

## Electronic Supporting Information

### **A luminescent-water soluble inorganic co-crystal for a selective picomolar range Arsenic(III) sensor in water medium**

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**General:** Copper(II) acetate monohydrate, n-butylmalonic acid, 2,2'-bipyridine, sodium arsenate dibasic heptahydrate, cacodylic acid, and chloride salts of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Zn}^{2+}$  were purchased from Sigma-Aldrich chemical company and used as received. A primary stock solution of arsenite, used as the standard for As(III), was prepared from American Chemical Society (ACS reagent) primary standard grade Arsenic(III) Oxide,  $\text{As}_2\text{O}_3$  (purchased from Sigma-Aldrich chemical company) dissolved in hydrochloric acid for ultratrace analysis (purchased from Fluka chemical company).<sup>1</sup> Double distilled water was used throughout. Elemental analysis (C, H, N) were carried out using a Perkin-Elmer 240C elemental analyzer. Aqueous phase FT-IR spectra were measured in a Perkin-Elmer Spectrum 100FT-IR Spectrometer with a  $\text{CaF}_2$  window. Solid-phase IR spectroscopy was measured on Shimadzu FTIR-8400S spectrometer between 400 and 4000  $\text{cm}^{-1}$ , using the KBr pellet method. Absorption and fluorescence spectra of both the solid and the aqueous solution of **ICC** were measured in a Shimadzu UVPC-3200 spectro-photometer and a Perkin-Elmer LS55 fluorimeter, respectively. Electrospray ionisation mass spectroscopy (ESI-MS) experiments were carried out on a Water's QtoF Model YA 263 spectrometer in positive ion ESI mode.

**Crystallographic data collection and refinement:** Suitable single crystal of the complex was mounted on a Bruker SMART diffractometer equipped with a graphite monochromator and  $\text{Mo-K}\alpha$  ( $\lambda = 0.71073\text{\AA}$ ) radiation. The structure was solved using Patterson methods using SHELXS97. Subsequent difference Fourier synthesis and least-squares refinement revealed the positions of the remaining non-hydrogen atoms. Non-hydrogen atoms were refined with independent anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and their displacement parameters were fixed to be 1.2 times larger than those of the attached non-hydrogen atom. All calculations were carried out using SHELXS97,<sup>2</sup> SHELXL97,<sup>3</sup> PLATON 99,<sup>4</sup> ORTEP-32<sup>5</sup> and WinGX system Ver-1.64.<sup>6</sup> Data collection and structure refinement parameters and crystallographic data for the complex is given in Table S1. The selected bond lengths, and bond angles are given in Table S2 and S3.

**Spectral Study:** The fluorescence response (shown in Fig. 2) of the aqueous solution of **ICC** in presence of increasing concentrations of different aqueous solutions of  $[\text{As}^{3+}]$  (i.e. 0, 49.8 pM, 99 pM, 196 pM, 476 pM, 566 pM, 740 pM, 909 pM, 1110 pM, 1300 pM, 1660 pM, 2000 pM, 3330 pM, 3750 pM, 4440 pM are concentrations of  $\text{As}^{3+}$  in the aqueous solutions containing **ICC** and  $\text{As}^{3+}$ ). Each reading has been obtained just after the addition of  $\text{As}^{3+}$ .

A comparative study of fluorescence intensity ratios (plot of  $I/I_0$  vs concentration ( $[\text{M}^{n+}] = 243.9$  pM) of different metal ions) of the aqueous solution of **ICC** in presence of different metal ions have also been done (shown in Fig. 4). Here, initially, 243.9 pM of each metal solution has been added to the water solution of **ICC** ( $[\text{ICC}] = 1.7 \times 10^{-4}$  M) and then after taking fluorescence emission spectra of this mixture, further 243.9 pM water solution of  $\text{As}(\text{III})$  has also been added to the each mixture containing respective metal ions and **ICC**, and then fluorescence spectral run has been performed again. Each reading has been taken just after the addition of each metal ion. In this bar-graph presentation (shown in Fig. 4), blue coloured bars represent the presence of metal ions including  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{As}^{5+}$ , Organic As (cacodylic acid) with the water solution of **ICC** and the every next red coloured bar, in immediate vicinity of the former blue coloured bar, is for the solution containing respective metal ion, **ICC** and  $\text{As}^{3+}$ .

**Table S1:** Crystallographic data of ICC

Formula	C <sub>34</sub> H <sub>36</sub> Cu <sub>2</sub> N <sub>4</sub> O <sub>8</sub> ·2(C <sub>17</sub> H <sub>20</sub> CuN <sub>2</sub> O <sub>5</sub> ), 6(H <sub>2</sub> O)
Formula Weight	1655.62
Crystal System	Triclinic
Space group	P-1 (No. 2)
a[Å]	10.4804(4)
b[Å]	13.7007(5)
c[Å]	14.5785(5)
α[°]	75.368(1)
β[°]	76.086(1)
γ[°]	70.713(1)
V [Å <sup>3</sup> ]	1883.27(12)
Z	1
D(calc) [g/cm <sup>3</sup> ]	1.460
μ(MoKα) [ /mm ]	1.194
F(000)	860
Crystal Size [mm]	0.08 x 0.08 x 0.12
Temperature (K)	293
Radiation [Angstrom]	MoKα 0.71073
Theta Min-Max [Deg]	1.5, 29.9
Tot.	17452
Uniq. Data	7040
R(int)	0.037
Observed data [I > 2.0 sigma(I)]	4050
Nref	7040
Npar	469
R	0.0568
wR2	0.1712
S	0.92
Max. and Av. Shift/Error	0.00, 0.00
Min. and Max. Resd. Dens. [e/Å <sup>3</sup> ]	-0.31, 0.57

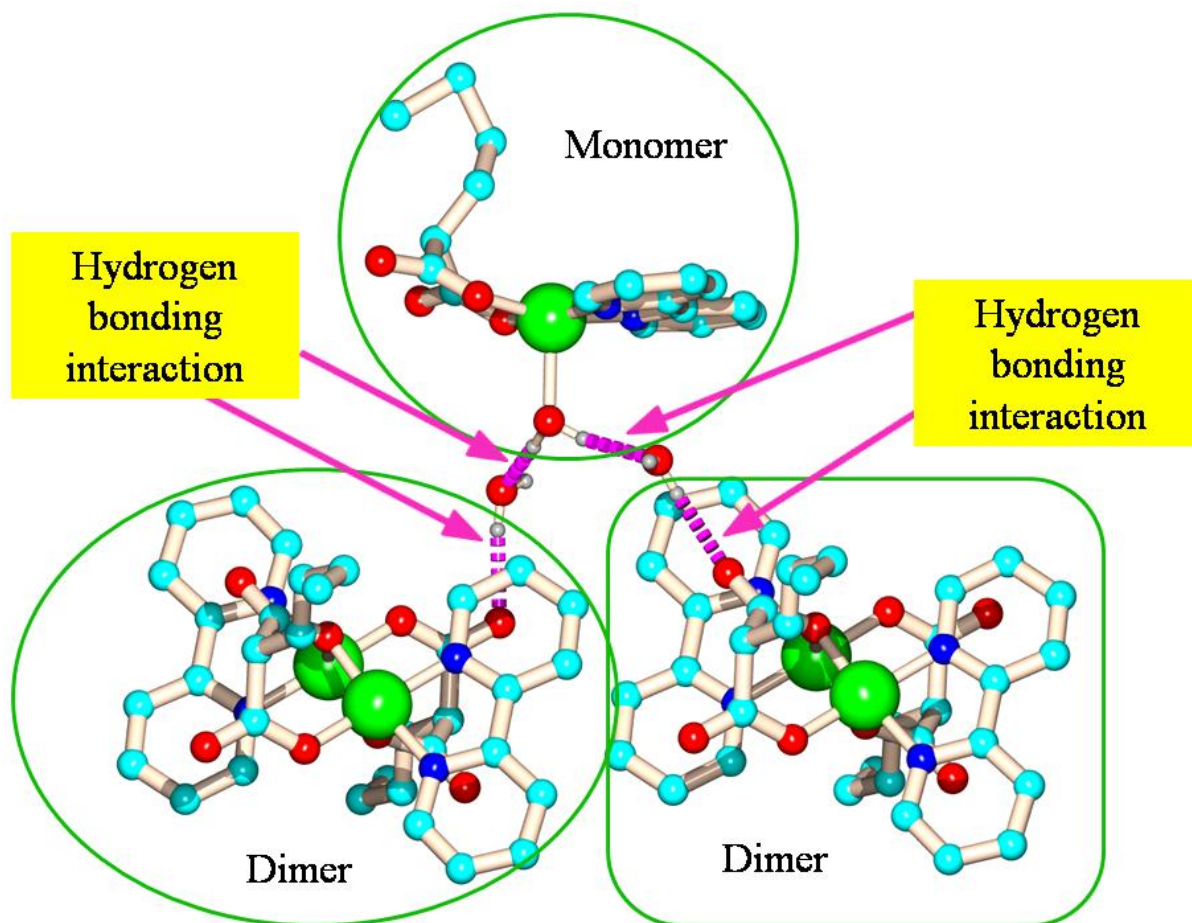
**Table S2:** Some selected bond lengths of ICC

Bonds	Distances (Å)	Bonds	Distances (Å)
Cu1-O1	1.922(5)	Cu1-O3	1.941(4)
Cu1-N1	1.984(5)	Cu1-N2	1.987(4)
Cu1-O3 <sup>a</sup>	2.362(4)	Cu2-N4	2.008(4)
Cu2-O5	1.937(3)	Cu2-O7	1.942(4)
Cu2-O1W	2.214(4)	Cu2-N3	1.992(4)

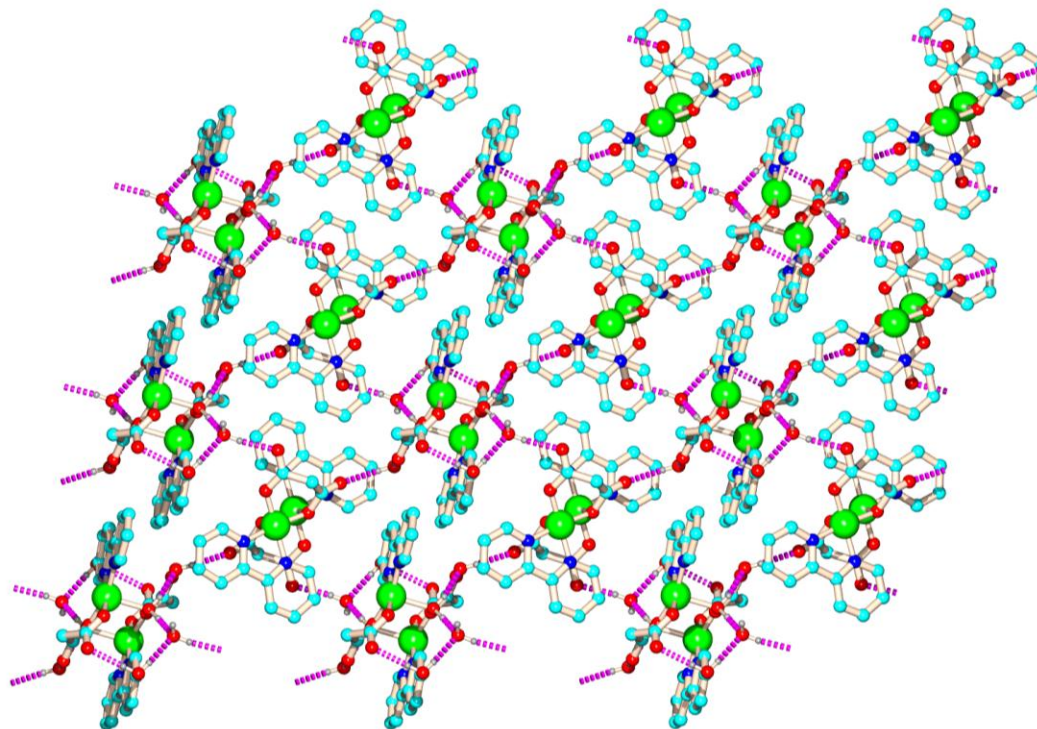
**Table S3:** Some selected bond angles (°) of **ICC**

O1-Cu1-O3	92.73(18)	O1-Cu1-N1	92.62(19)
O1-Cu1-N2	166.5(2)	O1-Cu1-O3 <sup>a</sup>	100.84(18)
O3-Cu1-N1	174.36(17)	O3-Cu1-N2	93.20(17)
O3-Cu1-O3 <sup>a</sup>	80.38(15)	N1-Cu1-N2	81.20(18)
O3 <sup>a</sup> -Cu1-N1	100.37(18)	O3 <sup>a</sup> -Cu1-N2	92.07(18)
O1W-Cu2-N3	96.52(16)	O1W-Cu2-N4	94.58(15)
O5-Cu2-O7	92.12(14)	O5-Cu2-N3	91.78(14)
O5-Cu2-N4	163.54(17)	O7-Cu2-N3	170.16(17)
O7-Cu2-N4	93.12(16)	N3-Cu2-N4	80.75(16)
O1W-Cu2-O7	91.61(16)	O1W-Cu2-O5	100.87(16)

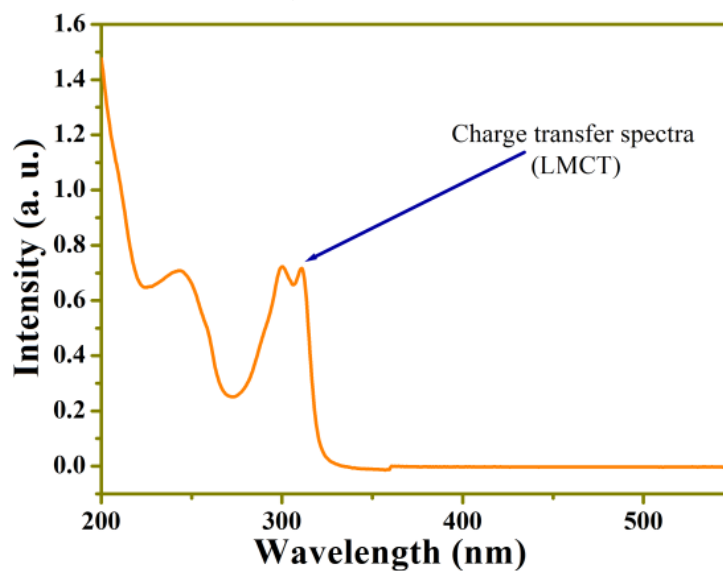
\*a= 1-x, 1-y, 1-z



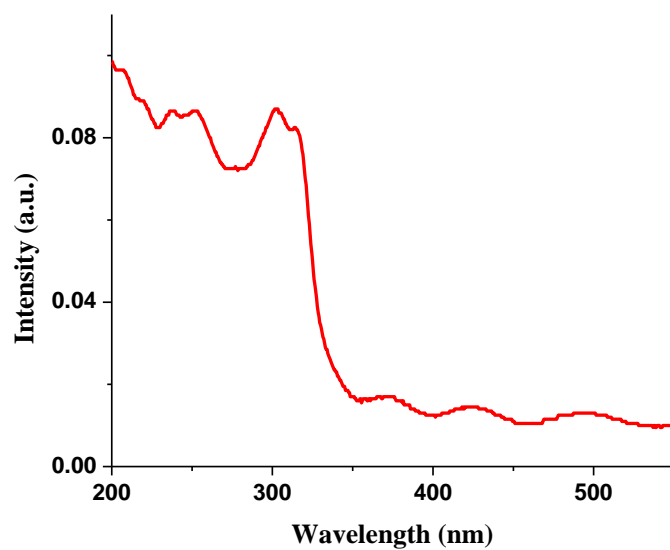
**Fig. S1** Monomeric unit is connected to two dimeric units of ICC through hydrogen bonding interactions (magenta color) *via* guest water molecules



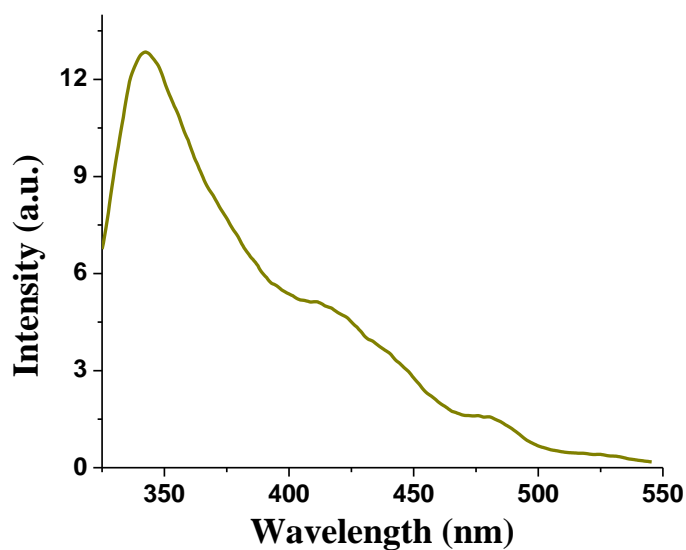
**Fig. S2** 2D supramolecular structure of **ICC** formed by hydrogen bonding interactions (magenta color)



**Fig. S3** UV-absorption spectra of the dilute aqueous solution of **ICC** ( $[\text{ICC}] = 1.7 \times 10^{-4} \text{ M}$ ) exhibits an intense broad absorption band centered at 310 nm at 298 K and atmospheric pressure

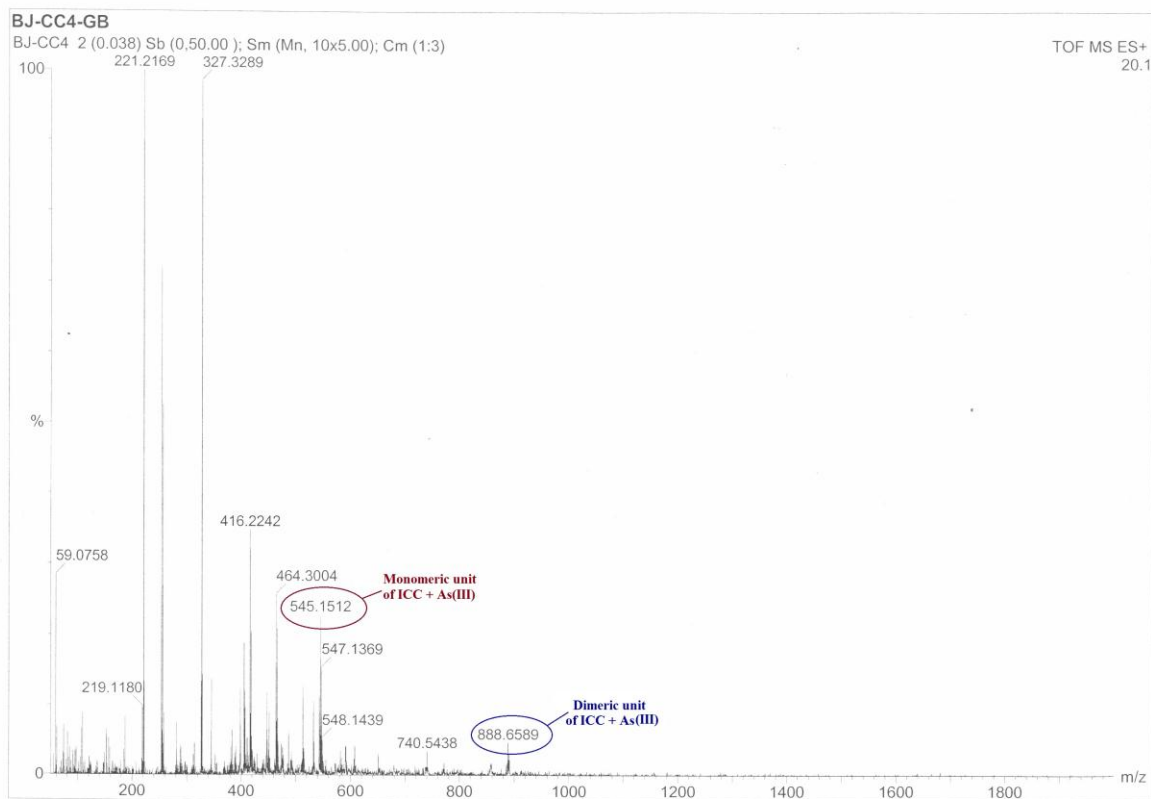


**Fig. S4** UV-absorption spectra of the solid **ICC** exhibits an intense broad absorption band centered at 310 nm at 298 K and atmospheric pressure



**Fig. S5** Fluorescence spectra of the solid **ICC** exhibits a fluorescence emission maximum at 350 nm ( $\lambda_{\text{ex}} = 310$  nm) at 298 K and atmospheric pressure





**Fig. S6** ESI-MS spectra of the complex formed by water solution of **ICC** and As(III)

Here, water is used as solvent for the ESI-MS measurements, as the **ICC** is highly soluble in the water medium. So, there is a chance of easy breaking of hydrogen bonding interactions (See Fig. S1) connected the monomeric and dimeric Cu(II) units of the co-crystal (**ICC**). Consequently, one peak has been found for the complex made of monomeric Cu(II) unit of **ICC**+As(III) and another peak has been obtained for the complex of the dimeric Cu(II) unit of **ICC**+As(III) in the ESI-MS spectra.

### Solid State Infrared spectroscopy:

The band at  $3485\text{ cm}^{-1}$  can be assigned to the stretching vibration,  $\nu$  (O-H), of the hydroxyl groups in the water molecules. The band at  $3304\text{ cm}^{-1}$  can be assigned to the stretching vibration,  $\nu$  (N-H), of the primary aromatic amine. The next band at  $2947\text{ cm}^{-1}$  corresponds to the stretching vibration,  $\nu$  (C-H), of the malonate ligands.  $\nu_{\text{as}}$  (OCO) and  $\nu_{\text{s}}$  (OCO) absorptions appeared at  $1620\text{ cm}^{-1}$ ,  $1394\text{ cm}^{-1}$  respectively.  $\delta$  (OCO) absorptions were located at  $837$  and  $771\text{ cm}^{-1}$  (Figure S7).

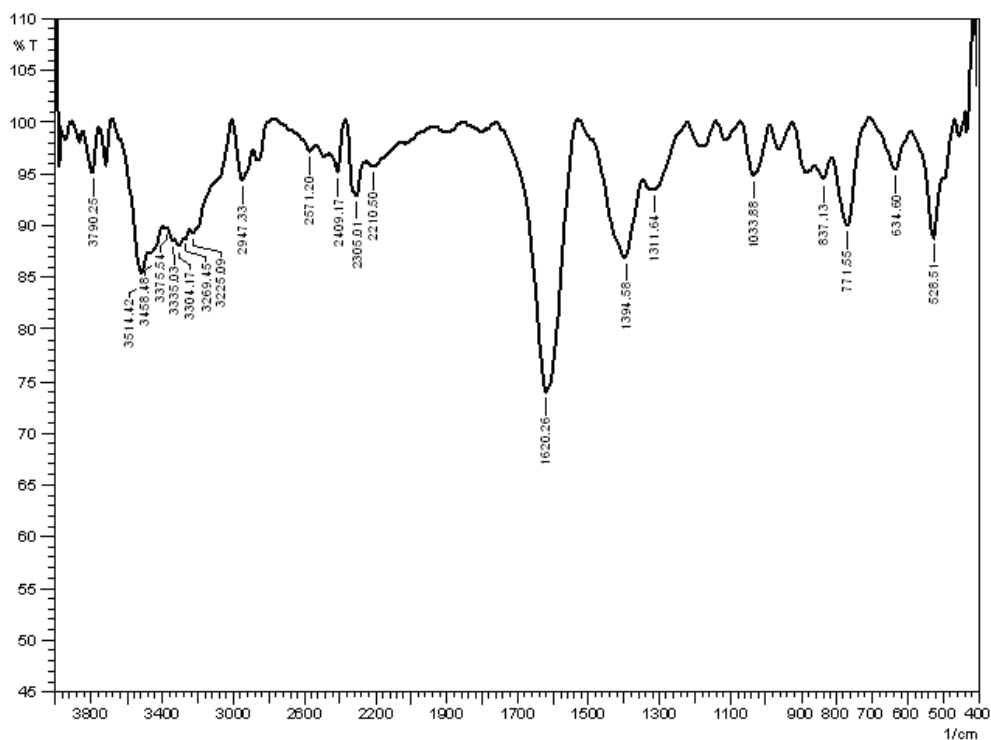


Fig. S7 Solid-phase IR spectra of pure ICC

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