorescence intensity at 463 nm gradually decreases.

To confirm the deprotonation of imidazole NH of chemosensor **1** caused by Hg^{2+} addition, we carried out ^1H NMR titrations of chemosensor **1** using Hg^{2+} ions in DMSO. It has been observed that, on addition of 0.5 equiv. of mercury perchlorate to a solution of chemosensor **1**, the imidazole NH proton nearly disappeared alongwith downfield shift from δ 13.06 to δ 14.86 (Fig. 3). This indicates that deprotonation of the NH proton is taking place in the presence of Hg^{2+} ions.

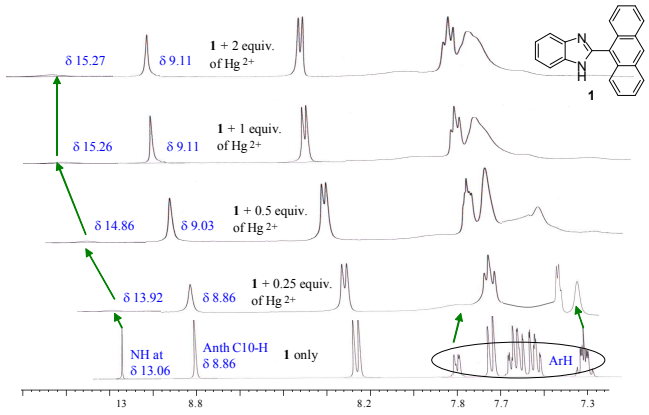


Fig. 3 Partial ^1H NMR spectra in DMSO-d_6 upon addition of different equivalents of Hg^{2+} ions in solution of **1**.

In addition to metal ion binding properties, we also investigated the fluorescence behaviour of chemosensor **1** towards different anions such as F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^- and SO_4^{2-} added as their tetrabutylammonium as the counter cation. No significant variation in the fluorescence intensity was found upon addition of various anions to the CH_3CN-buffer (9:1, v/v; pH= 7.0) solution of **1** (Fig. S5).

Stoichiometry of the complexation

The stoichiometry for the complexation of chemosensor **1** with Hg^{2+} has been studied using Job's continuous variation method. Job's plot obtained from the fluorescence measurements shows the formation of **1**.Hg^{2+} complex in 2:1 stoichiometric ratio (Fig. S6). Assuming a 2:1 complex formation, the binding constant[38] is calculated to be 2.2 x 10^9 M^{-2}.

Application in real samples

The practical application of the designed chemosensor has been evaluated by determination of Hg^{2+} in drinking water, river water and tap water samples. The water samples were first filtered to remove insoluble substances. To keep a stable system at given solvent ratio and pH, HEPES buffer was added to maintain the pH 7.0. All the samples with or without addition of Hg^{2+} at different concentrations as shown in table 1 were analyzed by chemosesnor **1** and the results obtained are found in good agreement with the concentration of Hg^{2+} ions in the system. As shown in table 1, it can be confirmed that recovery studies of Hg^{2+} based on **1** are satisfactory with RSD values ranging from 1.2 to 2.6%. This indicates the suitability and practicality of the present chemosensor **1** for the detection of Hg^{2+} from real water samples without any interferences from other environmentally relevant competitive metal ions.

Table 1. Results of Hg^{2+} sensing in drinking water, tap water and river water samples with **1**.

Sample	Hg^{2+} added/mol L^{-1}	Hg^{2+} found/mol L^{-1}	Recovery (%)	RSD (%)
Drinking Water	0	Not detected	–	–
	7.50 x 10^{-6}	7.44 x 10^{-6}	99.2	1.4
	12.00 x 10^{-6}	11.9 x 10^{-6}	99.4	1.2
	18.00 x 10^{-6}	18.4 x 10^{-6}	102.8	2.0
	30.00 x 10^{-6}	29.6 x 10^{-6}	98.8	1.2
	37.50 x 10^{-6}	38.6 x 10^{-6}	102.9	1.2
Tap Water	0	Not detected	–	–
	7.50 x 10^{-6}	6.55 x 10^{-6}	87.3	2.6
	12.00 x 10^{-6}	11.2 x 10^{-6}	92.9	1.6
	18.00 x 10^{-6}	18.2 x 10^{-6}	100.8	1.4
	30.00 x 10^{-6}	31.5 x 10^{-6}	104.9	–
	37.50 x 10^{-6}	37.4 x 10^{-6}	99.8	2.3
River Water	0	Not detected	–	–
	7.50 x 10^{-6}	7.9 x 10^{-6}	105.3	2.2
	12.00 x 10^{-6}	11.95 x 10^{-6}	99.6	1.4
	18.00 x 10^{-6}	18.00 x 10^{-6}	100.0	1.4
	30.00 x 10^{-6}	30.6 x 10^{-6}	102.0	–
	37.50 x 10^{-6}	37.25 x 10^{-6}	99.3	2.3

Fluorescence turn-on sensing for iodide

We utilized the deprotonated species formed on the addition of Hg^{2+} to chemosensor **1**, as a platform for detection of I^- ion due to known high stability of HgI_2. The fluorescence spectra of **1**-Hg^{2+}-**1** in aqueous acetonitrile solution in the presence of various amounts of iodide is shown in figure 5. Upon addition of incremental amounts of I^- ions (0-7 equiv.) to solution of **1**-Hg^{2+}-**1**, a significant fluorescence enhancement has been observed at 463 nm along with change in the color of the fluorescence back to bluish-green (Fig. 4).

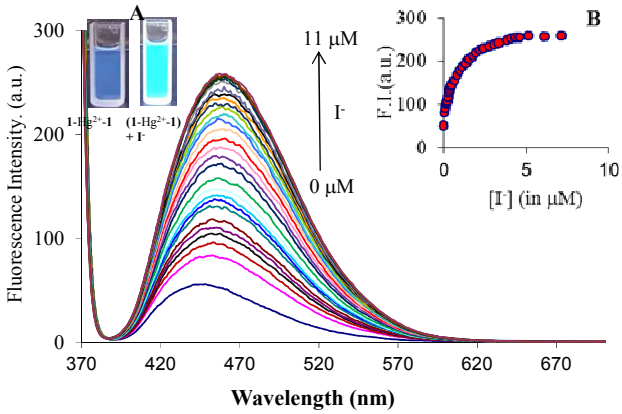


Fig. 4 Fluorescence response of **1**-Hg^{2+}-**1** (1.5 μM) on addition of I^- ions (0-11 μM) in CH_3CN-buffer solution (9:1, v/v, pH 7.0); λ_{ex} 365 nm. Inset A: fluorescence color change before and after the addition of I^- ions. Inset

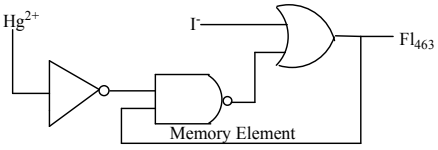
B: Change in the fluorescence intensity of **1**-Hg^{2+}-**1** as a function of I^- ion concentration

Addition of OH^- ions also cause decomplexation of **1**-Hg^{2+}-**1** complex in similar manner as done by I^- ions due to formation of stable $Hg(OH)_2$ complex (Fig. S6). So, for same reason, the effect of pH on **1**-Hg^{2+}-**1** complex cannot be accurately evaluated.

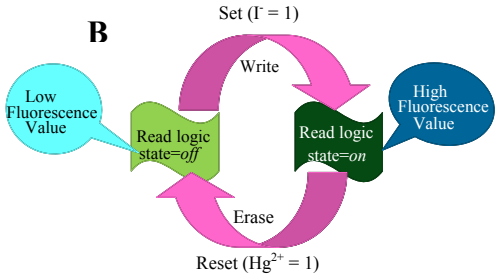
Elaboration of Set/Reset flip-flop

Recently, the conversion of chemically encoded information into optical (fluorescence / absorbance) signals for the development of sequential logic devices, has attracted tremendous attention for unconventional computing. Sequential circuits are the memory devices having capability of storing information. These usually operate through feedback loops, where one of the outputs of the device functions as an input and is memorized as a "memory element"[39]. Therefore, using Hg^{2+} and I^- ions as the chemical inputs, and fluorescence signal as the output, set/reset flip-flop can be constructed. The chemical inputs of Hg^{2+} and I^- are designated as In_1 and In_2, respectively. The threshold value of the fluorescence emission recorded at 463 nm is 60. A fluorescence intensity higher than the threshold value is assigned as "1" and an intensity lower than that value is assigned as "0", corresponding to the "on" and "off" states for the output signals, respectively. Different output values observed at 463 nm on sequential addition of Hg^{2+} and I^- ions as summarized in truth table (Fig. 5C) represent set/reset flip-flop corresponding to the memory device shown in figure 5A. The reset input (In_1 = 1) results in the fluorescence turning off at 463 nm and this encoded information is "read" in the system as "erased" and the logic operation is saved as "Output = 0". The stored information is "written" by the set input (In_2 = 1), where the fluorescence is turned on at 463 nm, this information is written by the system and the logic operation is saved as "Output = 1". The reversible and reconfigurable sequence of the set/reset logic operations in the feedback loop demonstrates a memory feature with "write–read–erase–read" functions (Fig. 5B) through the output signal at 463 nm. The sequential circuits construct memory devices and thus, generate a system that can store encoded information.

A



B



C

In_1 (Hg^{2+})	In_2 (I^-)	Out (Fl_{463})
0	0	1
1	0	0
0	1	1
1 (1st)	1 (2nd)	1
1 (2nd)	1 (1st)	0

Fig. 5 Logic symbol (A) for Set/Reset flip-flop and Schematic representation of the reversible logic operations for the memory element possessing "Write-read-erase-read" functions (B) and truth table (C)

Conclusions

In conclusion, the experimentation revealed that a much simpler (one step synthesis), cost-effective anthracene based highly selective fluorescent chemosensor for Hg^{2+} ions in the presence of other competitive metal ions. The sensing can be observed by fluorescence and ^1H NMR titrations pointing to Hg^{2+}-induced deprotonation of imidazole NH. Furthermore, deprotonated species **1**-Hg^{2+}-**1** can behave as a chemosensing system for the "turn on" detection of I^- ions and all the fluorescence changes involve naked eye fluorescence color change. Practical applications carried out in real water samples further indicate that the sensing system has great potential for facile real-time monitoring of Hg^{2+} ions. In addition, the synthesized chemosensor mimics the function of set/reset flip-flop, with inputs of Hg^{2+} and I^- ions, at the molecular level.

Experimental

General experimental conditions: All the solvents, reagents, metal and anion salts were purchased from Sigma-Aldrich Ltd and were used as received. Acetonitrile (CH_3CN) was of HPLC grade. Deionized water was used throughout the experiments. All fluorescence spectra were recorded on Hitachi F-7000 spectrophotometer. Melting point was determined in capillary and is uncorrected. ^1H and ^{13}C NMR spectra were recorded on a BRUKER AVANCE 400 and 100 MHz instrument using tetramethylsilane as an internal standard. All the metal ions such as Na^+, K^+, Mg^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+} and Cd^{2+} were added as their perchlorate salts whereas all the anions such as F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^- and SO_4^{2-} were added as their tetrabutylammonium salts for the different fluorescence spectroscopic experiments. Stock solution of the chemosensor **1** (1 x 10^{-3} M) was prepared in DMSO. This stock solution was diluted with CH_3CN-H_2O (9:1, v/v) and used further for different spectroscopic experiments. The excitation was carried out at 365 nm for chemosensor **1** with 5 nm excitation and emission slit widths in fluorometer. For fluorescence measurements, 1 cm width and 3.5 cm height quartz cells were used.

General procedure for ^1H NMR experiments: For ^1H NMR titrations, two stock solutions were prepared in DMSO-d_6 (5 x10^{-2} M), one of them containing host only and the second one containing an appropriate concentration of guest. Aliquots of the two solutions were mixed directly in NMR tubes, which then was diluted to 0.5 mL with DMSO-d_6 if need be.

Synthesis of chemosensor 1

Chemosensor **1** was synthesized by the refluxing 9-anthraldehyde

with phenylenediamine in PEG-400 under solvent-less conditions at 110 ^{o}C[31]. Solid, Yield 83%; mp 150 ^{0}C, FTIR (cm^{-1}): 3052.03 ($\nu_{Aromatic\ C\text{-}H\ str.}$),1615.14 ($\nu_{C=N\ str.}$), 1519.11, 1445.37 ($\nu_{Aromatic\ C\text{-}C\ str.}$), 1394.34 ($\nu_{C\text{-}C\ str.}$), 1329.26 ($\nu_{C\text{-}N\ str.}$); ^{1}H NMR (DMSO, 400 MHz) δ (ppm): 7.35 (d, 2H, *J* = 6.0 Hz, ArH), 7.52 (t, 2H, *J1=J2* = 6.0 Hz, ArH), 7.56-7.63 (m, 3H, ArH), 7.69 (d, 2H, *J* = 6.57 Hz, ArH), 7.83 (d, 1H, *J* = 5.04 Hz, ArH), 8.22 (d, 2H, *J* = 6.27 Hz, ArH), 8.86 (s, 1H, ArH), 13.1 (s, 1H, NH); ^{13}C NMR (DMSO + $CDCl_3$, 75 MHz) δ (ppm): 121.91, 125.39, 125.56, 125.73,126.51, 128.32, 128.64, 130.61, 149.46, 162.23, 185.79 (Fig. S8 and S9); MS: *m/z* (relative abundance (%), assignment) = 295.1 [100, $(M+1)^{+}$].

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