Electronic Supporting Information (ESI)

A Newly Developed Highly Selective Zn^{2+}-AcO^{-} Ion-pair Sensor through Partner Preference: Equal Efficiency under Solitary and Colonial Situation

Monaj Karar[1], Suvendu Paul[1], Bhaskar Biswas[2], Tapas Majumdar[1]*, and Arabinda Mallick[3]*

[1]*Department of Chemistry, University of Kalyani, Nadia, West Bengal- 741235, India*

[2]*Department of Chemistry, Surendranath College, Kolkata, West Bengal -700009, India*

[3]Department of Chemistry, Kashipur Michael Madhusudan Mahavidyalaya, Purulia, West Bengal -723132, India.

E-mail AM: ampcju@yahoo.co.in; TM: tapasmju@gmail.com

Contents

Characterization of HBP:

1. NMR result:

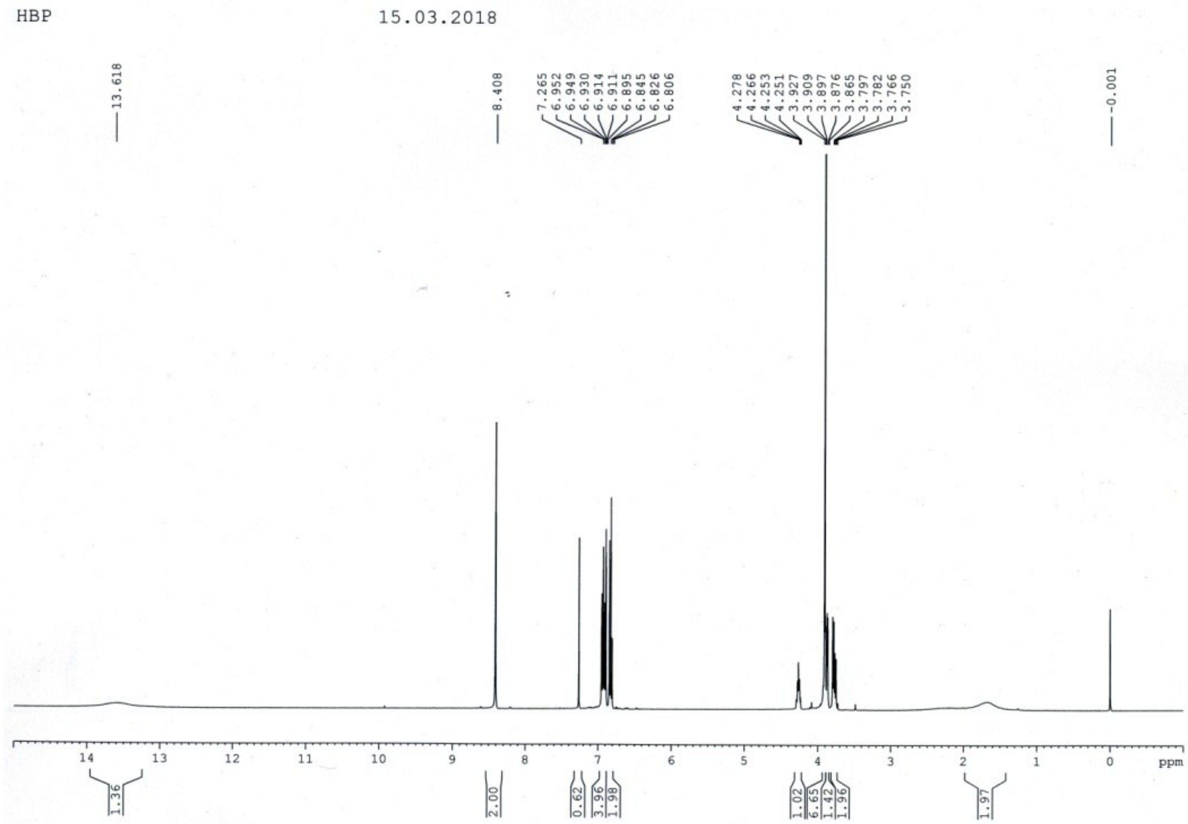


Figure S1: ^{1}H NMR spectrum of HBP in $CDCl_3$ at 298K.

2. IR spectral data:

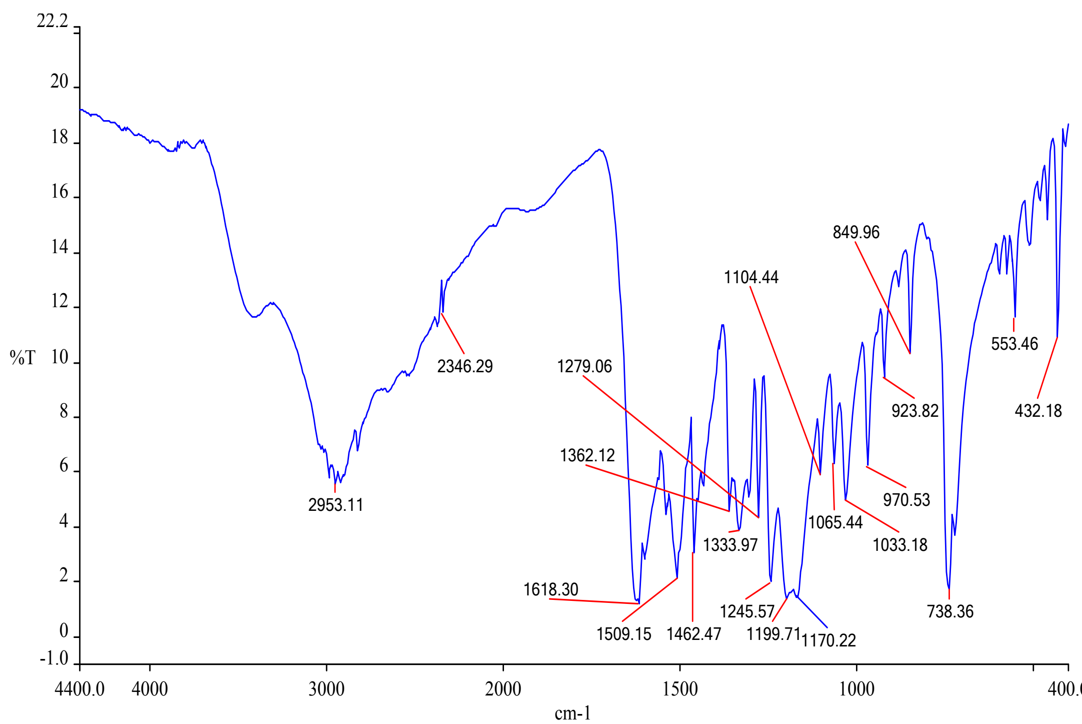
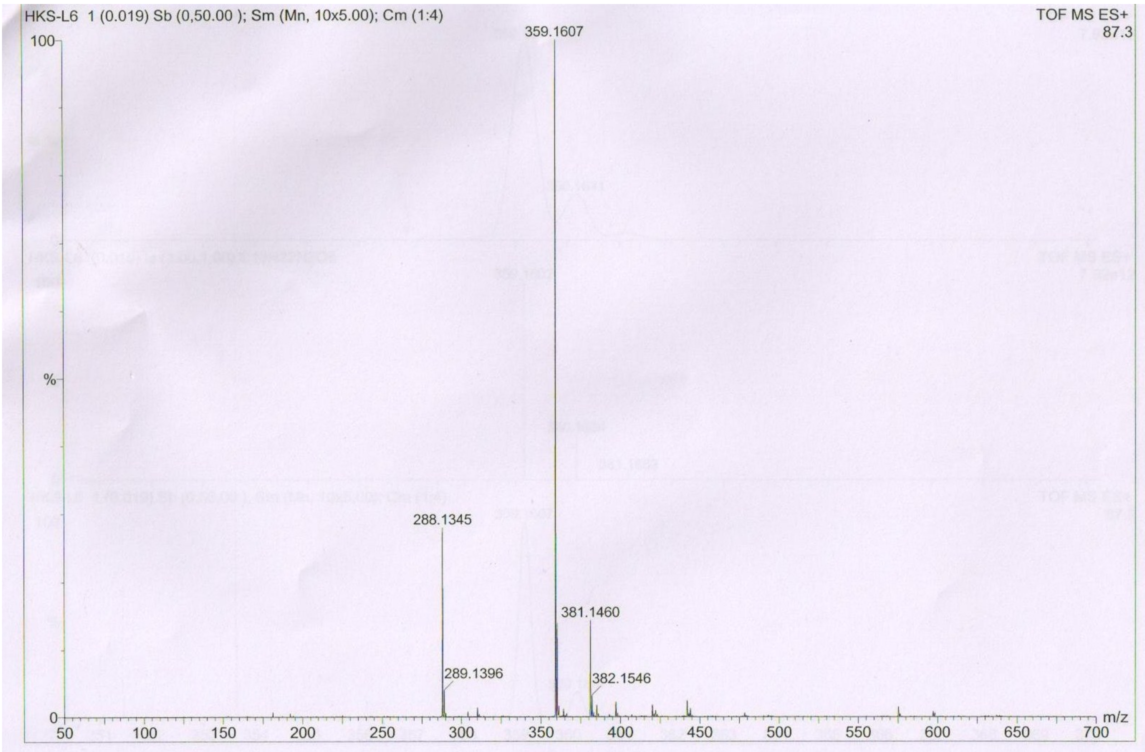


Figure S2: IR spectrum of HBP.

3. Mass data:



4. Elemental analysis data of HBP:

INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE
Department of Inorganic Chemistry

Name of applicant:......A. Mondal......
Date of report :......3/12/12......**Analysis No.**......

Ref.No.	Carbon(%)	Hydrogen(%)	Nitrogen(%)
PMN	31.39	3.26	9.99

Analyst...................... **In-Charge of Elemental Analyzer, CSS**

5. 3D Emission response:

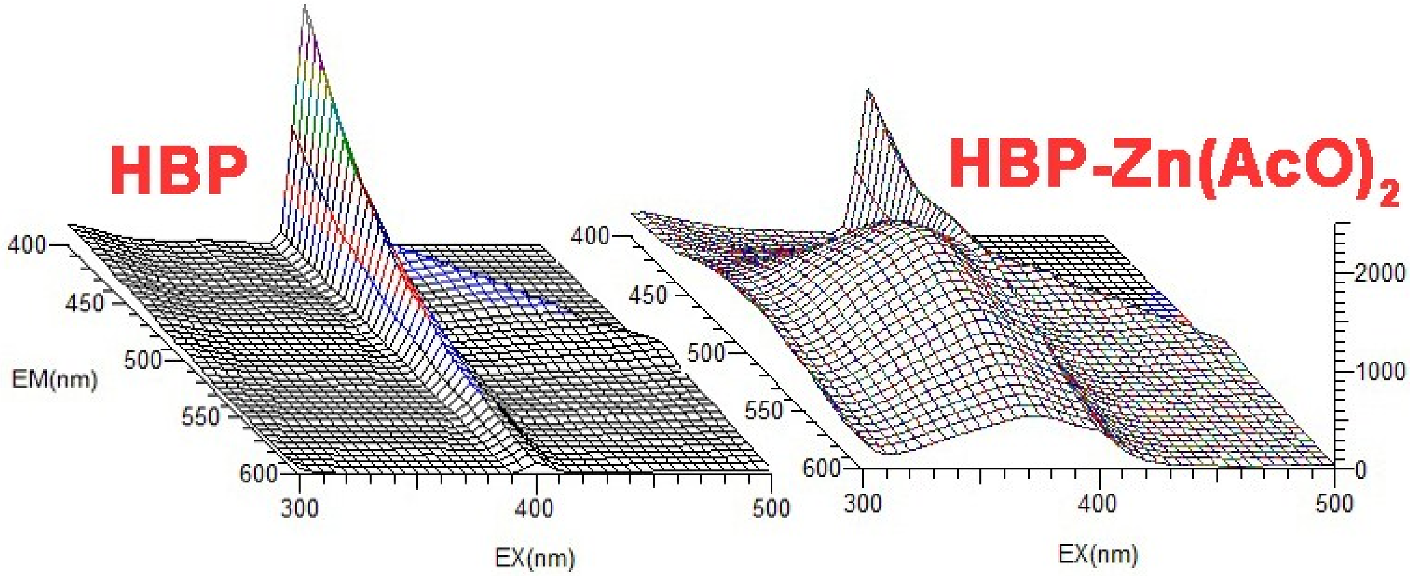


Fig. S4: 3D emission spectra of HBP (left) and its Zinc acetate complex (right) varying excitation wavelength from 300 nm to 500 nm with emission wavelength ranging between 400 nm - 600 nm ; [HBP] = 9.9 μM; $[Zn(AcO)_2]_{Final}$ = 106 μM; Temp 298K.

6. Solvent effect on emission spectra of HBP:

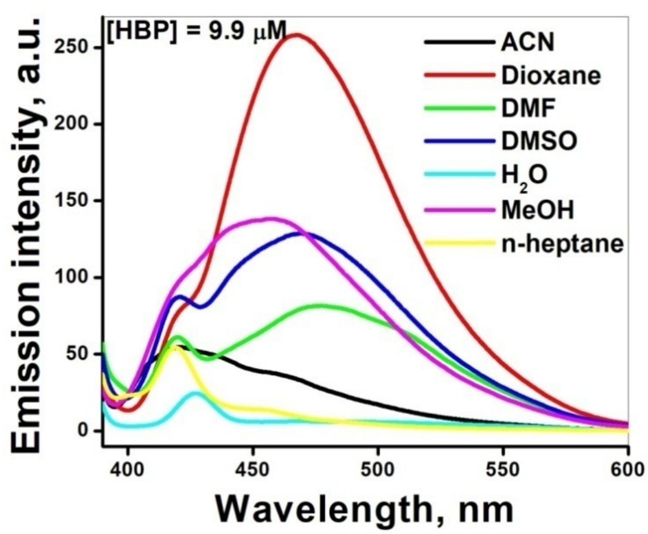


Fig. S5 Effect of solvent polarity on the emission spectra of HBP in solvents with different polarities (ε_{ACN} = 5.8; ε_{Dioxan} = 4.8; ε_{DMF} = 6.4; ε_{DMSO} = 7.2; ε_{Water} = 10.2; ε_{MeOH} = 5.1; $\varepsilon_{heptane}$ = 0.1); λ_{ex} = 370 nm; [HBP] = 9.9 μM; Temp 298K.

7. Selectivity of HBP towards $Zn(AcO)_2$ in 1:1 condition

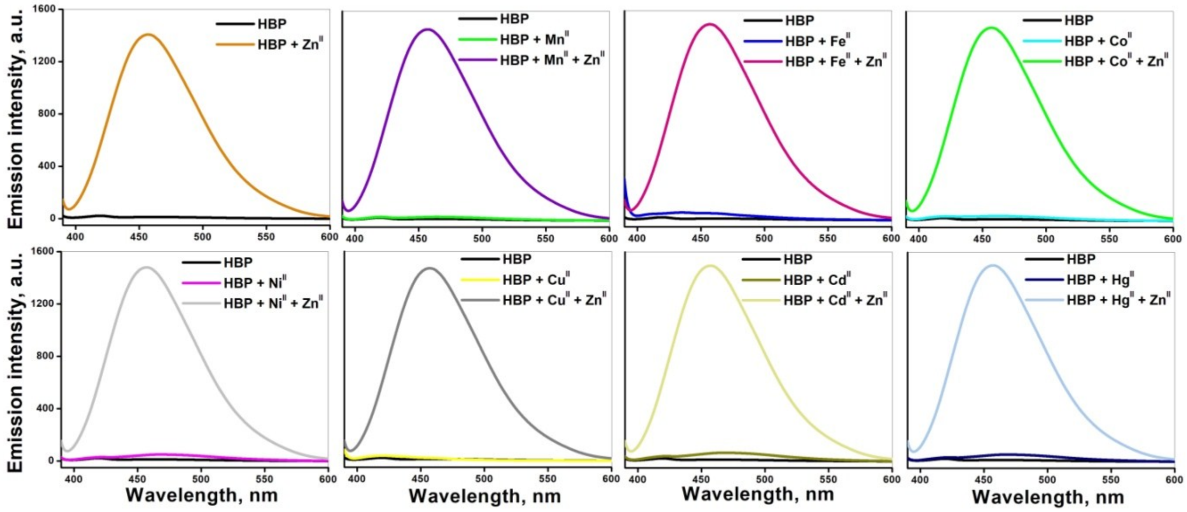


Fig. S6: Emission spectra of cation selectivity for Zn^{II} sensing of HBP for (a) 1:1 ion-pair situation; λ_{ex} = 370 nm; λ_{em} = 457 nm; [HBP] = 9.9 μM; $[M(AcO)_2]_{Final}$ = 106 μM; Temp 298K. (M = metal ions).

8. Selectivity of HBP towards $Zn(AcO)_2$ in the presence of other competitive metal salts

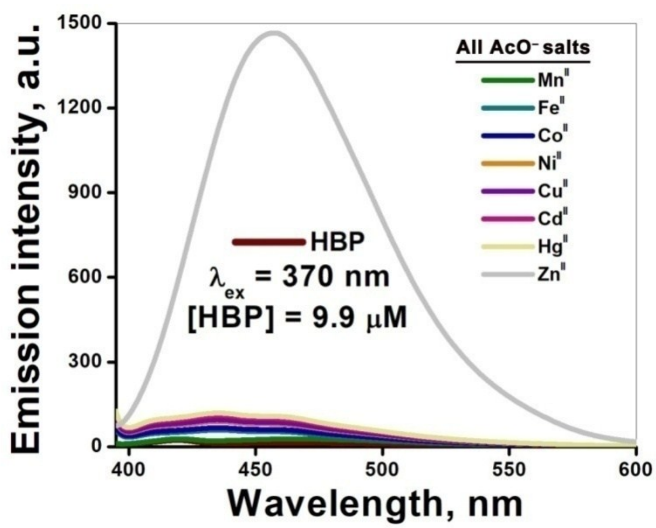


Fig. S7: Emission spectra to show the Zn^{II} specificity within the diversified crowd of common and similar cations (Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Cd^{II} & Hg^{II}) including 1st transition metal series and some from the group where Zn^{II} belongs; λ_{ex} = 370 nm; λ_{em} = 457 nm; [HBP] = 9.9 μM; $[Zn(X)_n]_{Final}$ = 106 μM; Temp 298K. (M = metal ions; X = different anions).

9. Selectivity of HBP towards Zn^{II} and AcO^{-} ion-pair from independent source

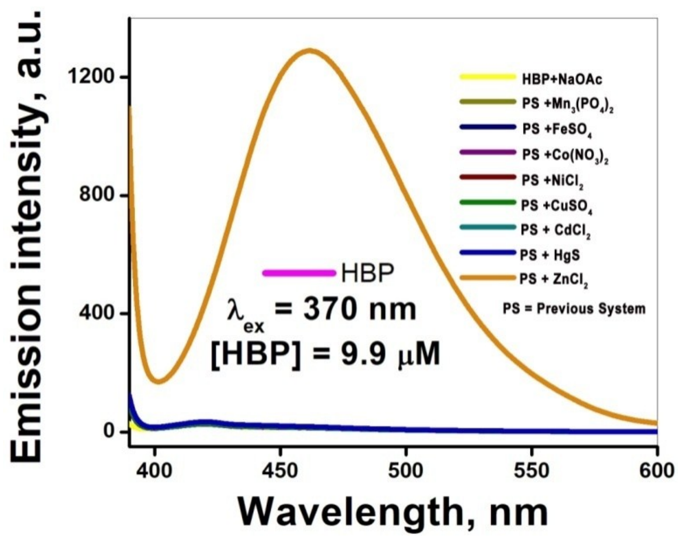


Fig. S8: Emission spectra of selectivity of HBP towards $Zn(AcO)_2$ where the anionic part of the salt came from NaAcO and the cationic part was contributed by $ZnCl_2$ within their addition, various types of other metal salts were added (≈12 equivalent of all salts added; λ_{ex} = 370 nm; λ_{em} = 457 nm; [HBP] = 9.9 μM; $[M(X)_n]_{Final}$ = 106 μM; Temp 298K.(M = metal ions; X = different anions).

10. Fluorescence Quantum yield measurements

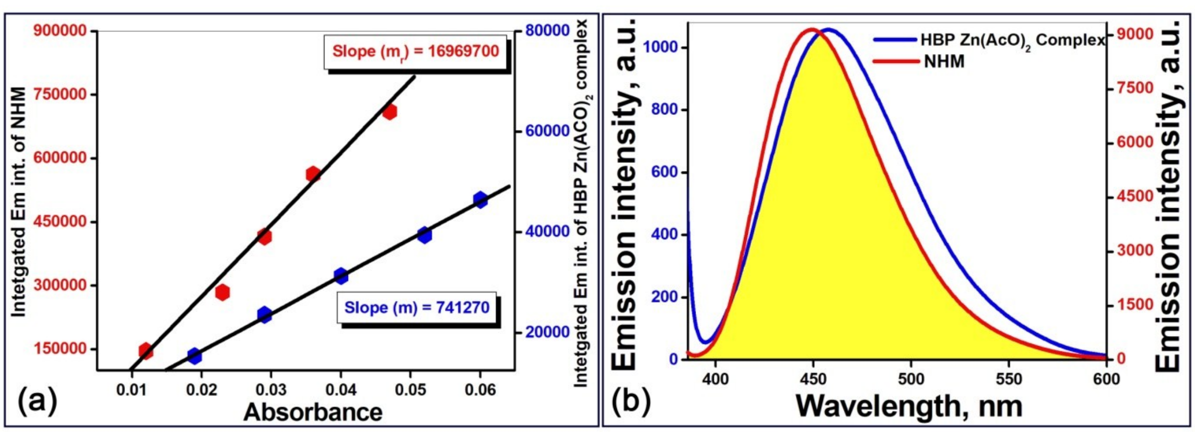


Fig. S9: (a) Plot of integrated emission intensity vs absorbance for norharmane (Standard) and HBP-$Zn(AcO)_2$ complex; Fig. S9(b) represented the choice of norharmane as reference for HBP-$Zn(AcO)_2$ complex indicating significant spectral overlap of emission spectral pattern with 370 nm excitation wavelength for both.

11. Limit of Detection (LOD):

To calculate the limit of detection, the $\frac{I_x - I_0}{I_{max} - I_0}$ values were plotted along abscissa and the $Zn(AcO)_2$ concentrations (at lower range) were plotted along ordinate following the data set below.

$I_0 = 15.54$, $I_{max} = 1466$, $I_{max} - I_0 = 1450.46$.

Table S1:

Conc. of $Zn(AcO)_2$ (μM)	$\boldsymbol{I_x}$	$\boldsymbol{I_X - I_0}$	$\boldsymbol{(I_X - I_0)/(I_{max} - I_0)}$
5.83	109.6	94.06	0.064848393
11.3	156.4	140.86	0.097114019
17.3	178	162.46	0.112005846
23	197.8	182.26	0.125656688
28.7	224.6	209.06	0.144133585
34.1	266.0	250.46	0.172679426

Then, the data points were fitted following the equation $Y = A + B^{*}X$ (The best fitted line cut the X axis at 0.049 μM. Hence, the limit of detection for $Zn(AcO)_2$ by HBP is considered to be 49 nM.

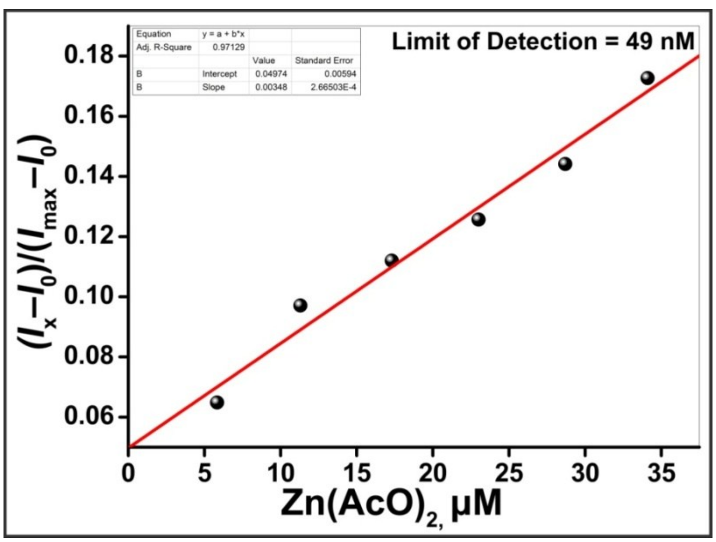


Fig. S10: The normalized emission intensity vs concentration of $Zn(AcO)_2$ plot for calculating the limit of detection for $Zn(AcO)_2$ by HBP ([HBP] = 9.9 μM, Temp. = 298K)