Supporting information

Facts and reality of multi-component organic ionic-cocrystals of di-topic conjugate acid-base

Abhay Pratap Singh, Jubaraj B. Baruah

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Experimental section: General

Infrared spectra of the solid samples were recorded on a Perkin-Elmer Spectrum-Two FT-IR spectrophotometer in the region 4000 - 400 cm^{-1} using attenuated total reflectance method. The ^{1}HNMR spectra were recorded on a BRUKER Ascend-600 MHz NMR spectrometer using TMS as the internal standard. The thermogravimetric analyses were done on PerkinElmer TGA 4000, under nitrogen gas flow. Fluorescence emission spectra in solution were recorded on a Horiba Jobin Yvon Fluoromax-4 spectrofluorometer.

Preparation of the ionic-cocrystals:

The *Chloroanthraimmida* was prepared by reported procedure. [S1]

S1: A. P. Singh and J. B. Baruah, ACS Omega, 2024, 9, 47848 - 47856.

[(H$_2$chloroanthraimmida)$^{2+}$][2(H35pdc)$^-$]·4H$_2$O (**1**) was prepared by dissolving equimolar (1 mmol) amount of the *Chloroanthraimmida* and $H_2$35pdc in 25 mL methanol containing about 1 % water at 28◦ - 35◦C. The solution was kept undisturbed for three to four days, which yielded crystals of the ionic-cocrystal.

[(H$_2$chloroanthraimmida)$^{2+}$][2(H35pdc)$^-$]·(IFbenz)·4H$_2$O (**2**) was prepared in methanol containing about 1% water (25 mL) by dissolving equimolar (1 mmol) amounts of the three components, namely, *chloroanthraimmida*, *$H_2$35pdc* and *IFbenz*. Upon standing of the solution in open air, the crystals of the ionic-cocrystal **2** appeared. The crystals were collected on a tissue paper and dried in open air.

[(H$_2$chloroanthraimmida)$^{2+}$(35pdc)$^{2-}$]·(IFbenz)·2CH$_3$OH (**3**) was prepared by addition 1,3-dihydroxybenzene to the solution having *chloroanthraimmida*, *$H_2$35pdc* and *IFbenz* (1 mmol each). The solution upon standing for 3 days resulted in the crystallization of **3**. The supernatant liquid was decanted to collect the crystals and the crystals were dried over a filter paper.

The spectroscopic details of the ionic-cocrystals:

[(H$_2$chloroanthraimmida)$^{2+}$][2(H35pdc)$^-$]·4H$_2$O : Isolated yield: 68 %. 1H NMR (600 MHz, DMSO-d6): 9.15 (s, 2H), 8.61 (s, 1H), 8.56 (d, J = 6 Hz, 2H), 8.50 (d, J = 6 Hz, 2H), 7.75 (t, J = 6 Hz, 2H), 7.70 (t, J = 6 Hz, 2H), 7.64 (s, 1H), 7.15 (s, 1H), 6.91 (s, 1H), 4.93 (s, 2H), 4.10 (t, J = 6 Hz, 2H), 3.09 (t, J = 6 Hz, 2H), 2.12 (p, J = 6 Hz, 2H). IR (KBr, cm-1): 3093 (w), 1708 (m), 1610 (s), 1578 (s), 1446 (m), 1362 (m), 1278 (m), 1137 (w), 1024 (m), 929 (m), 751 (s), 704 (m), 582 (m), 488 (m).

[(H$_2$chloroanthraimmida)$^{2+}$][2(H35pdc)$^-$]·(IFbenz)·4H$_2$O : Isolated yield: 63 %. 1H NMR (600 MHz, DMSO-d6): 9.17 (s, 4H), 8.62 (s, 2H), 8.58 (d, J = 6 Hz, 2H), 8.52 (d, J = 6 Hz, 2H), 7.76 (t, J = 6 Hz, 2H), 7.72 (t, J = 6 Hz, 2H), 7.71 (s, 1H), 7.18 (s, 1H), 6.95 (s, 1H), 5.08 (s, 2H), 4.07 (t, J = 6 Hz, 2H), 3.18 (s, 6H), 2.97 (t, J = 6 Hz, 2H), 2.06 (p, J = 6 Hz, 2H). IR (KBr, cm-1): 3117 (w), 3062 (w), 1710 (s), 1578 (w), 1465 (m), 1371 (w), 1305 (m), 1249 (m), 1127 (w), 1043 (w), 939 (s), 751 (s), 680 (m), 582 (m), 479 (m).

[(H$_2$chloroanthraimmida)$^{2+}$(35pdc)$^{2-}$]·(IFbenz)·2CH$_3$OH : Isolated yield: 53 %. 1H NMR (600 MHz, DMSO-d6): 9.15 (s, 2H), 8.61 (s, 1H), 8.56 (d, J = 6 Hz, 2H), 8.50 (d, J = 6 Hz, 2H), 7.75 (t, J = 6 Hz, 2H), 7.70 (t, J = 6 Hz, 2H), 7.64 (s, 1H), 7.15 (s, 1H), 6.91 (s, 1H), 4.93 (s, 2H), 4.10 (t, J = 6 Hz, 2H), 3.09 (t, J = 6 Hz, 2H), 2.12 (p, J = 6 Hz, 2H). IR (KBr, cm-1): 3371 (br, w), 3108 (w), 2817 (w), 1598 (s), 1549 (s), 1465 (s), 1344 (s), 1259 (w), 1146 (w), 1024 (m), 933 (m), 751 (s), 714 (s), 639 (m), 555 (m), 423 (w).

Density functional theory study:

For **density functional theory** calculations, the Gaussian 09 software was used by using B3LYP level. In each case the energy of the structure from the individual crystallographic information file. To generate alternate structure gauss view was used to replace at desired position of the .mol file generated and energy of the thus newly generated .mol files were calculated. The energies of the different forms of the ionic-cocrystal 1 were calculated by using 631G + (d,p) basis-set, whereas for the **2** and **3** were performed with LanL2DZ as basis-set

Crystallographic study:

The X-ray single crystal diffraction data for the salts were collected by Oxford SuperNova diffractometer at room temperature. Data refinement and cell reductions were carried out by CrysAlisPro.118 SMART software. Data reduction and cell refinements were performed using SAINT and XPREP software. Structures were solved by direct methods using SHELXS-14 and were refined by full-matrix least-squares on F^2 using SHELXL-14. All non-hydrogen atoms were refined in anisotropic approximation against F2 of all reflections. Hydrogen atoms were placed at their geometric positions by riding and refined in the isotropic approximation. The crystallographic parameters are listed in the Table 1S.

Table 1S: Crystal and refinement parameters of the ionic-cocrystals of ***Chloroanthraimmida***.

Parameters	***[(H_2chloroanthraimmida)$^{2+}$][2(H35pdc)$^-$]·4H_2O***	***[(H_2chloroanthraimmida)$^{2+}$][2(H35pdc)$^-$]·(IFbenz)·4H_2O***	***[(H_2chloroanthraimmida)$^{2+}$(35pdc)$^{2-}$]·(IFbenz)·2CH_3OH***
Formula	$C_{35}H_{38}N_5O_{12}Cl$	$C_{38}H_{38}N_5O_{12}ClF_2I$	$C_{36}H_{33}N_4O_6Cl$ F4 I2
CCDC	2396359	2396360	2403207
Mol.wt.	756.15	957.08	982.91
Crystal system	monoclinic	triclinic	Monoclinic
Space group	P 2_1/c	$P\bar{1}$	P 2_1/n
a(Å)	11.0457(16)	8.8096(5)	13.111(6)
b(Å)	31.235(4)	11.2696(6)	15.861(8)
c (Å)	11.3942(17)	21.1324(12)	18.599(9)
α (°)	90	85.724(2)	90
β (°)	117.679(5)	81.896(2)	90.667(14)
γ (°)	90	72.086(2)	90
V (Å^3)	3481.3(9)	1975.30(19)	3867(3)
Density, g cm^{-3}	1.443	1.609	1.688
Abs. coeff., mm^{-1}	0.183	0.958	1.764
F (000)	1584	970	1936
Total no. of reflections	6122	7768	8453
Reflections, I > 2σ(I)	4999	6522	7028
Max. θ/°	24.999	26.018	25.242
Ranges (h, k, l)	−13 ≤ h ≤ 13 −37 ≤ k ≤ 37 −13 ≤ l ≤ 13	−10 ≤ h ≤ 10 −13 ≤ k ≤ 13 −26 ≤ l ≤ 26	−16 ≤ h ≤ 16 −20 ≤ k ≤ 20 −23 ≤ l ≤ 23
Complete to 2θ (%)	99.9	99.8	99.6
Data/restraints/parameters	6122/0/494	7768/0/545	8453/0/486
GooF (F^2)	1.098	1.122	1.038
R indices [I > 2σ(I)]	0.0832	0.0408	0.0422
wR_2 [I > 2σ(I)]	0.2077	0.0775	0.1053
R indices (all data)	0.0957	0.0551	0.0543
wR_2 (all data)	0.2147	0.0852	0.1187

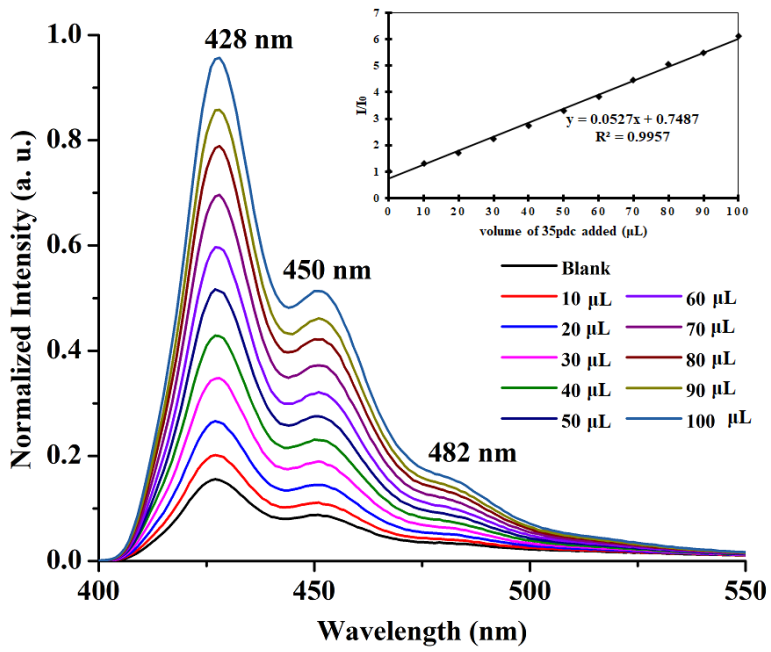


Figure 1S: Fluorescence titration (λ_{ex}, 300 nm) of ***chloroanthraimmida*** (10^{-5} M in methanol, 2mL) with *$H_2$35pdc* (10 µl aliquot of 10^{-5} M in methanol)

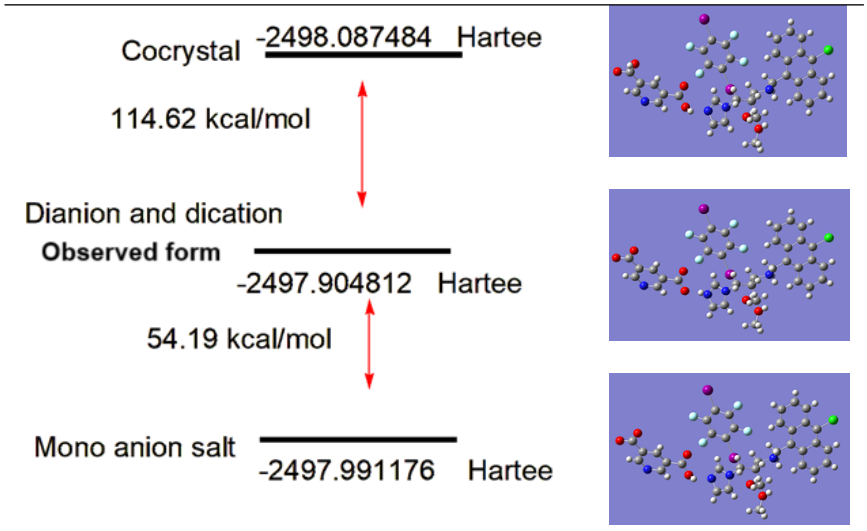
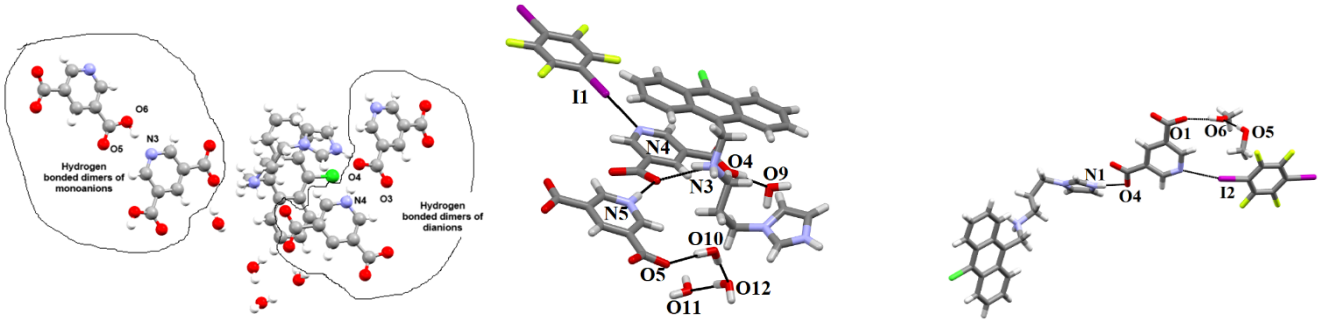
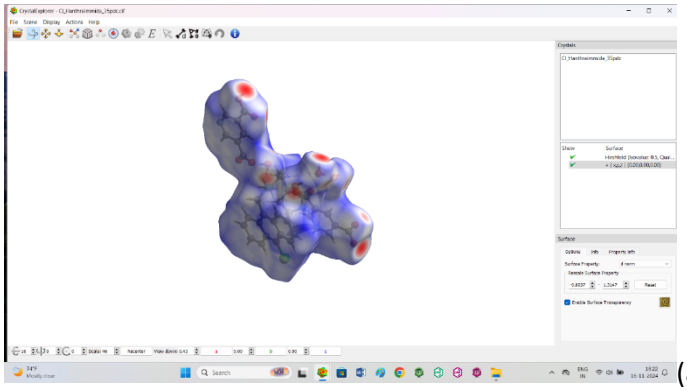


Figure 2S: The DFT calculated energy of **3** and its two other theoretically constructed forms

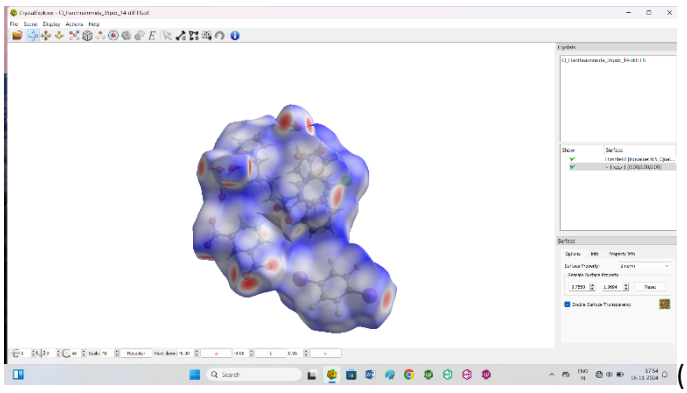


(a) (b) (c)

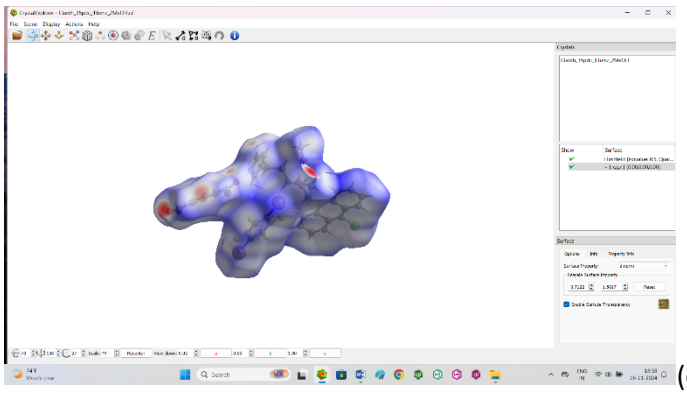
Figure 3S: (a) A part of the self-assembly of ionic-crystal 1 showing the hydrogen bonded dimers of anions. The crystal structure of (b) ***[(H_2chloroanthraimmida)$^{2+}$][2(H35pdc)$^-$].(IFbenz)·4H_2O,*** (c) Asymmetric unit of ***[(H_2chloroanthraimmida)$^{2+}$(35pdc)$^{2-}$].(IFbenz)·2CH_3OH***



(a)



(b)



(c)

Figure 4S: Hirshfeld surfaces of the (a) **1**, (b) **2**, (c) **3**

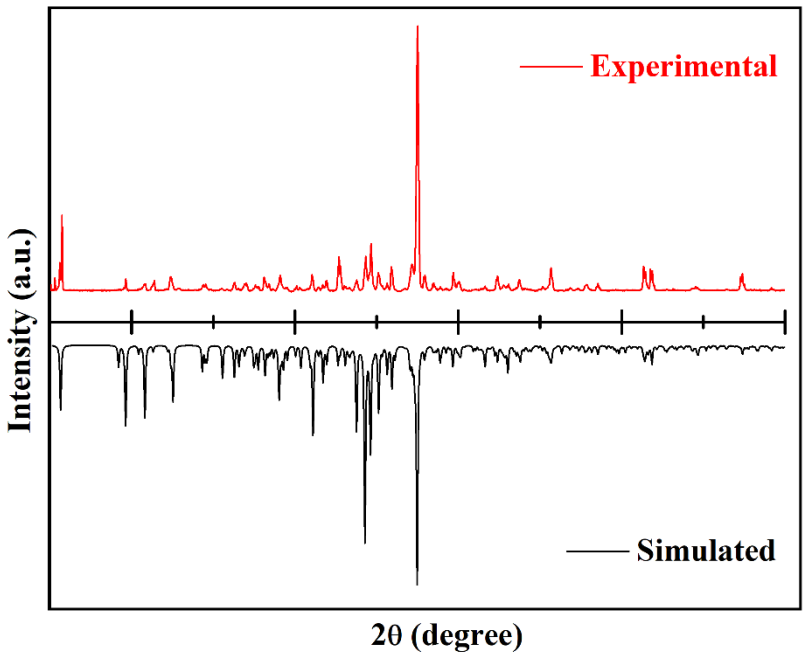


Figure 5S: PXRDs of ***[(H$_2$chloroanthraimmida)$^{2+}$][2(H35pdc)$^-$].4H$_2$O*** (Red = Experimental, Black = Simulated pattern generated from CIF file (50 ≤ 2θ ≤ 500)

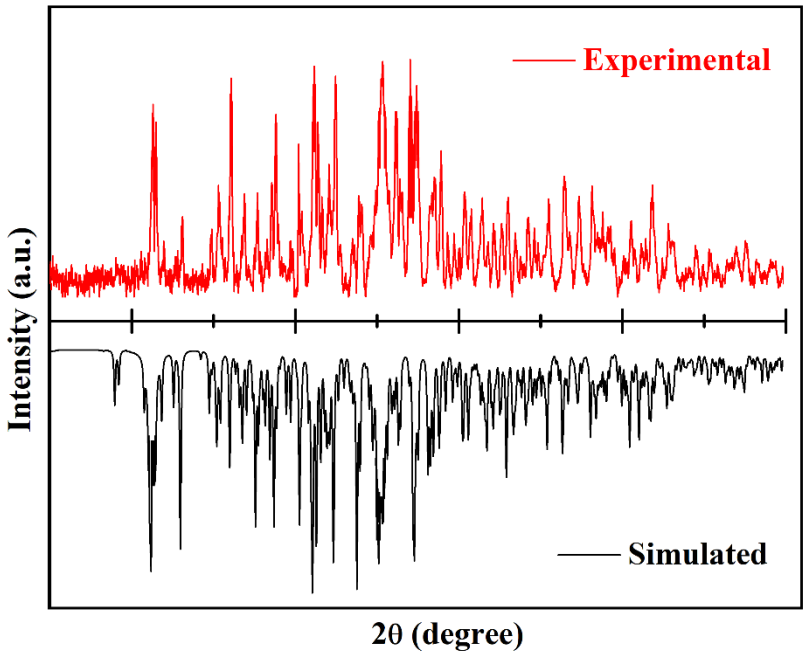


Figure 6S: PXRDs of ***[(H$_2$chloroanthraimmida)$^{2+}$][2(H35pdc)$^-$].(IFbenz)·4H$_2$O*** (Red = Experimental, Black = Simulated pattern generated from CIF file (50 ≤ 2θ ≤ 500)

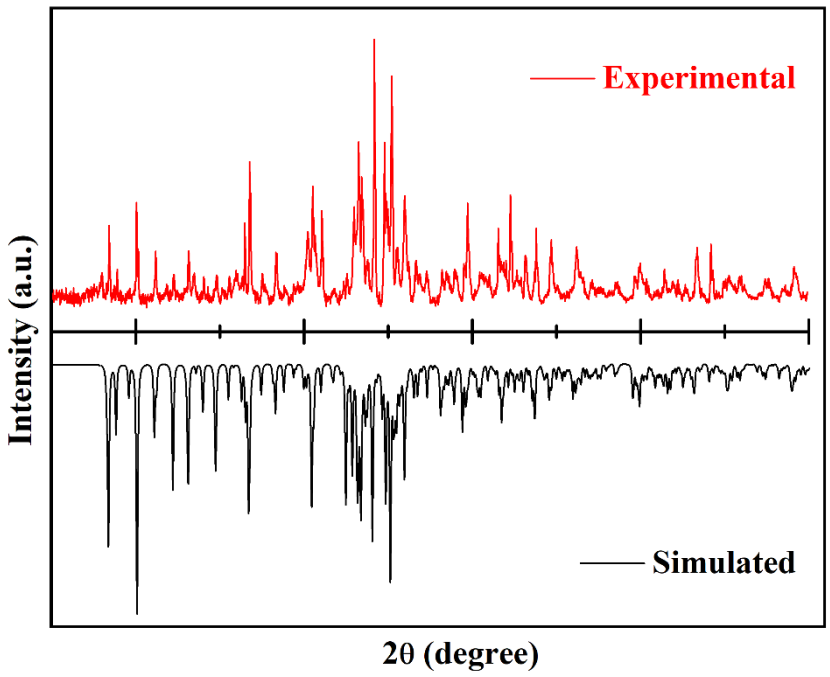


Figure 7S: PXRDs of ***[(H$_2$chloroanthraimmida)$^{2+}$(35pdc)$^{2-}$]·(IFbenz)·2CH$_3$OH*** (Red = Experimental, Black = Simulated pattern generated from CIF file (50 ≤ 2θ ≤ 500)

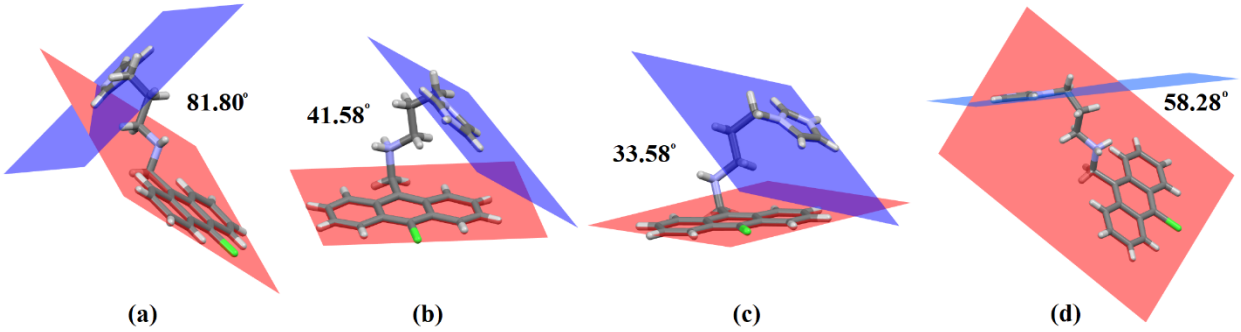


Figure 8S: The angle between planes of imidazole and Chloroanthracene of (a) ***chloroanthraimmida***, (b) ***[(H$_2$chloroanthraimmida)$^{2+}$][2(H35pdc)$^-$].4H$_2$O***, (c) ***[(H$_2$chloroanthraimmida)$^{2+}$][2(H35pdc)$^-$].(IFbenz)·4H$_2$O*** and (d) ***[(H$_2$chloroanthraimmida)$^{2+}$(35pdc)$^{2-}$]·(IFbenz)·2CH$_3$OH***

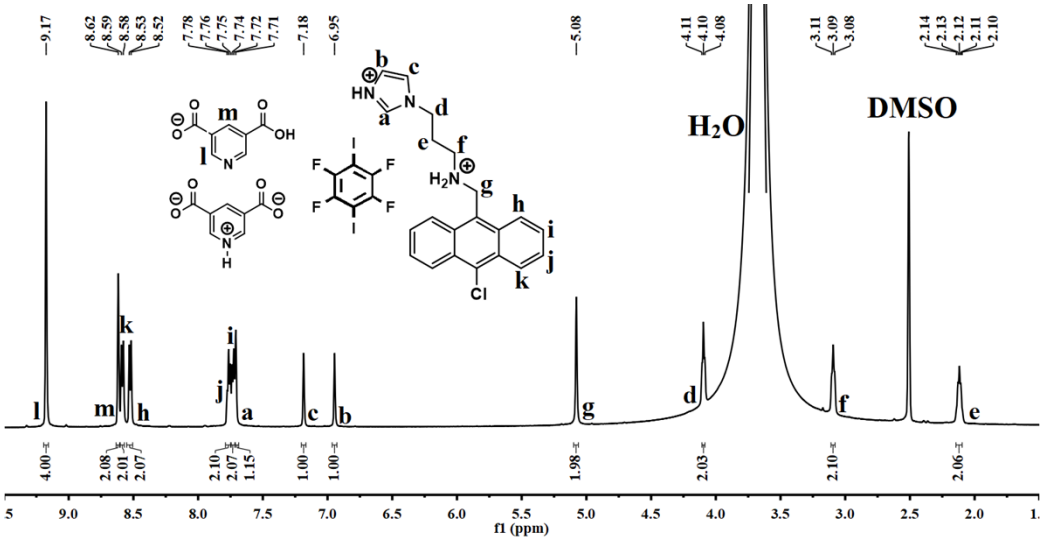


Figure 9S: ^{1}HNMR (600 MHz, DMSO-d_6) spectra of the ***[(H$_2$chloroanthraimmida)$^{2+}$][2(H35pdc)$^{-}$].(IFbenz)·4H$_2$O***.

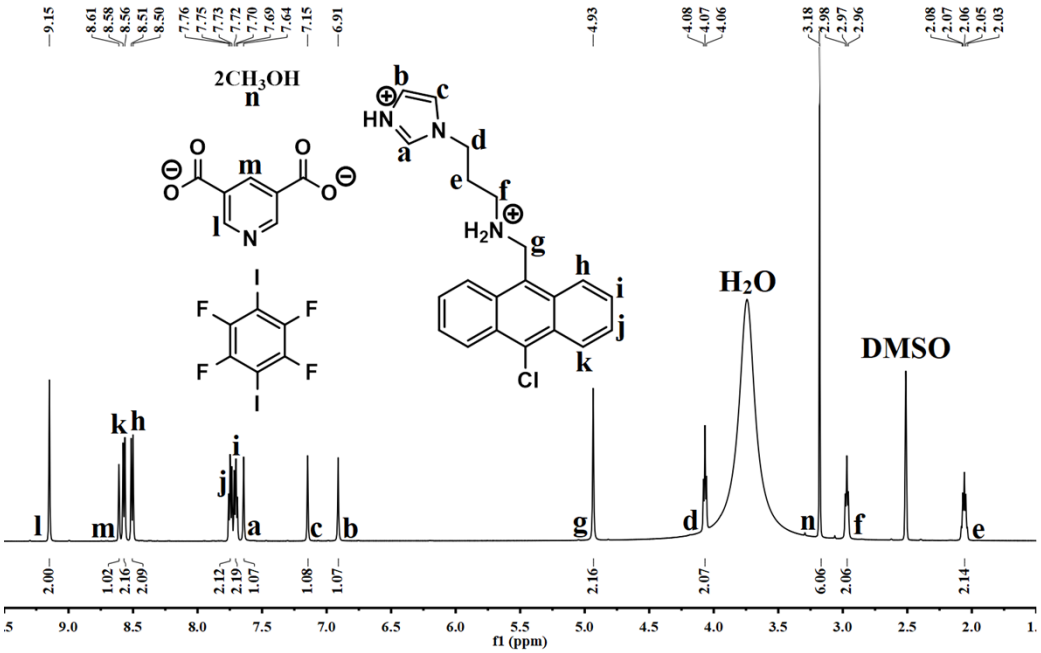


Figure 10S: ^{1}HNMR (600 MHz, DMSO-d_6) spectra of the ***[(H$_2$chloroanthraimmida)$^{2+}$(35pdc)$^{2-}$]·(IFbenz)·2CH$_3$OH***.

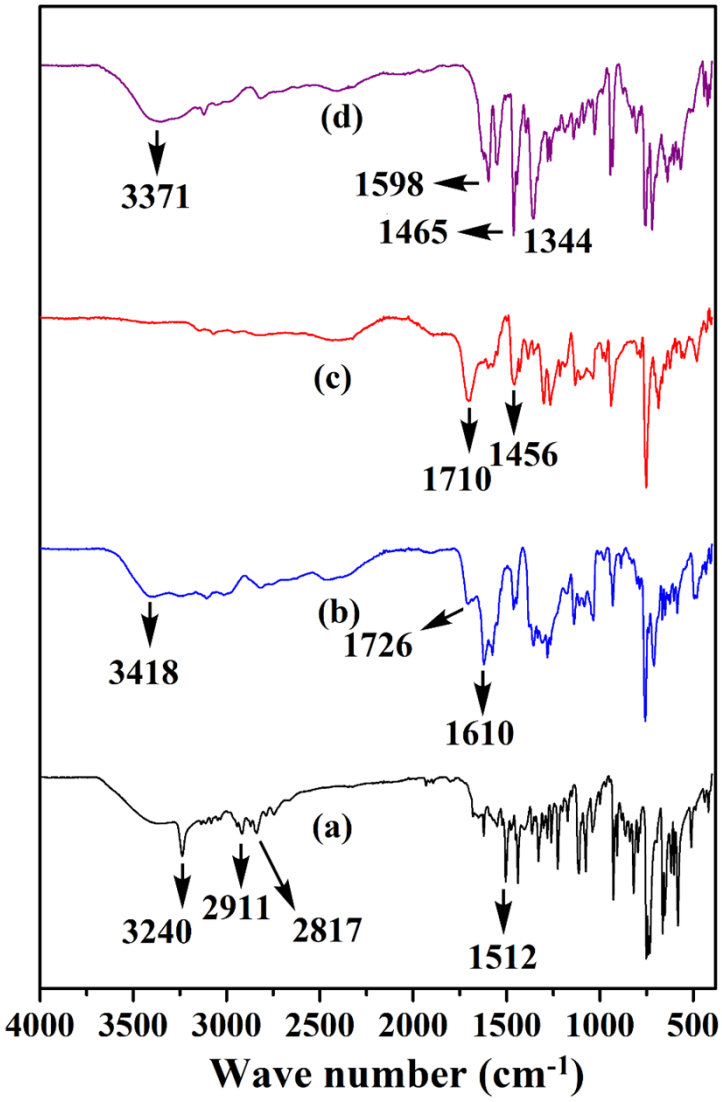
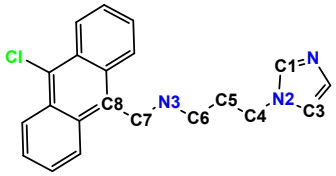


Figure 11S: IR spectra of (a) ***chloroanthraimmida***, (b) ***[(H$_2$chloroanthraimmida)$^{2+}$][2(H35pdc)$^-$].4H$_2$O***, (c) ***[(H$_2$chloroanthraimmida)$^{2+}$][2(H35pdc)$^-$].(IFbenz)·4H$_2$O*** and (d) ***[(H$_2$chloroanthraimmida)$^{2+}$(35pdc)$^{2-}$]·(IFbenz)·2CH$_3$OH***

Table 2S: Torsion angles of the flexible part of the ***chloroanthraimmida***

Torsion angles 	**1**	**2**	**3**
C1-N2-C4-C5	-77.8(5)	81.6(4)	-115.08
C3-N2-C4-C5	97.6(5)	-96.2(4)	70.23
C6-C5-C4-N2	-58.4(5)	57.6(4)	60.92
N3-C6-C5-C4	-178.6(3)	174.9(3)	158.34
C7-N3-C6-C5	-177.9(3)	179.5(2)	177.39
C6-N3-C7-C8	61.3(4)	66.2(3)	164.17